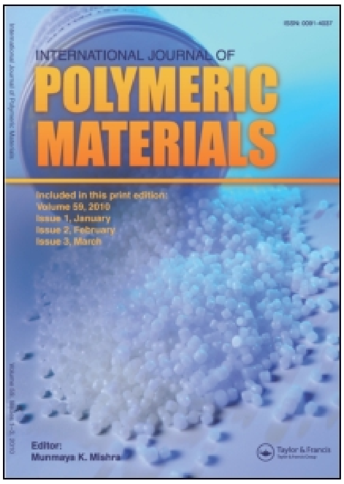

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The Chemical Polyfunctional Additives for the Heterochain Polymers

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The Chemical Polyfunctional Additives for the Heterochain Polymers

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The possibility of simultaneous dyeing and stabilizing against UV-radiation of a variety of polymers is explored.

KEY WORDS Polyfunctional additives, dyeing, cellulose acetate

INTRODUCTION

The heterochain polymers, cellulose acetate (CA), polyamides, polyesters, are now widely used in various industrial branches such as fibers, films, and construction materials.

Increases in the production of these polymers is limited by the raw material stocks and energy resources. Consequently "prolongation of the life" of polymer goods is equivalent to increasing their production.

Since during molding and use, the heterochain polymers are subjected to various actions which deteriorate their performance characteristics, an investigation of the mechanism of these actions on the polymers is one of the important problems of polymer science.

There are various known stabilization mechanisms: filtration of UV-radiation, inhibition of the reactions of degradation, neutralization of products of degradation.[1,2]

Stabilization is realized by two methods: 1) by the physical and chemical modification of polymers; 2) by the addition of special additives (stabilizers).

In the first case the physical/mechanical properties often deterioriate and changes in the technology of polymer manufacture are required.

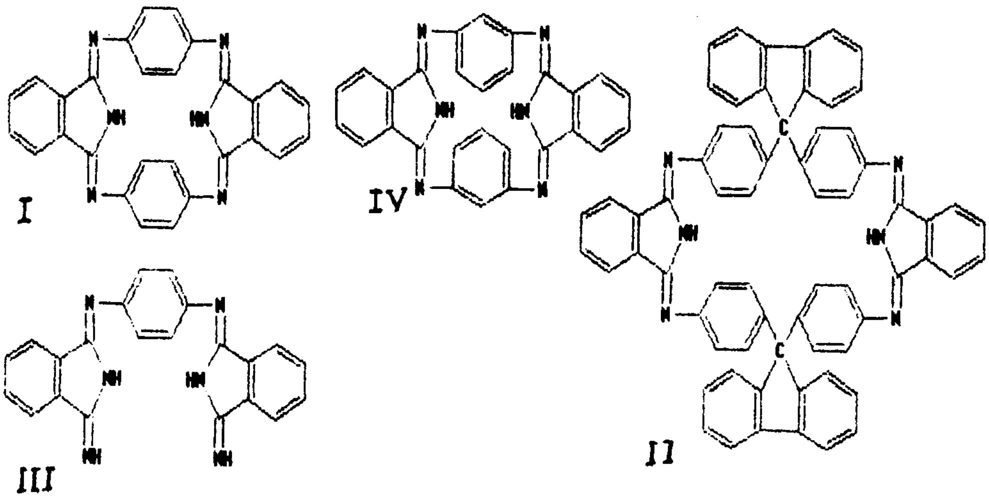
The second method supposes the creation of polymer compositions with the special additives, small amounts of which inhibit degradation. In that case, the problems of additive selection and their compatibility with polymer solution or melts arise.

The application of stabilizing additives has great advantages, since it does not require changes to the technology of polymer production. In this connection the creation of polymer compositions with polyfunctional additives (stabilizers, dyes, antistatics, plasticizers, etc.) is of great interest. The search for these chemical additives is a serious scientific problem. Our attention was attracted to the chemical additives, namely stabilizers on the basis of dyes.

The aim of this article is an investigation of the photo- and thermostabilizing action of a new polyconjugated chemical additive on heterochain polymers.

