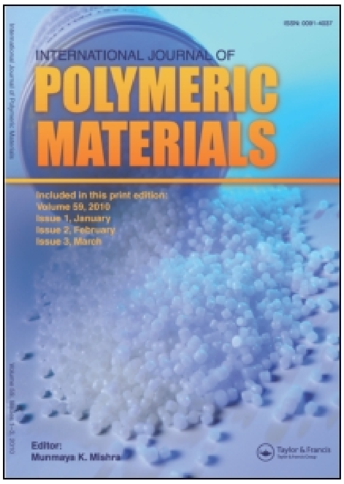

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Photodegradation in Aqueous Solution of a Polyamidehydroxyurethane Type Polymer. Temperature Effect on the Process of Degradation

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The present research shows some aspects of temperature effect on the process of photodegradation in aqueous solution of a polyamidehydroxyurethane type polymer. The process of photodegradation in aqueous solution of the studied polymer proceeds with chain scissions, what is promoted at elevated temperatures. At the temperatures 45 °C and 65 °C the values of the number average of chain scissions, S, and of the quantum yield of chain scission, Φ_{cs}, are greater at the initial moments of the process than the correspondent values at 25 °C and 35 °C. At elevated temperatures there is an increase in the probability of the process of recombination of macroradicals, formed during chains scission. The values of S at 45 °C and 65 °C by the end of the process are smaller than those at 35 °C and 25 °C. It can also be noticed, that the values of Φ_{cs} at 45 °C and 65 °C continuously decrease after the initial moments of irradiation till the end of the process of degradation, while at 25 °C the values of Φ_{cs} increase practically during the whole process. At 35 °C the behaviour of the system is more unusual.

Keywords: Photodegradation; polyamidhydroxyurethane; aqueous solutions; temperature effect

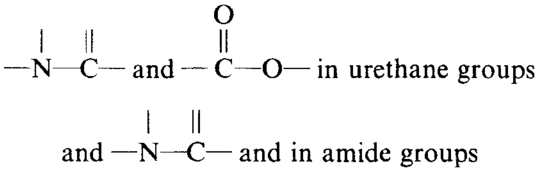
INTRODUCTION

One of the most important factors, contributing the modification of the properties of polymers with time, is the degradation, caused by ultraviolet radiation. The study of this phenomenon is particularly interesting from two points of view: to obtain polymeric materials, stable at the action of ultraviolet radiation, and to solve the problem of polymeric waste and to obtain photo-, biodegradable and biocompatible polymers [1–5].

Polyurethanes represent a class of polymers of great importance from the practical point of view. Therefore, the problem of their photodegradation becomes more frequently the object of study [6–10].

The mechanism of photodegradation of polyurethanes is similar to the mechanism of degradation of polyamides [11].

The polymer under concern is a polyamidehydroxyurethane type polymer. The degradation of this polymer is due to the fact that its macromolecules possess ketone groups (in urethane and amide groups) which absorb in the region of wavelengths of near 270–330 nm [11]. Ultraviolet radiation can initiate some photochemical reactions in the polymer. In this case the break of the bonds



$$-\overset{|}{N}-\overset{\|}{C}-\text{ and }-\overset{\overset{O}{\|}}{C}-O-\text{ in urethane groups}$$

$$\text{and }-\overset{|}{N}-\overset{\|}{C}-\text{ and in amide groups}$$

can lead to the chain scissions of the polymer with free radicals formation. In the case of photodegradation of polymers with ketone groups more often take place primary photochemical processes, which present Norrish type I and II reactions [12].

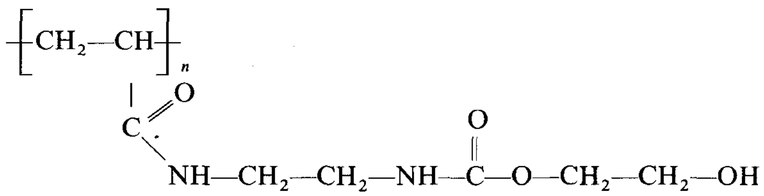
The process of the chain scission with free radicals formation (Norrish type I reaction) is promoted at elevated temperatures [13]. The formed free radicals can recombine. The latter process is also facilitated at elevated temperatures. Since irradiation of PAHU solution with ultraviolet light is carried out in the presence of oxygen, the degradation with the photochemical break combines with the photooxidation, proceeding with formation and decomposition of hydroperoxids [14]. This process, in its turn, is also facilitated at elevated temperatures [11].

