

Polymer Communication

# Kinetic effects of photoexposed isotactic polypropylene in the presence of some hindered-amine light stabilisers

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## Abstract

A chemiluminescence study on photo-irradiated isotactic polypropylene in the presence of three new HALS compounds, mercapto-1,3,5-triazinic phenolic stabiliser (antioxidant T) and Tinuvin 770 as standard was carried out. The oxidation prevention was assessed by the calculation of the main kinetic parameters of thermal degradation process (oxidation induction time and maximum oxidation rate). Supplementary stability tests were performed on i-PP containing four stabiliser couples (triazine + HALS) and the cooperative factors resulting from the synergistic activities of oxidation prevention couple were determined. A kinetic treatment of the chemiluminescence data obtained from thermal ageing of stabilised isotactic polypropylene is presented. © 2000 Elsevier Science Ltd. All rights reserved.

**Keywords:** Polypropylene; Hindered-amine light stabilisers; Triazine

## 1. Introduction

There is a considerable interest in the thermal stabilisation of commercial polyolefins, for example polypropylene, because their service life depends on a large extent by the stabilisation efficiency of additives. The expansion of polymer market and the progress in the synthesis of new thermal stabilisers involve sustained tests on the thermal behaviour of protected materials.

Several studies have been performed on the thermal stabilisation of polyolefins. Various stabiliser classes and assay methods have been selected for the evaluation of structural changes that occurred in degrading materials. One of the most sensitive procedures used for the determination of antioxidative ability is chemiluminescence. The pioneering chemiluminescence studies on solid polymers [1–3] have provided reliable information on exothermal termination reactions of alkyl peroxy radicals. The kinetic treatment of polymer stability were also reported [4–10]. The protection of polymers to UV light and thermal degradation can be satisfactorily achieved by various long-term antioxidants during the application stage.

The photodegradation of polymers is another essential problem in the science and technology of polymers. Hindered-amine light stabilisers (HALS) are the most

known efficient compounds largely used in photooxidation prevention [11–14]. The polymer materials like various sorts of polyethylene and polypropylene undergo a fast ageing process when they are exposed to sunlight. The improvement in their chemical resistance is promoted by HALS; they are two to six times more effective than nickel chelate light stabilisers and four to ten times more effective than ultraviolet absorbers [15].

The inhibition of polymer oxidation via free radical reaction with molecular oxygen is the main goal of the increase in material durability when the fabricated polymer products are subjected to various environmental conditions. Consequently, this paper presents a study on the photo and thermal oxidation of isotactic polypropylene containing various oxidation prevention systems. The chemiluminescence procedure was selected for an accurate determination of process characteristics (oxidation induction time, maximum oxidation rate, cooperative factors).

## 2. Experimental

The polymer used in this investigation was isotactic polypropylene (Moplen<sup>®</sup>, Himont, Italy). It was purified by precipitation with cold methanol poured from a hot *o*-xylene solution. After the removal of the remaining solvent, the i-PP powder was washed with acetone and dried in vacuum at room temperature. The additives were brought into the

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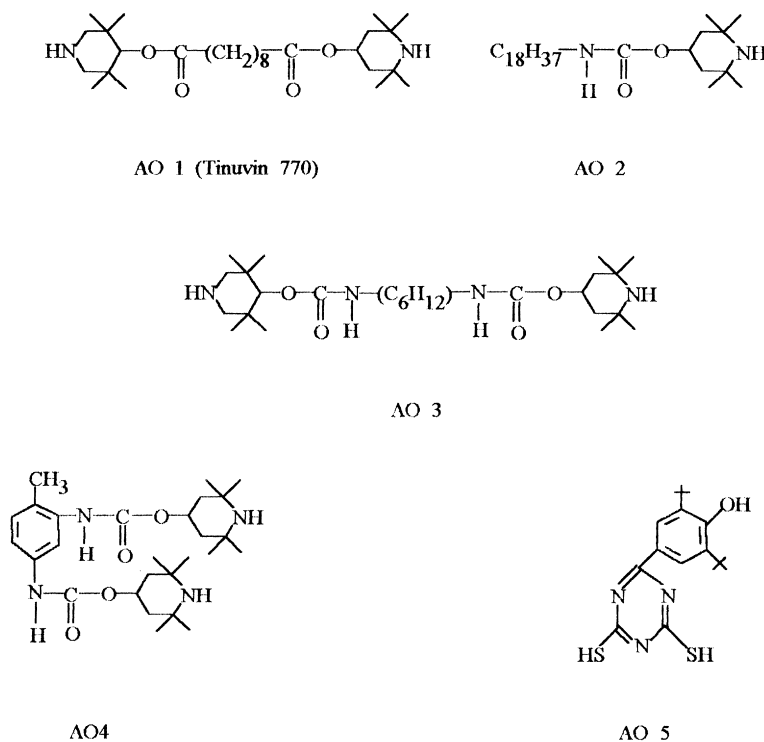


