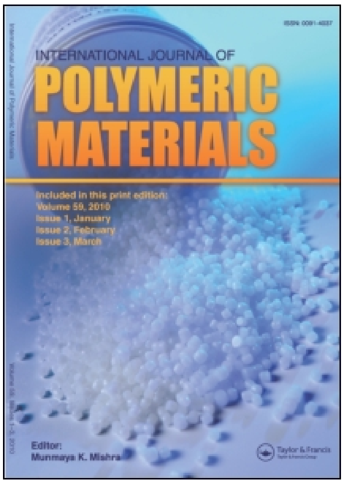

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Photostabilizing Thermostable Dyes for Polycaproamide and Polyethylenterephthalate

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Photostabilizing Thermostable Dyes for Polycaproamide and Polyethylenterephthalate

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Photostabilizing properties of thermostable dyes and bulk-dyed polymeric materials are considered. Photostabilizing dyes based on aroylenbenzimidazol derivatives used in polycaproamide and polyethylenterephthalate are discussed. The photostabilizing action of the above dyes is related to their own photostability and is manifested through UV-shielding, quenching of excited states of the polymer and inhibition of photooxidative reactions.

KEY WORDS Dyes, polycaproxamide, polyethylenterephthalate, thermal stability, photostability.

INTRODUCTION

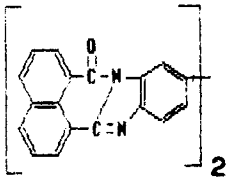
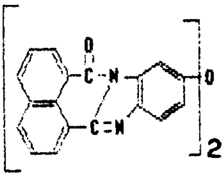
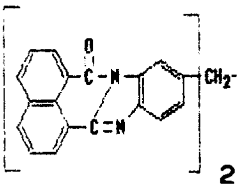
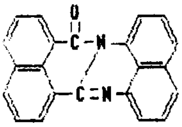
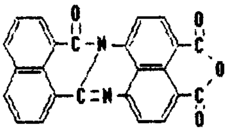
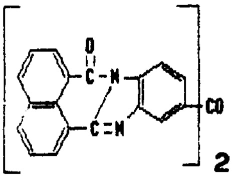
The mutual influence in the "dye-polymer" system is known to take place during the photooxidative degradation of dyed fiber forming polymers, so that the dye may cause either a stabilizing or a sensibilizing effect on the degradation of polymer materials.[1,2] Thermoplastic fiber-forming polymers such as polycaproamide (PCA) and polyethylenterephthalate (PET) are retreated into the fiber from the melts. Hence, the most ecologically clean method of imparting the dye to the fiber is by means of bulk dyeing, which in its turn demands high thermostability of dyeing agents. Benzimidazole derivatives are recognized stabilizing agents of polymeric materials. We were attracted by thermostable aroylenbenzimidazols which can be used for dyeing.

This paper presents results of an investigation of thermostabilizing properties of some naphthoylenbenzimidazoles that are thermostable dyeing agents for bulk dyeing of PCA and PET. The general method of their synthesis is designed on the basis of bicyclic bis(o-nytroanylines) and corresponding anhydrides of tetracarbonic acids of naphtalene.[3,4]

Characteristics of the investigation naphthoylenbenzimidazoles are presented in Table I.

TABLE I

The characteristics of the tested naphthoylenbenzimidazols

Compound	Structure	T melt	T decomp	MM	Abs max	Emis max
I		435–437	588	538	425	510
II		335–337	395	554	418	525
III		295–296	370	552	415	530
IV		293–295	375	320	460	480
V		433–436	538	342	282	310
VI		337–339	395	566	425	510

1. PHOTOSTABILIZING THERMOSTABLE DYEING AGENTS OF THE POLYCAPROAMIDE

The range of dyeing agents having thermostable properties in relation to the corrosive reductive medium of the PCA is rather limited. To solve this problem we used in our investigation compounds I–V, which blended satisfactorily with the polymer melt and produced a blended evenly-dyed PCA fiber. The fibers, which contained 0.5–2.0% dye, were then irradiated with the UV-light of the medium-pressure mercury-quartz lamp PRC-2.

The presented data (Table II) on the molecular mass and physico-chemical factors of dyed and undyed PCA fiber before and after the irradiation show a significant increase of photooxidative stability of the dyed PCA fiber. At the same time physico-mechanical factors are independent of the way the additive is introduced. For example, the fiber containing 0.6% by weight of compound III was obtained using a polymer concentrate of the dyeing agent synthesized by polyamidation, whereas in other cases the dyed fibers were obtained using conventional techniques, such as introducing dyeing agent III to the polymer melt. The stabilizing effect of III on the UV-irradiation depends on its concentration. This effect is explained by the fact that the increase of additives concentration provides: a) the absorption of photons due to the increase of the concentration of chromophore groups; b) the change of overmolecular arrangement of the polymer itself.