The present research shows some aspects of temperature effect on the process of photodegradation in aqueous solutions of a polyamidehydroxyurethane (PAHU) with the molecular weight of approximately

18700 g/mol. Previous investigations, made by the authors, were connected with the study of photodegradation in aqueous solutions of the same polymer under isothermic conditions [15].

EXPERIMENTAL

The synthesis of the PAHU has been described in one of the previous works [16]. The obtained polymer has the following structure:



- The molecular weight of the polymer both irradiated with ultraviolet light and not irradiated was determined by osmometry, using a membran osmometer "Knauer" [15]. The measurements were carried out in aqueous solutions of the polymer (with concentration 0,1–1,0 g/dl) at 25 °C. The number average molecular weight of the polymer was $\bar{M}_n = 18700$ g/mol.
- Changes, that occured during the irradiation of the polymer with ultraviolet light, were observed by means of viscosimetry [11]. The authors used an Ubbelohde Type viscometer. The same viscometer serves as a reactor during the irradiation of polymer solutions. The lower part of the viscometer-reactor is made of the Pyrex glass, transparent in the used region of wavelengths. The jacket of thermosetting permits to maintain a constant temperature.

  Irradiation of PAHU aqueous solutions and the correspondent viscometric measurements were carried out at the temperatures 25 °C, 35 °C, 45 °C, 65 °C ± 0,25 °C. The volume of the solutions was equal to 50 ml.
- For irradiation of the PAHU solutions there were used medium pressure mercury lamps Type HQE-40, emitting in the ultraviolet and visible region of the spectrum (the emission bands in the UV region are 3650–3663; 3126–3122; 3022–2967; 2662–2655 Å).

The light intensity from the sources of light was measured by means of the actinometry, using potassium ferri-oxalate [12]. The light intensity from the used sources of light is $I_0 = 11,69 \cdot 10^{16}$ quanta/s.

The intensity of the light, absorbed by the polymer in solution, I_a, was determined according to procedure described in [12] and appeared to be $I_a = 9,933 \cdot 10^{14}$ quanta/s·cm^3.

The process of degradation was observed by determining the intrinsic viscosity, $[\eta]$, at different times of irradiation.

The intrinsic viscosity was calculated by means of the single-point equation, deduced by the authors for the present polymer in water: [15]

$$\log[\eta] = \log\left(\frac{\eta_{sp}}{c}\right) + 0,017\eta_{sp},$$

where η_{sp} is specific viscosity; c is concentration of solution, g/dl.

The quantum yield of chain scission, Φ_{cs}, was calculated, using the equation: [11]

$$\Phi_{cs} = \frac{cN_A}{M_{n(0)}} \cdot \frac{\left([\eta]_0/[\eta]_\tau\right)^{1/a} - 1}{I_a \cdot \tau},$$

where $M_{n(0)}$ is number average molecular weight of the not irradiated polymer, g/mol; c is concentration of the polymer in solution, g/cm^3; N_A is Avogadro's number, $N_A = 6,023 \cdot 10^{23}$ molecules/mol; τ is time of irradiation, s; I_a is intensity of the light, absorbed by the polymer in solution, quanta/s·cm^3; $[\eta]_0$ and $[\eta]_\tau$ are the intrinsic viscosities of the polymer solution at the moment $\tau = 0$ of irradiation and at the correspondent time τ; a is exponent from Mark-Houwink equation for the used pair of polymer-solvent. For PAHU in water the authors determined $a = 1,32$ [15].

RESULTS AND DISCUSSION

During irradiation of PAHU in aqueous solutions with ultraviolet light there was observed a decrease in solutions viscosity with the time of irradiation at all the temperatures.