Fig. 1. The chemical structures of the tested hindered-amine light stabilisers.

polypropylene mass by thorough wet grinding. An appropriate solution of additive was poured on purified polypropylene powder in order to obtain a concentration of 0.5 wt%. The mixtures were dried at room temperature for 24 h before melting on aluminium trays (0.02 g of sample; 40 s at 180°C). Thin and homogenous films of 350  $\mu\text{m}$  were obtained.

The tested stabilisers belong to the hindered amine compounds: AO 1: bis(2,2,6,6-tetramethyl-4-piperidinyl) sebacate (Tinuvin 770, Ciba Geigy) and AO 2–AO 4: three new HALS [16]. Their molecular structures are shown in Fig. 1. They were individually added. For synergistic assay the four antioxidants were accompanied by a mercapto-*S*-triazine (AO 5) (Fig. 1). Both additive concentrations were 0.5 wt%.

UV irradiation was carried out using a laboratory type medium-pressure mercury lamp operating without a glass envelope (250 W). The total ultra-violet output expressed in units of  $\text{Nh}\nu$  at wavelengths shorter than 380 nm was of the order of  $5 \times 10^{-5}$  s/cm the arch length. During UV exposure the sample temperature did not exceed 30°C.

Isothermal chemiluminescence measurements were performed in air at 180°C in a laboratory equipment, Oxyluminograph OL-94; the details on chemiluminescence unit were previously presented [18]. The stabilised isotactic polypropylene and the purified polymer (control) samples were placed inside an oven provided with the electronically controlled temperature device (mean error:  $\pm 0.5^\circ\text{C}$ ). Thus the dependencies of counts on oxidation time could be

recorded. The polymer samples were immediately analysed after the end of the exposure.

### 3. Results and discussion

The proportionality between the photon numbers and the accumulation of peroxy radicals allows us to follow the progress in oxidative degradation of polymers by chemiluminescence. UV radiation supplies enough energy to a polymer matrix that excites chemical bonds. Free radicals are generated, their reaction with molecular oxygen follows and the accumulation of excited carbonyls will accompany the degradation of material. The photon emitted by the triplet state of oxygen can be measured and the increase in counted photons number describe the evolution of material ageing. The dependencies of CL intensity on measuring time may be divided into three stages: the induction period when the count number is quite small so it is impossible to detect photons, the propagation stage characterised by a constant oxidation rate and the end of process when maximum chemiluminescence intensity is attained. The longer the induction time the higher the stabilisation efficiency. At this early stage of oxidative degradation the antioxidant depletes. After the shorter induction periods a larger amount of stabiliser remained unconsumed. It becomes available for the second step of oxidation and a higher maximum intensity, which is lesser, is determined.

Fig. 2 presents the chemiluminescence curves for

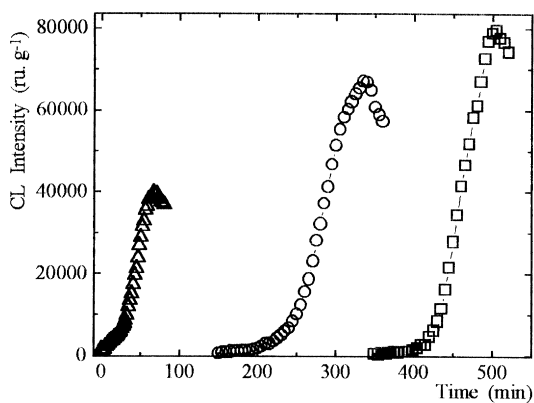


Fig. 2. The chemiluminographs of i-PP (180°C in air) stabilised with 0.5 wt% AO 4 ( $\Delta$ ), 0.5 wt% AO 5 ( $\circ$ ) and 0.5 wt% AO 4 + 0.5 wt% AO 5 ( $\square$ ).

