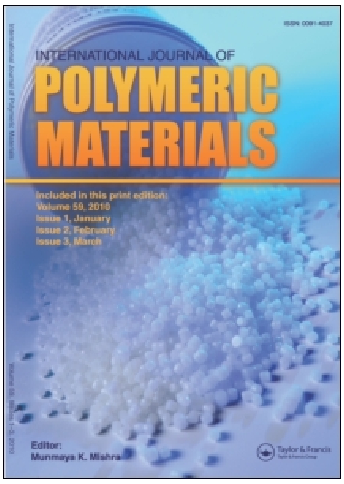

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Photooxidative Destruction and Stabilization of Polycaproamide by Bis-Aroilenbenzimidazole Derivatives

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To cite this Article Kalontarov, I. Ya , Niyazi, F. F. and Chajko, Yu. V.(1990) 'Photooxidative Destruction and Stabilization of Polycaproamide by Bis-Aroilenbenzimidazole Derivatives', International Journal of Polymeric Materials, 13: 1, 53 — 61
To link to this Article: DOI: 10.1080/00914039008039461
URL: http://dx.doi.org/10.1080/00914039008039461

Intern. J. Polymeric Mater., 1990, Vol. 13, pp. 53–61
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Printed in the United Kingdom

Photooxidative Destruction and Stabilization of Polycaproamide by Bis-Aroilenbenzimidazole Derivatives

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Some derivatives of bis-naphthoylenebenzimidazoles have been studied as light stabilizers of polyamide-6 and polyethylene terephtalate. These stabilizers are stable in the melts of these polymers for long times at 260–280°.

The light-stabilizing effect of compounds studied is discussed.

KEYWORDS: Photodegradation, oxidation, polycaproamide, bis-aroilen-benzimidazoles, methods of investigations, stabilization

Polyamides are widely used in manufacturing fibres, films, construction materials. While in service these items are subjected to various physico-chemical affects as well as they are exposed to the atmosphere (primarily light and heat).

At present a great deal of actual information has been accumulated on luminosity and thermostructure of aliphatic polyamides. There is a number of works on their luminosity and thermostability[1] But there arise certain difficulties in incorporating stabilizing additives into polyamides, particularly into polycaproamides, because most items are manufactured from melt polymers.

In the light of the said above new stabilizing additives are to be searched among thermoresistive compounds capable of withstanding heating up to 260–300°C for an extended period of time and resistive to a reactive reduction media of melt PCA. Of particular interest is the combination of both stabilizing and dying properties in one and the same compound. The importance of incorporating additives into the polymer mass is also dictated by the problems of protection of environment since in this case the question of wasteless production is practically realized and the need for drainage cleaning falls away. Therefore PCA stabilization by incorporating new thermoresistant additives as well as impassing the polymer fast colouring is of important scientific and practical significance.

The purpose of this work was to obtain dyed polymeric compositions stable to photo-thermooxidative degradation through the incorporation of bifunctional additives into PCA on the basis of bis-aroilenbenzimidazole and also to study their stabilizing effect.

1. STUDY OF BIS-AROILENBENZIMIDAZOLE

Compounds given in Table I possess high thermoresistivity ($T_{\text{melt}} = 295\text{–}335°\text{C}$ and $T_{\text{decomp.}} = 327\text{–}395°\text{C}$). which is indicative of potential feasibility to incorporate compounds I–VII into PCA melt, since their thermoresistivity exceeds the termperature of producing PCA fibre.

In order to reveal stability and compatibility of bis-aroilenbenzimidazole with PCA melt investigations have been carried out on the solubility and stability of compounds I–VII at the stage of polymerization-caprolactam; ability of PCA melt to mould (form) fibre was well as molecular mass (MM) mean viscosity of dyed and undyed polymer has been determined. In order to determine the reductive media of PCA melt visual and spectral investigations of solid compounds I–VII in PCA have also been carried out.