The latter hypothesis is confirmed by electron-microscopy. Plastic and spherolytic formations can be seen on the photographs of the dyed fiber, giving it a more ordered overmolecular structure, which positively affects the photooxidative stability of the polymer (Figure 1).

The absence of the crystal structure in undyed samples is associated with the fact that derivatives of bis-naphthoylenbenzimidazoles may play a peculiar role as crystal nuclei, providing a change of molecular orientation in the fiber during its formation, i.e. when the overmolecular structure characteristic of the oriented state begins to form.

These conclusions are confirmed by the data of large-angle ionization meridian X-rayograms (Figure 2). The analysis reveals the identity of diffraction maxima which are the evidence of the constant character of interplane distances of the polymer crystallites on addition of bis-aroylenbenzimidazoles, i.e. the additives are introduced into the amorphous region, resulting in packing of the structure. Some

TABLE II

The conservation of molecular weight and physico-mechanical properties of PCA-fibers stabilized by bis(aroylenbenzimidazols) after 24 hours irradiation by UV-lamp PRC-2

Samples	[η], dl/g	M.M	Breaking tension σ, MPa	Breaking elongation ε, %	Conservation, %		
					M.M	Tension	Elongation
PCA	1,02/0,53	35000/15040	325,68/154,99	122/86	42.7	47.60	70.5
PCA + I	1,07/1,00	37590/33480	331,38/302,11	115/104	91.7	91.17	89.6
PCA + II	1,02/0,98	35410/33880	341,73/317,12	116/106	94.3	92.80	91.4
PCA + III	1,05/0,97	36700/32810	335,83/294,86	110/99	89.4	87.80	90.0

Note. The numerator, represent the value of parameters before and after irradiation.

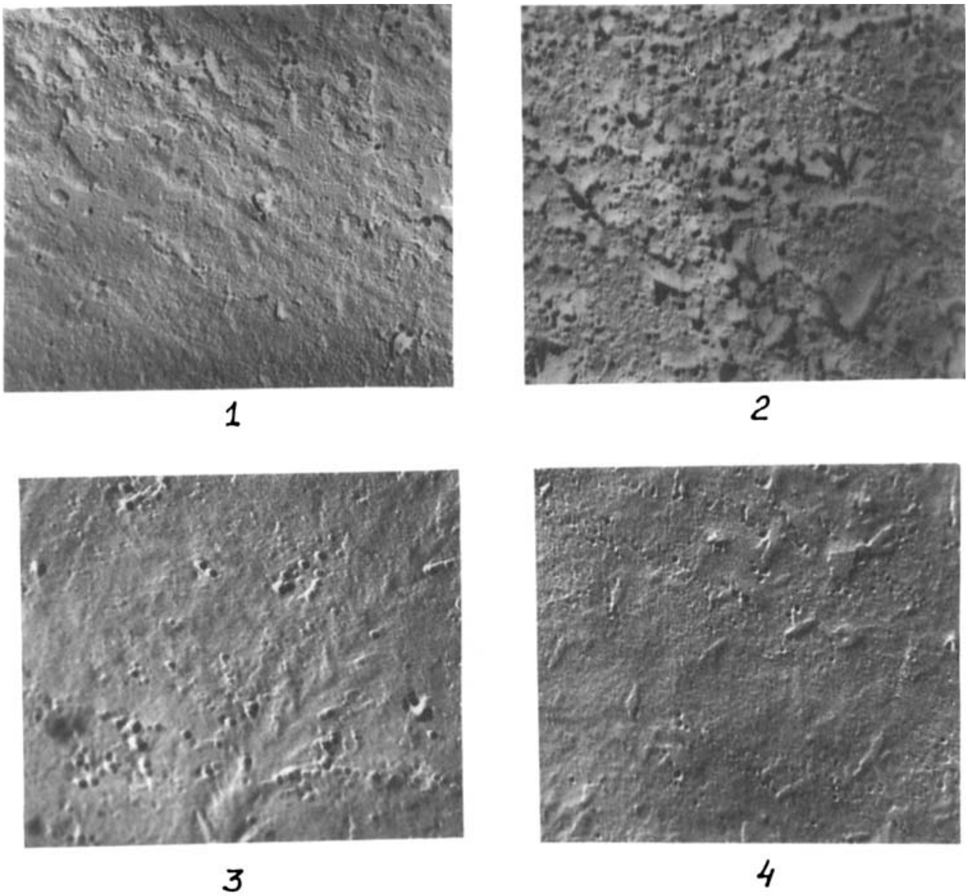


FIGURE 1 Electron micrographs of PCA-fibers. 1—initial fiber; 2—the same UV-irradiated fibers; 3—fiber dyed by III; 4—the same, UV-irradiated.

increase of the crystallinity upon UV-irradiation is associated with the adjustment (contraction) of the inhibitor to polymer crystallites as well as with a possible "burn-out" of the amorphous portion of the polymer, resulting in the packing of the structure.