isotactic polypropylene stabilised with AO 4 (HALS) and/or AO 5 (mercapto-*S*-triazine derivative). This example is representative for this study that intends to demonstrate the cooperation potential of these classes of antioxidants during the degradation of i-PP. It can be remarked that the oxidative protection of these two stabilisers is noteworthy. An analogous behaviour was displayed by the other stabilisation systems checked in this paper (Table 1). In the case of the simultaneous presence of AO 3 and triazine (AO 5) in polymer samples a simple addition could be calculated. In the cases of AO 2 + AO 5 and AO 4 + AO 5 we suppose that this synergistic activity would be due to the regeneration of phenoxy radicals by the hydroxylamine derivatives resulting from oxidation of piperidine. The results listed in Table 1 prove that over the early stage of oxidation (oxidation induction time) the cooperation in material stabilisation is less efficient than during the propagation step. In addition, the sterically hindered amines AO 1–AO 4 displayed a weaker effect on oxidative protection in the presence of

Table 1

The main kinetic parameters of thermal oxidation (180°C, air) obtained for stabilised i-PP

Additive <sup>a</sup>	$\tau_i^b$ (min)	$V_{ox}^{maxb}$ (r u g <sup>-1</sup> min <sup>-1</sup> )	Cooperative factor	
			$\theta_{\tau_i}^c$	$\theta_{\tau_v}^{maxd}$
Free of stabiliser	4	5071	–	–
AO 1	6	1954	–	–
AO 2	11	1586	–	–
AO 3	14	965	–	–
AO 4	19	920	–	–
AO 5	172	1609	–	–
AO 1 + AO 5	201	1335	1.13	2.67
AO 2 + AO 5	260	1059	1.42	3.02
AO 3 + AO 5	195	934	1.05	2.76
AO 4 + AO 5	302	1157	1.58	2.19

<sup>a</sup> The concentration for all additives was 0.5 wt%.

<sup>b</sup> The parameters calculated from chemiluminescence records.

<sup>c</sup> The values calculated from oxidation induction times [21].

<sup>d</sup> The values calculated from oxidation rates [21].

the second compound, mercapto-triazine (Table 1, last two columns). The chain break reaction between nitroxy units and alkyl radicals would decrease the efficiency in oxidation inhibition of the tested amines.

In the literature these kinds of heterosynergistic effects showed by HALS either with the chain break antioxidants or with the prevention ones have been reported. Thus, during the thermal oxidation of polypropylene (testing temperature 130°C) Tinuvin 770 exhibits synergistic effects with Irganox 1010 ( $\theta_{V_{ox}^{max}} = 1.71$ ), Topanol CA ( $\theta_{V_{ox}^{max}} = 2.20$ ), Goodrite 3114 ( $\theta_{V_{ox}^{max}} = 3.14$ ) or Weston 618 ( $\theta_{V_{ox}^{max}} = 1.68$ ); an additivity in oxidation prevention behaviour with Cyanox 2246 ( $\theta_{V_{ox}^{max}} = 1.00$ ), Cyanox 1790 ( $\theta_{V_{ox}^{max}} = 0.98$ ) or Irganox 1076 was established. An antagonistic activity was found for the systems consisting of sterically hindered amine and Plastomax STDP ( $\theta_{V_{ox}^{max}} = 0.69$ ) [19,20].

The chemiluminescence emission intensity presented by the polymer is proportional to the rate of the bimolecular reaction for the peroxy radical recombination [21]:

$$I_{CL} = G\Phi k_{II} C_{RO_2}^2 \quad (1)$$

where  $I_{CL}$  represents the chemiluminescence intensity,  $G$  the geometry factor,  $\Phi$  expresses the quantum yield,  $k_{II}$  is the rate constant of the bimolecular reaction and  $C_{RO_2}$  symbolises the peroxy radical concentration. According to Billingham [22], the geometry factor,  $G$ , is the multiplication of the number of photons that reach the photocathode and the emitted photon fraction that are caught by the photocathode; the quantum yield,  $\Phi$ , is the multiplication of the reaction fraction that generates excited states and the process fraction that expels the excess energy as light emission.