MACROCYCLIC DYES AS CELLULOSE DIACETATE PHOTOSTABILIZERS

The macrocyclic dyes, derivatives of hexazocyclanes (HC), dye cellulose diacetate (CDA) various colours from yellow to brown. They are quite compatible with CDA, without deteriorating the film properties at concentration up to 5–7%. At the same time HC have a stabilizing action on CDA photodegradation. We investigated the rate of photo-oxidative degradation of CDA with HC incorporated based on phthalodinitrile and *p*- and *m*-phenylene diamine. Among various types of HC available, the HC's having the following structures were chosen as CDA stabilizers:



I IV II III

Hexazocyclane I and its isomer IV are conjugated planar systems, compound II is an unconjugated HC based on phthalodinitrile and 9,9-bis(-4-dianiline)fluorene. To ascertain the impact of the structure of the macrocyclic stabilizer on its properties we also investigated the products of linear condensation of phthalodinitrile and *p*-phenylene diamine (III).[3]

The total effect of the rise in the light stability $A = w_0/w_s \cdot i_\varphi$, where w_0 and w_s are the formation rates of acetic acid (the main volatile product of CDA degradation under the action of UV-irradiation) with and without the presence of a stabilizer; i_φ is the coefficient that shows to what extent the stabilizer decreases the light absorption of the polymer. Since the formation rate of acetic acid is proportional to the light intensity, at $A = 1$ the dye acts according to a screening mechanism; at $A < 1$ by a sensitizing mechanism and if $A > 1$ there are complementing mechanisms over the screening.

In Figure 1 it is seen, that at concentrations <1% wt. HC-I acts as a UV-screen, because $A = 1$. At a higher concentration the efficiency is 1.5–3 times lower than the screening effect, indicative of a sensitizing action of the additive.

TABLE I

Dependence of the total rise of light stability of the composition of the structure HC (5% mass)

Compound	HC-I	HC-II	HC-III	HC-IV
A	0.40	0.31	0.21	0.67

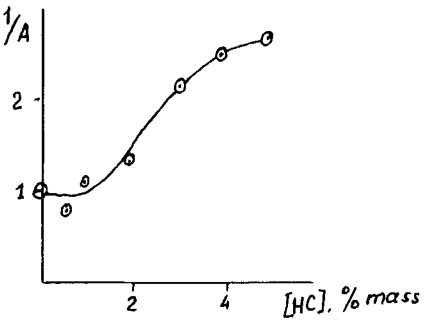
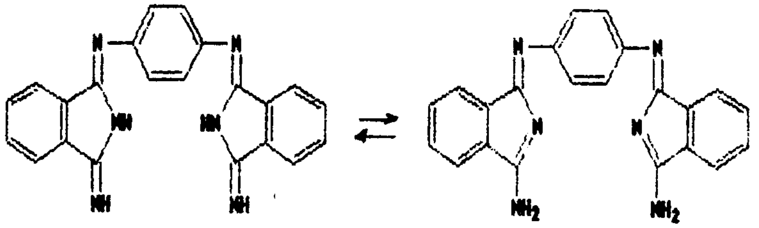


FIGURE 1 The influence of HC concentration on photodegradation CDA.

It is seen from Table I that for all the investigated compounds the value *A* is <1. This gives cause to believe that the stabilizers act not only as UV-screens but also as photosensitizers. The highest photosensitizing activity is manifested by the photosensitizer III. This seems to be explained by the fact that compound III has two resonance states, in one of which it contains free amino groups:



These amino groups act as photostabilizers of CDA to photodegradation. This agrees with the data from the literature.[2]

By its light stabilizing activity, HC-II is superior to compound III but inferior to HC-I and HC-IV. That is probably associated with a shorter length of the conjugated chain and a decrease in the aromaticity of the system in the case of HC-II.

The most effective photostabilizers are HC-I and HC-IV, which have high light stabilizing activity that can be caused by both UV-screening and inhibition effects.