Figure 1 presents the change of relative viscosity, η_{rel}, of PAHU solutions with the time of irradiation at the temperatures 25 °C, 35 °C, 45 °C, 65 °C. There we note a decrease in η_{rel} with the time of irradiation until a point is reached when further decrease in η_{rel} doesn't occur. The time, after which the decrease in η_{rel} with the time of irradiation is not observed, is different for each temperature and is longest at 25 °C (840 minutes). With the rise of the temperature, the time of the degradation process of the polymer decreases; at 35 °C the process ends in 600 minutes, at 45 °C it ends in 480 minutes, and at 65 °C is completed in 360 minutes of irradiation.

Figure 1 also shows that the rate of the degradation of PAHU increases with temperature, with the exception of the case at 35 °C. According to the curve at 35 °C (Fig. 1) it can be seen, that the decrease in η_{rel} with the time of irradiation is not uniform: at the certain moments (at 10 minutes and 60 minutes of irradiation) a slight

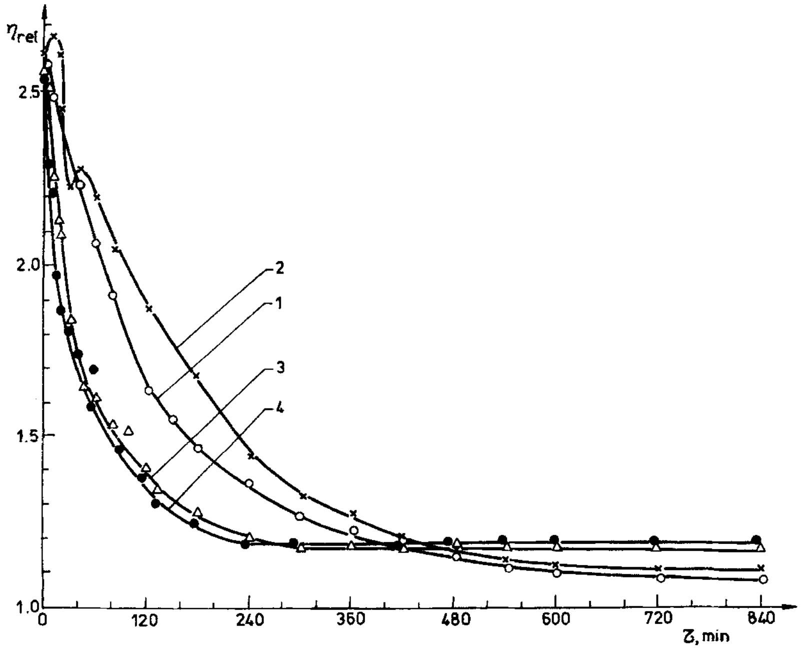


FIGURE 1 The change of relative viscosity of aqueous solutions of PAHU as function of time of irradiation at the different temperatures: 1–at 25 °C; 2–at 35 °C; 3–at 45 °C; 4–at 65 °C.

increase in viscosity of PAHU solutions occurs. This phenomenon is reproducible.

Parallel to the above experiments we carried out viscometric measurements for PAHU solutions with the concentration 0,1 g/dl at the temperatures 25 °C, 35 °C, 45 °C, 65 °C without irradiation at times, that corresponded the times of measurements in the presence of irradiation. In this case there were observed no changes in viscosity of PAHU solutions at any temperature.

The decrease in viscosity of PAHU solutions during ultraviolet irradiation could be explained by the fact, that under the irradiation with ultraviolet light the processes of chain scissions and changes of chain conformation take place [15]. Conformation changes of PAHU macromolecules can be caused by the break of some hydrogen bonds at irradiation.

The studied polymer, having in its structure amide, urethane and hydroxyl groups, can form a great deal of hydrogen bonds, both intramacromolecular and intermolecular ones between macromolecules of the polymer, PAHU molecules and water molecules. The presence of a great number of hydrogen bonds also explains the high viscosity of PAHU aqueous solutions even at small concentrations of the polymer. It has been reported, that the presence of hydrogen bonds contributes to the increase in viscosity and in activation energy of the viscous flow of polymer melts and solutions [17–19].

The values of the number average of chain scissions, S, were calculated from viscosity data using the equation

$$S = \left(\frac{[\eta]_0}{[\eta]_\tau}\right)^{1/a} - 1$$

Owing to the relative low molecular weight of the polymer and the fact, that the chain scission can take place also in amide groups, situated in side-chains of the macromolecules, it could be possible to expect an increase in the probability of secondary radical processes – radical recombination or crosslinking. These processes are favored at elevated temperatures.