The UV irradiation of polymers in the presence of oxygen is characterised by the formation rate of the peroxy radicals that can be expressed as follows:

$$\frac{dC_{RO_2}}{dt} = R_{UV} - k_{II} C_{RO_2}^2 \quad (2)$$

where  $R_{UV}$  denotes the rate of the photoinitiating reaction involving peroxy radicals. In Eqs. (1) and (2) we have assumed that  $I_{CL}$  increases with the UV irradiation time. It attains a saturation value because of the balance between the rate of generation of the peroxy radicals and their rate of decay. In this condition, the left member of Eq. (2) equals zero. During the propagation stage of degradation

$$I_0 = G\Phi R_{UV} \quad (3)$$

where  $I_0$  is the saturation chemiluminescence intensity. Eq. (3) proves that  $I_0$  is proportional to the initiation rate of the photoinduced peroxy radicals.

The degradation step that occurred on the descendant region of sigmoidal  $I = f(t)$  may be characterised by the following relationship:

$$\frac{dC_{RO_2}}{dt} = -k_{II} C_{RO_2}^2 \quad (4)$$

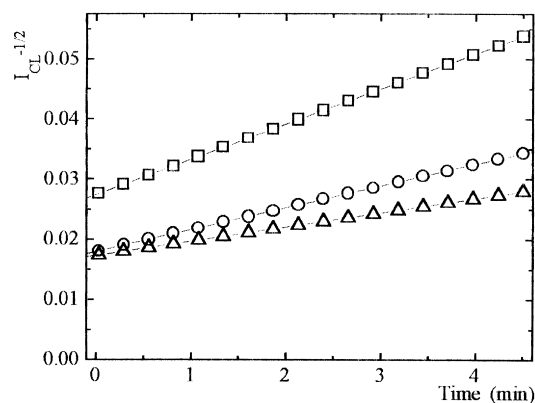


Fig. 3. The postirradiation time dependencies  $1/\sqrt{I_{CL}}$  on time for i-PP stabilised with 0.5 wt% AO 4 ( $\Delta$ ), 0.5 wt% AO 5 ( $\circ$ ) and 0.5 wt% AO 4 + 0.5 wt% AO 5 ( $\square$ ) (exposed for 90 min and CL tested at 180°C in air).

and after integration this last relationship provides:

$$\frac{1}{C_{RO_2}} - \frac{1}{C_{RO_2}^0} = k_{II}t \quad (5)$$

But the concentration of the peroxy radical can be obtained from Eq. (1):

$$C_{RO_2} = \sqrt{\frac{I_{CL}}{G\Phi k_{II}}} \quad (6)$$

Eq. (5) becomes:

$$\frac{1}{\sqrt{\frac{I_{CL}}{G\Phi k_{II}}}} - \frac{1}{\sqrt{\frac{I_{CL}^0}{G\Phi k_{II}}}} = k_{II}t \quad (7)$$

or, under the other form:

$$\frac{1}{\sqrt{I_{CL}}} = \sqrt{\frac{k_{II}}{G\Phi}}t + \frac{1}{\sqrt{I_{CL}^0}} \quad (8)$$

Eq. (8) emphasises that the reciprocal square root of chemiluminescence is proportional to the UV exposure time.

Fig. 3 presents the dependence of  $1/\sqrt{I_{CL}}$  on the post-

Table 2  
Chemiluminescence intensity attained at saturation by i-PP in the presence of tested compounds

Additive <sup>a</sup>	$I_{CL}^0$ (r u g <sup>-1</sup> )	Cooperative factor ( $\theta_{CL}^0$ )
Free of stabiliser	12600	–
AO 1	8244	–
AO 2	8613	–
AO 3	8769	–
AO 4	4525	–
AO 5	4000	–
AO 5 + AO 1	3800	3.22
AO 5 + AO 2	8125	1.55
AO 5 + AO 3	3850	3.32
AO 5 + AO 4	4200	2.03

<sup>a</sup> All concentrations were 0.5 wt%.

irradiation heating time carried out in air at 180°C for isotactic polypropylene stabilised with AO 4, AO 5 and their couple. The straight line dependencies (correlation factors 0.96–0.98) proves the validity of Eq. (8).