Thus, the addition of bis-aroylenbenzimidazoles provides an improvement of overmolecular arrangement of PCA products, thereby providing enhanced photooxidative stability.

The stabilizing effect attributable only to shielding by additives is found to be small compared to the total effect of stabilization obtained using bis-naphthoylenbenzimidazoles. Hence, the investigated stabilizers I–III protect the PCA not only by the shielding mechanism.[5] Other possible mechanisms of stabilization may be presented, such as quenching of PCA excited states and inhibiting radical processes. Bis-aroylenmidazoles exhibit fluorescence similar to some other benzimidazole derivatives, with UV-irradiation allowing for quenching of the polymer excited states.

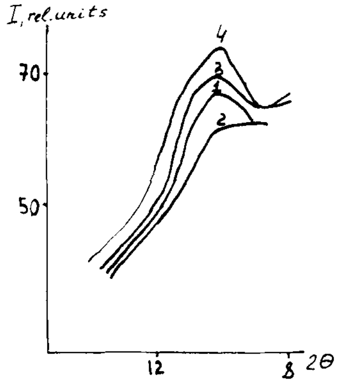


FIGURE 2 The large-angle ionization meridian X-rayograms PCA-fibers; 1—initial, unirradiated fiber; 2—the same, irradiated for 10 hours; 3—unirradiated fiber dyed by III; 4—the same, irradiated for 10 hours.

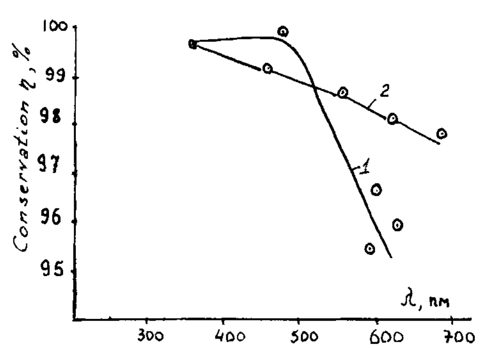


FIGURE 3 The conservation of specific viscosity of dyed (1) and undyed (2) PCA-fibers with the wavelength of the light irradiation for 45 days.

The PCA products being subjected to a wide-spectrum UV-irradiation, it was interesting to investigate the effect of the long-wavelength irradiation on dyed aroylenbenzimidazole compounds of the PCA fiber. It should be noted that additives I–III essentially do not absorb the effective irradiation in the region with $\lambda = 480$ nm.

The dependence of viscosity variation of undyed PCA fiber and those dyed by II with the wavelength of the light irradiation is shown in Figure 3. Depending on the wavelength of the effective irradiation, the dye III is seen to exhibit both the stabilizing and the sensibilizing properties.

On irradiation of the dyed PCA fiber with the full spectrum of the daylight lamp LCD-80 it is found that increase of the exposure time results in decrease of the absorption intensity of the additive at $\lambda = 420$ nm, and the dye is completely consumed within 8 days under irradiation.

On the basis of the above findings it can be concluded that the total effect of quenching, shielding, and sensibilization is exhibited in the UV-region. The dyes act as sensibilizers outside the absorption spectrum of the aroylenbenzimidazol itself where shielding and quenching effects are not exhibited. The latter conclusion

TABLE III

The effect of irradiation by UV- and daylight on the viscosity properties of PCA-fibers

Irradiation source	PCA-fiber	Specific viscosity, η Before irradiation	After irradiation	Conservation of η, %
Daylight lamp, LDC-60	Initial	2.16	1.15	53.24
	Dyed by IV	2.18	1.69	77.52
	Dyed by II	2.17	0.88	39.36
UV-mercury-quartz, lamp, PRK-2	Initial	2.16	0.93	43.18
	Dyed by IV	2.18	1.22	55.96
	Dyed by II	2.17	2.04	94.30

was confirmed during the comparative study of the effect of additives, III and IV, identical to each other by structural features except for the fact that the absorption of the additive IV occurs in the longer wavelength region with $\lambda_{\text{abs.}} = 460-560$ nm.

Table III shows that at long wavelength irradiation (the daylight lamp LCD-80), the PCA fiber dyed by IV exhibits stabilizing action twice that for the sample dyed by II.