The foaming-up of the polymer during polymerization has not been observed, while the additive has been evenly distributed in its mass having dyed PCA in a bright-colour even at a low concentration of the additive (0.5–1.0 mass %). It

TABLE I

Structural formulas and characteristic of bis-aroilenbenzimidazole derivatives

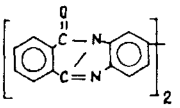
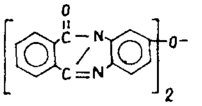
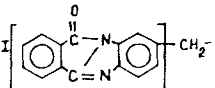
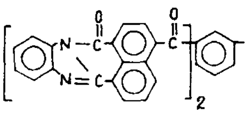
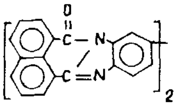
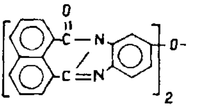
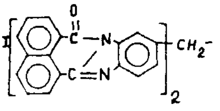
Formulas of compound	Melting temp. (°C)	Molecular mass	Colour
I 	385	438	yellow
II 	317	454	lemon-coloured
III 	307	452	light-yellow
IV 	315	670	yellow
V 	335	538	bright-yellow
VI 	335	554	lemon-coloured
VII 	295	552	light-yellow

TABLE II

Synthesized PCA molecular mass dyed with compound VI

Nos	Polymer sample	Additive concentration, mass %	Representative viscosity	MM
1.	Source—PCA	—	0.61	18135
2.	PCA + Dye VI	0.25	0.62	18610
3.	PCA + Dye VI	0.5	0.61	18225
4.	PCA + Dye VI	1.0	0.59	17460
5.	PCA + Dye VI	2.0	0.60	17840
6.	PCA + Dye VI	5.0	0.45	12340

must be noted that the formation of fibre containing I–YII compounds has been proceeding steadily and no difficulties have arisen when stretching. That is indicative of the fact that the incoropration of bis-aroilenbenzimidazole at the stage of polymerization neither worsens the PCA properties nor it disturbs the process technology of producing PCA fibres.

Table II shows PCA molecular mass data synthesized in the presence of compound VI, which demonstrates that a small quantity of the dye does not affect on MM polymer.

On the other hand, the dyes are stable in the polymer melt except IV, which even at 250°C transforms moulding form of teracotta, though it does not at all influence on the fibre-forming process.

2. PHOTO AND THERMORESISTIVITY OF DYED POLYCAPROMIDE

The breaking of basic macromolecular chain is mainly resposible for the loss of useful properties of PCA during photooxidative degradation. Based on MM values of the polymer before and after photooxidation the number of macrochain breakings has been calculated, PCA samples obtained by incorporating the dye of 0.25–5.0% from the polymer mass into the reactive mass of PCA have been investigated both at the stage of polyamidirization and by direct mixing it with polymer crubs (granulate).

Table III demonstrates the data on the retaining of molecular mass of dyed and undyed PCA fibres before and after irradiation. From Table III it follows that the source-polymer looses over 50% of its initial MM during 24 hrs of irradiation. AU additives exert stabilizing effect which is manifested by retaining MM from 85.6% to 94.3% depending on the structure of the dye. Having compared similar manner "bridged" group compounds of benzoilenbenzimidazole series (I–III) and naphtoilenbenzimidazole series (V–VIII) we have observed that it is a bridge-group that exerts a considerable influence on the stabilizing effect, but not a chromophor part.

It must be noted that stabilizing effect of additives depends on their concentration in the polymer, which is supported by the data in Figure 1. It shows the dependence of PCA macromolecular breaking number on the concentration of compound VI.

TABLE III

Retaining molecular-mass stabilized by bis-aroilenbenzimidazoles of polycaproamide fibres after 24 hrs of irradiation using PRK-2 lamp (additive content 1.0 mass %)

	Representative viscosity Ing/gr		Molecular mass			
Polymer sample	before irriation	after irradiation	before irradiation	after irratiation	Retaining of molecular mass %	Number of breakings
Source—PCA	1.02	0.53	35190	15040	42.7	1.34
PCA + Additive I	1.04	9,95	35900	32250	89.8	0.11
PCA + Additive II	0.97	0.92	32810	30650	93.4	0.07
PCA + Additive III	1.00	0.89	34300	29370	85.6	0.17
PCA + Additive IV	1.10	1.00	38800	34390	88.6	0.13
PCA + Additive V	1.07	1.00	37590	34480	91.7	0.09
PCA + Additive VI	1.02	0.88	35410	33380	94.3	0.06
PCA + Additive VII	1.05	0.97	36700	32810	89.4	0.12

When increasing the additive concentration up to 1 mass % the retaining of molecular mass increases and while further concentration some decreasing is observed. Such a trend of the curve can be accounted for by the fact that when increasing the additive content the light-absorption increases.