Table 2 lists the chemiluminescence intensity  $I_{CL}^0$  of all the specimens that were recorded after the elapse of the UV irradiation time (90 min). This table emphasises that the  $I_{CL}^0$  values for the stabilised polymer samples were smaller in comparison to the similar values obtained for unprotected polypropylene. On the other hand, a notable decrease in the CL saturation intensity,  $I_{CL}^0$ , for i-PP stabilised with triazine/HALS couples could be also observed. The use of triazine as an antioxidant is justified by its double function: scavenger of radicals by the phenolic units and decomposer of hydroperoxides by the –SH groups. These kinds of compounds may offer a self-synergism effect [17,23]. It is well known that the HALS compounds display a lower activity at the early stages of photooxidation; they act more efficiently in the hindrance of the propagation reactions involving free radicals [13]. The third column contains the cooperative factors obtained for the tested couple. All the four values of  $\theta_{CL}^0$  are greater than unity. It means that cooperative effects could be demonstrated and these values ( $\theta_{CL}^0 = 1.55$ – $3.32$ ) are noteworthy for their further application in polymer industry. This synergism is somewhat surprising if it takes into account the situation of antagonism between the antioxidants containing sulphur and HALS [24,25].

The cooperative efficiencies of tested HALS (AO 1–AO 4) and triazine (AO 5) determined for the photooxidation of i-PP can be placed in the following order:

$$AO 3 > AO 1 > AO 4 > AO 2 \quad (9)$$

After the end of the UV irradiation, i-PP containing couples AO 5/AO 1–AO 4 become yellowish. This colour change was not observed after the experiments on isotactic polypropylene free of AO 5 (triazine). This behaviour is expected to be brought about by the reaction between the phenol triazine compound with nitroxy radicals when coloured quinone structures would be formed.

Fig. 4 illustrates the increase in the oxidation induction time ( $\tau_i$ ) of i-PP obtained at different exposure times by chemiluminescence in air at 180°C on the samples stabilised with AO 5 (triazine) and AO 4 (HALS). Similar results were found for the other triazine/HALS couples (Table 3). It proves the involvement of various antioxidants in specific reactions and, simultaneously, the stabiliser depletion during the photooxidation stage of the experiments [26].

The relationship that correlates the oxidation induction time of the thermal degradation performed after the UV irradiation on the UV exposure time is:

$$\tau_i = k e^{-\epsilon t} \quad (10)$$

where  $\tau_i$  represents the remnant oxidation induction time,  $k$  a material constant,  $\epsilon$  the consumption factor of the stabiliser and  $t$  the UV irradiation time. The slopes calculated from  $\ln \tau_i$  vs  $t$  curves may be considered as a criterion of the

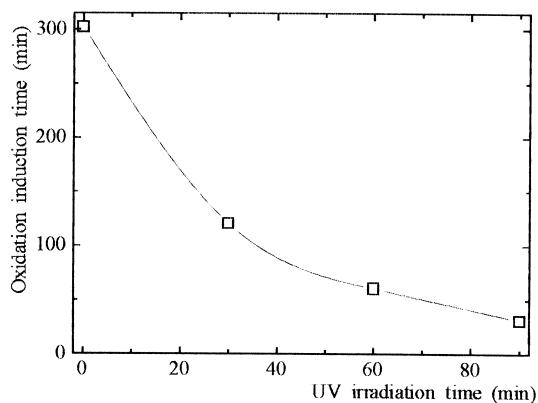


Fig. 4. The decrease in oxidation induction time determined for i-PP (180°C in air) stabilised with 0.5 wt% AO 4, 0.5 wt% AO 5 and 0.5 wt% AO 4 + 0.5 wt% AO 5 at various UV exposure times.

stabilisation ability during photooxidation. The greater the value of the consumption factor  $\epsilon$ , the more efficient the photodegradation inhibitor. Taking into account this factor of oxidation protection under UV exposure a series of tested compounds can be written:

$$\text{AO 4} > \text{AO 1} > \text{AO 3} > \text{AO 2} \quad (11)$$

In a previous paper [16] it has been reported that the stabilisation effect of tested HALS by spectroscopic determinations (carbonyl absorbency as a function of UV irradiation time) on PP films containing 0.3 wt% is the same HALS as used in this study. The following order was found:

$$\text{AO 3} > \text{AO 1} > \text{AO 4} = \text{AO 2} \quad (12)$$

This sequence is in a good agreement with the results describing the photostabilisation efficiency based on  $I_{CL}^0$  (Eq. (9)).