2. PHOTOSTABILIZING THERMOSTABLE DYES FOR POLYETHYLENTEREPHTHALATE

The obtained method of dyeing and stabilization of polyamides by derivatives (aroylenbenzimidazoles) turned out to be general enough. This conclusion is based on the results of investigating polymer composition properties based on the PET and compounds IV–VI (Table IV).

To describe sorption processes the following equation is used:

$$a = a_0 \exp[-(-PTh_i/E)^{0.7} - \alpha(T - T_0)],$$

TABLE IV

The conservation of specific viscosity and the sorption constants of the irradiated PET-fibers

Dye	Concentration, % mass	Conservation η, %	Unirradiated fiber a_0, %	Unirradiated fiber E, kJ/mol	Irradiated fiber a_0, %	Irradiated fiber E, kJ/mol
II	3.0	—	3.74	2.60	0.97	2.38
III	3.0	—	2.70	1.53	1.54	3.53
V	0.5	79.9	—	—	—	—
	1.0	83.4	—	—	—	—
	3.0	90.5	—	—	—	—
VI	1.0	82.6	2.98	2.40	1.34	1.59
—	0.0	71.3	1.41	1.60	—	—

where a is the equilibrium sorption,
a_0 is the maximum sorption from the vapor phase,
h_i is the relative vapor pressure of the sorbate,
E is the characteristic sorption energy.

This equation was selected because it satisfactorily describes sorption isotherms not only for water but organic matter as well with the mean-square error $\delta < 13\%$, and was successfully used to calculate sorption isothermas in PET-methanol, polyethylenesebacynate-water, and PET-water systems.[6,7]

The sorption constants of both irradiated and non-irradiated dyed PET fiber calculated from sorption isotherms for water (Table IV) by almost all tested additives are shown to be higher compared to the initial samples, which may owe to the plasticizing action of the dye. Irradiation significantly lowers the maximum sorption of the fiber, which may be caused either by packing of the polymer structure during the irradiation similar to the packing during the heat treatment or by the structurization which occurs during the irradiation by hard rays similar to the structurization in other polymers, polystyrene in particular.

The frequency dependence investigation of dielectric characteristics showed the maximum dielectric losses of the initial PET to lie in the 1 kHz range, whereas that of unmodified samples is shifted insignificantly towards higher frequencies and decreased in the absolute value. The maximum of the dielectric loss tangent related to the dipole-symmetry mobility for the initial PET is observed at 115°C. The position of this maximum on the temperature axis is unchanged by introduction of 0.1% of aroylenbenzimidazole while its absolute value is decreased by 0.5. The subsequent increase of the modifier concentration to 0.5% and 3% results in a sudden increase of $tg\delta$ and the down-shift of the maximum by 10°C and 25°C, respectively, revealing its plasticizing action.[8]

Despite some deterioration of dielectric properties and the increase of the electric conductivity, the modification of the polymer results in a significant improvement of the mechanical properties ($\sigma_{\text{break.}}$ and $P_{\text{break.}}$ are doubled), with the highest stability and break-up strain observed for samples containing 0.5% of naphthoylenbenzimidazols (Figure 4, where $P = \sigma_0/\sigma_{\text{st.}}\ 100\%$).

A significant increase of stability of modified films is also explained by the

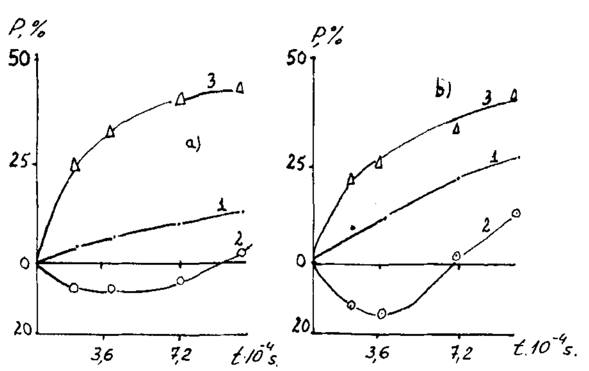


FIGURE 4 The dependence of the mechanical properties PET-fibers from the irradiation time: (a) λ = 254 nm; (b) λ = 313 nm. 1—initial PET fiber; 2—PET + 1% dye V; 3—PET + 1% dye VI.

additive's plasticizing action, which favors an even distribution of stresses and orientational hardening of the polymer.[9] The case of PET is an exception to the observed dependence of the incident light on the total effect of stabilization for PCA. This note provides a conclusion on the effect of the polymer environment on the type of the stabilizer action.

Thus, the potential of naphthoylenbenzimidazoles derivatives as thermostable dyes for both PCA and PET has been demonstrated.

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