Figure 2 shows the dependence of the values of S on the time of irradiation, τ, at various temperatures. If the effect of the irradiation with ultraviolet light caused only primary photochemical reactions, in

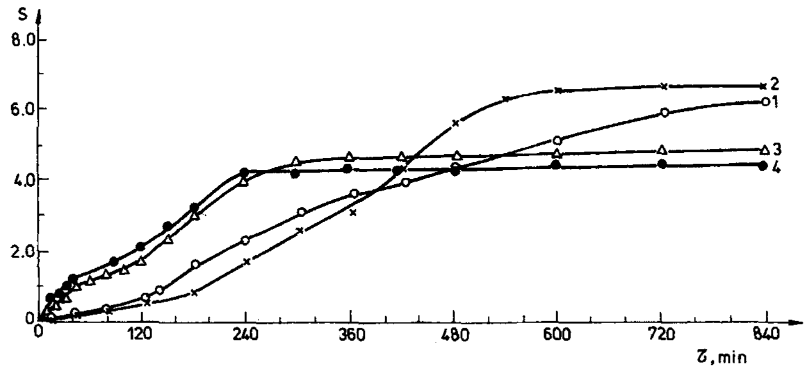


FIGURE 2 Dependence of number average of chain scissions on time of irradiation of aqueous solutions of PAHU: 1–at 25 °C; 2–at 35 °C; 3–at 45 °C; 4–at 65 °C.

$S-\tau$ coordinates a linear dependence would be observed. However, this is not the case even at the initial moments of irradiation. The examination of the curves in Figure 2 points to the existence of the induction periods at 25 °C and 35 °C (till ~ 20 minutes). It can be also noticed, that with temperature, the number average of chain scissions increases (at the same moments of irradiation), excluding 35 °C. By the end of the process, nevertheless, the values of S at 25 °C increase with the time of irradiation, remaining close to the values of S at 35 °C, and greater in comparison with those at 45 °C and 65 °C. Besides, at more elevated temperatures (including 35 °C) the degradation process is stabilized. This is reflected in the dependence $S=f(\tau)$ (the values of S reach some limits). The times τ corresponding to levelling off are smaller at elevated temperatures. Figure 2 also shows that the values of S by the end of the process decrease with temperature (at 45 °C and 65 °C in comparison with 25 °C and 35 °C).

This dependence can be explained by assuming, that the processes of chain scissions occur in amide and urethane groups with free radicals formation (Norrish type I reaction). These processes are strongly dependent on temperature [13,20].

Thus, with the rise of temperature, the number of free radicals increases and there radicals recombine because of elevated temperatures. This fact causes the lower degree of degradation by the end of the process at more elevated temperatures (at 45 °C and 65 °C) and even the achievement of a certain limit of degradability at temperatures above 25 °C. Since irradiation of PAHU solutions with ultraviolet light was carried out in presence of oxygen, it could be expected, that together with photodegradation of PAHU there take place photo-oxidation with formation and decomposition of intermediate hydroperoxides [14].

Figure 3 shows the dependence of quantum yield of chain scission, Φ_{cs}, on the time of irradiation, τ, at the temperatures 25 °C, 35 °C, 45 °C, 65 °C. It can be noticed, that at 25 °C the values of Φ_{cs} increase continuously after 40 minutes of irradiation almost to the end of the process. Values of Φ_{cs} are smaller in comparison with those at 45 °C and 65 °C, and larger in comparison with those at 35 °C. At 45 °C and 65 °C the values of Φ_{cs} abruptly increase at the initial moments of the process, reaching their maximum values ($1{,}66 \cdot 10^{-2}$ at 65 °C). This indicates, that the processes of chain scissions, facilitated by the temperature rise proceed more intensely at the initial period of the process. Afterwards, at 45 °C and at 65 °C we note some oscillations