#### 4. Conclusion

The individual and synergistic effects of triazine and

Table 3

The remnant induction time of thermal oxidation after UV irradiation of the tested stabilisation couples

Stabiliser couples	Oxidation induction time after UV exposure (min)				$\epsilon^a$
	0	30	60	90	
AO 5 + AO 1	201	142	93	75	0.0128
AO 5 + AO 2	260	206	151	9	0.0091
AO 5 + AO 3	188	113	107	7	0.0094
AO 5 + AO 4	302	120	67	31	0.0251

<sup>a</sup> Stabiliser consumption constant, Eq. (10).

HALS were assessed by chemiluminescence measurements. The kinetic treatment of degradation data allowed us to emphasise the consequences of UV exposure on the post-irradiation behaviour of the stabilised isotactic polypropylene. The comparison of various cooperative factors calculated for the initial stage of postirradiation degradation and for the propagation step of this ageing process reveals a difference in the stabilisation effectiveness. Thus, suitable parameters for oxidation prevention may be oxidation induction time and/or saturation chemiluminescence intensity. The durability of polypropylene can be successfully assured by the antioxidant couples of triazine and HALS.

#### References

- [1] Ashby GE. *J Polym Sci* 1961;50:99.
- [2] Schard MP, Russell CA. *J Appl Polym Sci* 1964;8:985.
- [3] Schard MP. *Polym Engng Sci* 1965;5:246.
- [4] Rychla LM, Rychly J, Vavrekova V. *Eur Polym J* 1978;14:1033.
- [5] Zlatkevich L. *J Polym Sci, Polym Phys* 1985;23:1691.
- [6] Jirakova LA, Verdu J. *J Polym Sci, Polym Chem* 1987;25:1205.
- [7] Billingham NC, O'Keefe ES, Then ETH. *Polym Mat Sci Engng* 1988;58:431.
- [8] Osawa Z, Tsurumi K, Konoma F. *Mater Life* 1990;2:162.
- [9] Jipa S, Setnescu R, Setnescu T, Cazac C, Budrugaec P, Mihalcea I. *Polym Degrad Stab* 1993;40:101.
- [10] Dudler V, Lacey DJ, Kröhnke Ch. *Polym Degrad Stab* 1996;51:115.
- [11] George GA, Egglestone G, Riddell SZ. *Polym Engng Sci* 1983;23:412.
- [12] Cen J, Konoma F, Osawa Z. *Polym Photochem* 1986;7:469.
- [13] George GA, Ghaemy M. *Polym Degrad Stab* 1991;34:37.
- [14] Kihara H, Yabe T, Hosoda S. *Polym Bull* 1992;29:369.
- [15] Pan JQ. *Polym Bull* 1992;3:138.
- [16] Lau WWY, Pan JQ. *Polym Degrad Stab* 1998;60:459.
- [17] Giurginca M, Herdan JM, Cira L, Văleanu G, Ivan G. *Polym Degrad Stab* 1992;36:53.
- [18] Jipa S, Zaharescu T, Setnescu R, Setnescu T, Brites MJS, Silva AMG, Marcelo-Curto MJ, Gigante B. *Polym Int* 1999;48:414.
- [19] Allen NS, Hamidi A, Loffelman FF, MacDonald P, Rauhut M, Sussi PV. *Plast Rubb Process Appl* 1985;5:259.
- [20] Allen NS, Hamidi A, Williams DAR, Loffelman FF, MacDonald P, Sussi PV. *Plast Rubb Process Appl* 1986;6:109.
- [21] Latocha C, Uhriat M, Baloerowich AW. *Polym Degrad Stab* 1984;7:189.
- [22] Billingham NC. *Polym Prepar* 1993;34:237.
- [23] Jipa S, Setnescu R, Setnescu T, Wurm D, Podina C, Giurginca M. Practical application of chemiluminescence at the oxidation of chemical systems. International Workshop, Smolenice (Slovakia), November 1998. p. 14.
- [24] Lind H, Loelinger. Mechanism of degradation and stabilization of hydrocarbon polymers, Nineteenth Symposium on Macromolecules, Prague, July 1989, poster M44.
- [25] \*\*\* Light stabilization of polymers. Part 2: polyolefin thick sections, CIBA-CEIGY General Guide, Publ. No. 28473/1/e, 1992. p. 3.
- [26] Toda T, Kurumada T, Murayama. In: Klemchuk PP, editor. *Polymer stabilization and degradation*, ACS Symposium Series 280, Washington DC: ACS, 1985. p. 37.