Similar results have been gained when physico-mechanical characteristics of stabilizing PCA fibres during photooxidation have been measured. In all the above cases the highest degree of retaining positive properties of the polymer is observed in PCA containing compound VI with 1 mass % concentration. Moreover physical and mechanical features of the polymer practically do not depend on the manner of incorporation of the additives into the polymer. Stabilized fibres have been produced both by incorporating additives at the stage of obtaining polymeric concentrate of the dye and by powdering a polymeric crumbs before melting and moulding.

For the determination of resistivity to thermooxidative destruction the PCA samples have been subjected to the effect of elevated temperatures with dynamic heating in the atmosphere within the intervals of temperature 20–600°C and isothermal heating at temperatures 150°C and 200°C.

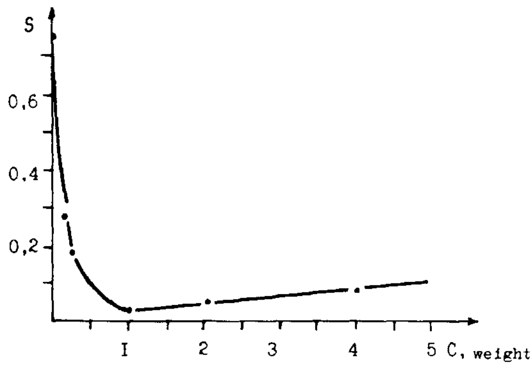


FIGURE 1 Dependence of the number of PCA macromolecular breakings (S) on compound VI concentration during 24 hours irradiation in the atmosphere using Lamp PRK-2.

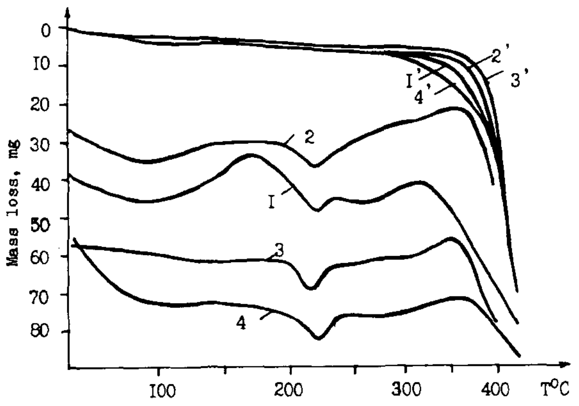


FIGURE 2 Thermogramms of nonstabilized (1, 1') and stabilized PCA fibres by compounds VI—(2, 2'); VII—(3); V—(4) in the atmosphere.

Based on the complex thermogravimetric analysis the study on the effect of bis-aroilenbenzimidazole derivatives upon thermooxidative degradation of PCA during dynamic and isothermal heating (Figures 2 and 3) has been carried out. Having examined the TG curves one could observe the decrease of polymer mass due to the removal of absorption water. This process is characterized by rather a wide exothermal curve peak on DTA within the temperature intervals 75–115°C. Moreover there is a difference in the volume of absorption water in different samples.

A considerable difference in the nature of thermal degradation of dyed and undyed PCA samples has been observed within the temperature intervals 325–360°C, where the process of depolymerization begins. In a source-sample this process begins even at 335°C, while the incorporation of the bis-aroilenbenzimidazole into PCA shifts the temperature of depolymerization by 10–25°C within the range of higher termperature, though in all cases the maximum rate of depolymerization corresponds to 450°C.