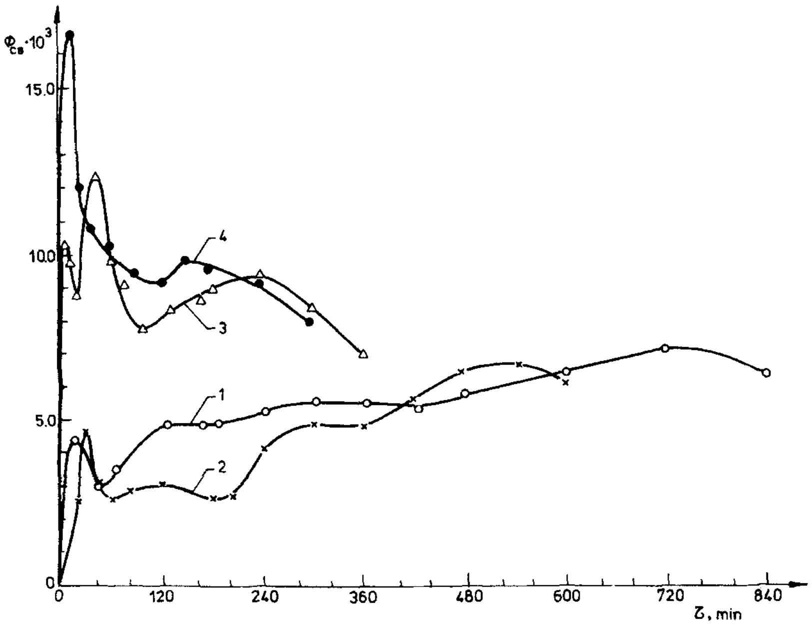


FIGURE 3 Dependence of quantum yield of chain scission on time of irradiation of aqueous solutions of PAHU: 1–at 25 °C; 2–at 35 °C; 3–at 45 °C; 4–at 65 °C.

and the further decrease in the values of Φ_{cs} with the time of irradiation nearly till the end of the process of photodegradation. This again confirms the occurence of processes of recombination of the radicals formed during chain scissions. And these processes proceed easier with increasing temperature. The values of Φ_{cs} by the end of the process of degradation are close for all temperatures.

Figures 1–3 shows that at 35 °C the process proceeds in a different way, than at 45 °C and 65 °C. Before 420 minutes of irradiation at 35 °C the process proceeds slower than at 25 °C (Fig. 1), the values of the number of chain scissions and the values of quantum yield of chain scission of the polymer at 35 °C are also less than at 25 °C (Figs. 2, 3).

However, after 420 minutes of irradiation the values of S and Φ_{cs} increase in comparison with the corresponding values at 25 °C, but remain less, than those at 45 °C and 65 °C. By the end of the process of photodegradation the values of S at 35 °C are close to those at 25 °C and they are higher in comparison with these values at 45 °C and 65 °C. Probably, such a behaviour of the system at 35 °C (till 420 minutes of irradiation) can be caused by the appearance of some steric effects, which can be caused by modifications of macromolecule conformations during the process.

We will define an apparent activation energy, E, [13], by the equation

$$\Phi_{cs} = \Phi_{cs(0)} \cdot e^{-E/RT},$$

where T is absolute temperature, K; $\Phi_{cs(0)}$ is quantum yield of chain scission at $T \to \infty$.

Figure 4 presents the dependence $\ln \Phi_{cs} = f(1/T)$ (the temperatures 25 °C, 45 °C, 65 °C). The value of E, calculated from the slope of the straight line is equal to $\sim$ 3,97 kcal/mol, and it is rather close to the value, obtained by Hartley and Guilett [13] for compounds, possessing ketone groups.

CONCLUSIONS

- Photodegradation of PAHU in aqueous solutions proceeds with chain scissions and free radicals formation. This process is facili-

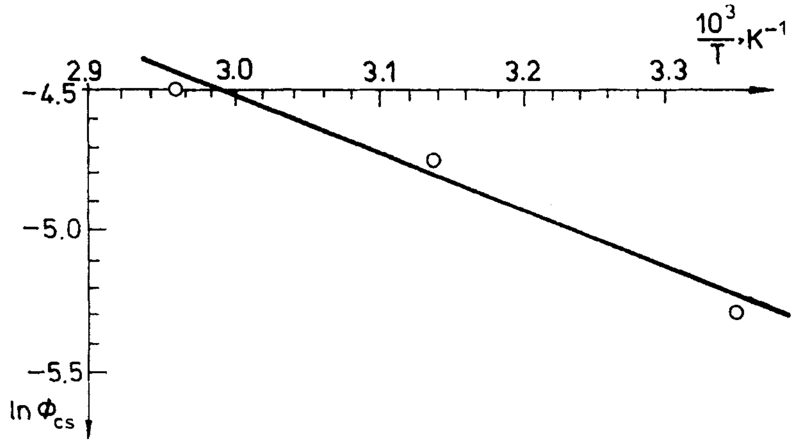


FIGURE 4 Dependence of ln Φ_{cs} on $1/T$ for the process of photodegration of PAHU in aqueous solutions.