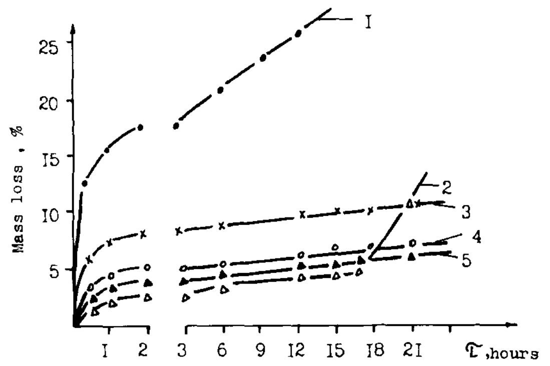


FIGURE 3 Kinetic curves of mass loss of nonstabilized (1) and stabilized PCA fibres by compounds IV—(2); V—(3); VI—(5); VII—(4) in isothermal conditions at T = 200°C in the atmosphere.

The DTA curves within the melting range of the polymer ($T_{\text{melt}} = 215$–$220°\text{C}$) have revealed considerable differences of dyed and undyed samples. In a source-PCA (Figure 2) exoeffect within the termperature interval is 160–215°C, while this effect is practically lacking in dyed samples. This is likely associated with the effect of compounds I–VII on the ordering of PCA super-molecular structure even during its formation, that is well consistent with the data of X-ray structure analysis.

Studies under isothermal conditions have been carried out in the atmosphere at 150°C and 200°C. Kinetic curves of samples mass loss warming-up (Figure 3) show that during 6 hrs an undyed sample loses about 3% of its mass. The induction period is manifested in dyed samples, while it lacks in a source-sample, and the most effect is observed in compounds containing oxygen in a bridge group. Based on the results of studies on photo and thermooxidative degradation of PCA one can draw a conclusion that compounds I–VII posses light and thermoprotective effect which is expressed in increasing photo and thermoresistivity of items manufactured from PCA.

3. MECHANISM OF LIGHT STABILIZING EFFECT OF BIS-AROILENBENZIMIDAZOLES

Taking into consideration the important role played by oxidative processes in light-aging of PCA, and in order to understand the mechanism of light-protecting effect, it has been expedient to investigate the absorption of oxygen by spruce and stabilized PCA fibre during longwave irradiation using filtered light from DRP-1000 Lamp. Since under the influence of longwave light, which is not absorbed by the chromophoric amide group of the polymer, the photooxidation of PCA is determined by an initiating effect of admixtures, products of oxidation, as well as by special additives (pigments, dyes etc.).

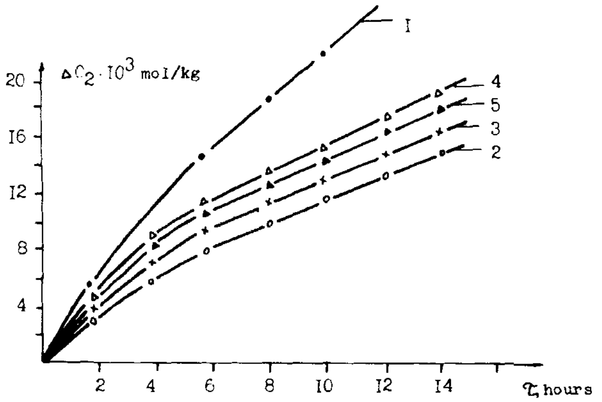


FIGURE 4 Kinetic curves of the absorption of oxygen by PCA samples: source sample (1) and samples containing 1 mass. % of bis-aroilenbenzimidazole derivatives: VI—(2); V—(3); IV—(4); VII—(5).

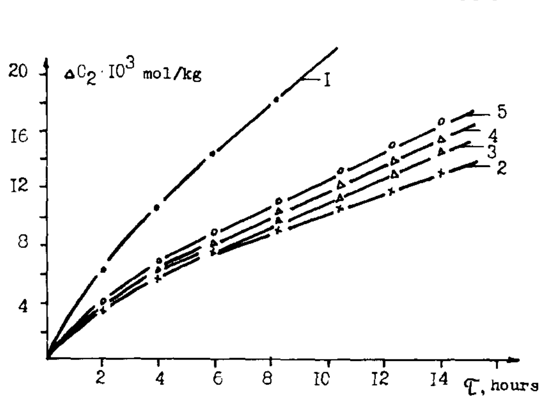


FIGURE 5 Kinetic curves of the absorption of oxygen by PCA samples: by source PCA (1) and PCA containing compound VI in different concentration: 2 mass. %—(2); 1 mass. %—(3); 0.5 mass. %—(4); 0.25 mass. %—(5).