tated at elevated temperatures. The values of S and Φ_{cs} increase with temperature, excluding 35 °C;

- reactions of chain scissions are accompanied by reactions of recombination of formed radicals. This process is also promoted at elevated temperatures. The values of S at 45 °C and 65 °C are less by the end of the process of degradation than at 25 °C and 35 °C. A certain stabilization of the process is observed at 45 °C and 65 °C. By the end of the process, at temperature above 25 °C, the degree of degradation is less and even approaches a certain limit of degradability. The values of Φ_{cs} at 45 °C and 65 °C begin to decrease after the initial moments of the process, and at 25 °C they increase permanently with the time of irradiation nearly till the end of the process;
- at 35 °C it can be observed a rather unusual behaviour of the system (in comparison with the behaviour of the process at 45 °C and 65 °C).
- during irradiation with ultraviolet light there can occur modifications of macromolecule conformations, caused by the rupture of some hydrogen bonds.

References

[1] Drazdh, M. (1991). *Plasty Komc.*, **28**(3), 78.
[2] Nagy, Y. (1992). Termeszet Viloga, **123**(8), 375.
[3] Tsunooka, M. (1992). Gosei Jushi, **38**(2), 4.
[4] Lenz, R. (1993). *Adv. Polym. Sci.*, **107**, 1.
[5] Hari, Y., Suzuki, M., Okida, I. and Imai, T. (1992). *Macromolecules*, **25**(19), 5117.
[6] Farkas, F. (1991). *Muanyages Gumi, RPU*, **18**(9), 262.
[7] Sato, H. and Fujii, K. *Jpn. Kokai Tokkyo Kaho* JP 04 72, 317(92, 72, 317) (CI C08 G18/42), 06 Mar. 1992, *Jp. Appl.*, 90/116, 358, 02 May 1990.
[8] Rek Vesna. (1992). *Pertanika*, **15**(2), 134.
[9] Chandro, R., Thapliyal, B. P. and Sani, R. K. (1993). *Polym. Degrdn. Stab.*, **39**(1), 93.
[10] Osawa, Z., Sunakami, T. and Fukuda, J. (1994). *Polym. Degrdn. Stab.*, **43**(1), 61.
[11] Ranby, B. and Rabek, J. F. (1975). "Photodegradation, Photo-oxidation and Photostabilization of polymers", John Wiley and Sons, London-New York-Sydney-Toronto.
[12] Calvert, J. G. and Pitts, J. N. (1968). "Photochemistry", John Wiley and Sons, New York-London-Sydney.
[13] Harthley, J. H. and Guillet, J. E. (1968). *Macromolecules*, **1**(5), 413.
[14] Rabek, J. F. (1974). in Comprehensive Chemical Kinetics, (Ed. C, H. Bamford and C. F. Tipper), Elsevier, Oxford, **14**.
[15] The datas on course of publication.
[16] Ciobanu, C., Farcas, A., Badea, N., Barladeanu, C., Culic, C. V. and Darie, A. Patent, RO 93572. 31.12.87.
[17] Vinogradov, S. N. and Linnell, R. H. (1971). Hydrogen Bonding, Van Nostrand Reinhold Comp, New York, Cincinnati, Toronto, London, Melburn.
[18] Blyler, J. I. and Hoos, T. W. (1969). *J. Appl. Polym. Sci.*, **13**, 2721.
[19] Lim, T. and Hoos, T. W. *Advan. Polym. Sci. Eng. Proc., Symp.*, 1972, 272; (*Chem. Abstr.*, **78**, 148553 (1973)).
[20] Golemba, F. J. and Guillet, J. E. (1968). *Macromolecules*, **1**(5), 413.