The analysis of the kinetic curves of the absorption of oxygen per mass unit of a polymer at a given temperature depending on the duration of irradiation (Figures 4 and 5) shows that at an initial stage photooxidation proceeds at a considerable speed, but after a certain period of time the above process slows down and finally it enters its operating conditions. Probably at an initial stage of irradiation there takes place oxidation of admixtures or side-products formed in the polymer during its production. It can be supposed that a great deal of role is played here by the formation and establishment of an operating concentration of ketoimide product. According to the recent data the initiating stage of radical transformation of polyamide runs along with the participation of an intermediate product of a *a*-ketoimide structure.

It should be noted that operating conditions in our experiments are established for 3–5 hours. After switching the light off, the oxidating process gradually slows down up to its complete cessation. But the repeat switching on the light brings about the establishments of operating conditions even in half an hour. This is indicative of the fact that photooxidation at its initial stage does not affect upon the further process of PCA oxidation. Therefore for a quantative evaluation of photooxidative resistivity of PCA fibres and films the oxidation rate under operating conditions can be used.

Table IV shows the values of the absorption rate of oxygen obtained during photooxidation destruction of PCA. All the compounds to be used to this or that extent slow down the absorption rate of oxygen (1.8–3.1 times). In this case as to their stabilizing activity depending on the type of a bridge group, the stabilizers are arranged in the following sequence: $A_r\text{—}O\text{—}A_r > A_r\text{—}A_r > A_r\text{—}CH_2\text{—}A_r$. We suppose that such sequence can be accounted for by the total effect of conjugate molecules and their effect of absorption. According to their conjugate effect they have to be arranged in the sequence as $A_r\text{—}A_r > A_r\text{—}O\text{—}A_r > A_r\text{—}CH_2\text{—}A_r$, and proceeding from the absorption spectras they are of $A_r\text{—}CH_2\text{—}A_r > A_r\text{—}O\text{—}A_r > A_r\text{—}A_r$ order. As a consequence bis-aroilenbenzimidazoloxide, occupying in both cases the intermediate position demonstrates the best stabilizing effect.

TABLE IV

Kinetic parameters of the absorption of oxygen by source and stabilized polycaproamide fibres

Polymer samples	C, mass. %	O_2 10^{-3} mol./kg · hr	(screening) γ_S	(braking) γ_B	γ_B/γ_S
Source—PCA	—	2.03	—	—	—
PCA + Compound IV	1.0	1.00	1.43	2.0	1.40
PCA + Compound V	1.0	0.98	1.48	2.0	1.35
PCA + Compound VII	1.00	0.96	1.32	2.1	1.59
PCA + Compound VI	1.0	0.81	1.53	2.5	1.63
PCA + Compound VI	0.25	1.10	1.18	1.8	1.54
PCA + Compound VI	0.5	0.92	1.25	2.2	1.60
PCA + Compound VI	2.0	0.65	1.70	3.1	1.82

Since compounds I–VII absorb the effective light, it has been necessary to estimate contribution by the screening effect to an overall effect of stabilization.

With this end in view the spectra of absorption of PCA solutions containing compounds I–VII have been taken; values of extinction and screening coefficients for a wavelength of the effective light ($\lambda = 365$ nm) have been calculated. The polymer itself within this range absorbs very little.

The comparison of the breaking factors of photooxidation (γ_B), which is determined as the relation between the absorption rate of oxygen by the polymer lacking (WO_2) and in the presence of (WO_2) and screening factors additives (γ_S) shows that the stabilizing effect attained only through screening by additives is less than the stabilizing effect observed (Table IV). Thus the stabilizers under study I–VII protect PCA not only in accordance with the screening mechanism. Other possible mechanism of light-stabilization could be considered as the extinguishing of excited states of a polymer and inhibition of radical processes.

One of the conditions for the process of energy transfer is the shutting down of the spectra of the absorption of an additive by the spectrum of the polymer luminescence, therefore before considering the effect of bis-aroilenbenzimidazole derivatives as extinguishers of excited states of the polymer, it is necessary to investigate the fluorescence of PCA itself. For this purpose PCA film and fibre samples have been subjected to cleaning, photoirradiation for 1–4 hours and heat treatment in the atmosphere at 90–110°C during 4–16 hrs prior to recording fluorescence spectra.

Spectrum data of nonirradiated and not subjected to heat-treatment films of PCA have shown that maximum fluorescence wavelength (λ^{em}_{max}): 375 nm, 425 nm and 430 nm correspond to different wavelength of the exciting light (290 nm, 350 nm, and 365 nm), within 430 nm band the intensity being two times higher than the others. This is indicative of the presence of several glowing fluorescence centres in PCA which can be associated both with impurities and products of polymer oxidation during its formation. Photo and heat treatment of the PCA film has resulted in a sharp increase of the peak intensity $\lambda^{em}_{max} = 430$ nm having subsequently returned to operating conditions. That confirms the hypothesis explaining PCA fluorescence by the formation of a ketoimidic compound in the polymer.

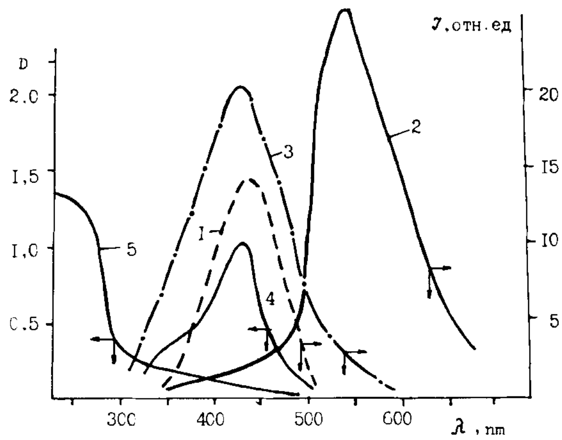


FIGURE 6 Spectral and luminescence properties of source PCA: spectra of: absorption (5); fluorescence (1) and PCA containing 1 mass. % of compound VI: spectra of: absorption (4); fluorescence (2); excitation (3) at excit = 365 nm.

Sharp decrease of the PCA fluorescence intensity is observed in PCA samples containing bis-aroilenbenzimidazole additives. With the increase of additive concentration the intensity of a polymer fluorescence also decreases down to its complete disappearence. Figure 6 shows the absorption spectra and fluorescence of the source and dyed PCA by compound VI. Characteristic fluorescence maximum of the source PCA $\lambda_{max}^{em} = 428$ nm (curve 1) is lacking in the dyed polymer (curve 2). At the same time there appears a new peak $\lambda_{max}^{em} = 530$ nm corresponding to the spectrum emitted by compound VI.

It should be noted that the excitation spectrum of the dyed PCA (curve 3) fully coincides with the fluorescence spectrum of the source PCA. Similar results have been obtained during the study of spectra of absorption, fluorescence and excitation of films and solutions of dyed and non-dyed PCA samples, as well as during the application of other dyes-stabilizer of that series.

The absence of fluorescence of dyed PCA in the spectrum, containing I mass % ($1 \cdot 8$–10^{-2} mol/kg) of the dye with the peak $\lambda_{max}^{em} = 428$ nm can be accounted for by a great fluorescence intensity of the dye itself. Since under such relatively high concentration of dye one cannot unambiguously judge about the extinguishing of PCA fluorescence, the samples with less additive concentration have been prepared. Complete disappearance of the PCA fluorescence maximum and the appearence of a true PCA fluorescence have been observed during additive concentration being $3.5 \cdot 10^{-3}$ mol/kg and higher therewith gradually decreasing the dye fluorescence intensity.

The whole complex of results obtained shows that:

— protective effects observed are not reduced to screening;

— dyes used undoubtedly play the role of quenchers of excited polymer states, but protection in addition to screening in these conditions cannot be provided by extinguishing only.