As we have seen earlier,[4] the HC-I stabilizer does not affect the CDA chain oxidation parameter, i.e., it is not an inhibitor that interacts with the polymer radicals and in that time the photoinitiation quantum yield P_i sharply decreases in the presence of HC-I. This shows that the transition from pure CDA to the stabilized CDA leads to a change in the photoinitiation mechanism: the macrocyclic dye becomes a photoinitiator instead of CDA. However, a marked decrease in P_i in the presence of HC-I is responsible for the total light protection effect.

The HC-IV, which is isomeric to HC-I, was obtained on the basis of phthalodinitrile and *m*-phenylenediamine and has a higher stabilizing activity. After 48 h of UV-irradiation of CDA, containing 3% wt of these additives, the retention of viscosity is 82.2% for HC-IV and 65.8% for HC-I. The decrease in acetic acid formation rate calculated from w_0/w_s is 4.8 (HC-IV) and 2.8 (HC-I), i.e., in the use of HC-IV acetic acid the formation rate is 1.7 times lower than for CDA stabilized by HC-I.

This difference seems to be explained by the greater structure planarity of HC-IV than HC-I, as follows from the computer models. The planar structure of HC-IV must be promoted by the HC-IV molecule's aggregation, which leads to a very effective quench of the excited states. The search for effective photostabilizers should be carried out among the planar macrocyclic aromatic compounds.

THE PHOTOSTABILIZATION OF CDA BY THE POLYCONJUGATED AZOMETHYNE DYES

The use of low molecular weight stabilizers has a very significant disadvantage. They do not provide a long protective period because of their rapid loss under UV-radiation, due to washing from the polymer and volatility.

In this connection the using of the high molecular stabilizers is very interesting. Among these compounds our attention was attracted to the polyconjugated azomethyn compounds (PAC), which characteristics are given in Table II.

The CDA photo transformations under the UV-irradiation are investigated by the acetic acid formation rate at the absence and the presence of PAC (Figure 2).

Depending on PAC-V concentration, the index $A = 1.3-1.7$, indicating some additional light stabilizing mechanism except UV-screening.

As follows from the above (Figure 2), the PAC light stabilizing properties are correlated to the molecular weight and effective conjugation.

Investigation of the kinetics of the radical processes showed that all PAC are polymerization inhibitors. This inhibiting activity of the oligomeric azomethyns is correlated with shifting of the maximum for the electronic absorption spectra to the long wavelength region.

As PAC contains *p*-electrons of *N*-heteroatoms, in the conjugation chain an electronic density redistribution occurs and the value of the effective conjugation decreases, explaining the hypsochromic shifting with increasing conjugation chain length.

It was established that the additional stabilizing effect of PAC is connected with the inhibition of CDA radical-chain degradation reactions and the increasing of the conjugation efficiency in the following order PAC-VII < PAC-V < PAC-III.

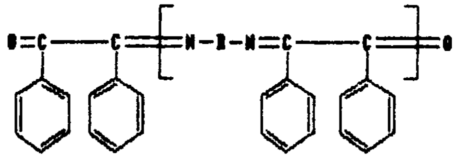
With the aid of PAC, which is quite compatible with CDA in a common solvent, bulk dyed acetate fibers were obtained.

Depending on PCA type and concentration the fibers were dyed an olive color of various shades.[5]

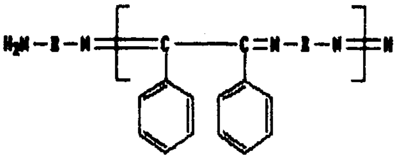
TABLE II

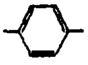
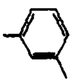
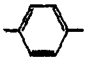
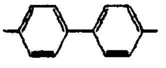
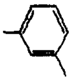
The structure and properties of PAC

A



B



PAC	Structure	R	MM	T melt., °C	λ max. in C_2H_5OH	Retention of η_{sp}, %
I	A		400	140–145	261; 360	81.0
II	A		800	180–186	266; 350	85.0
III	A		1400	116–120	352	82.5
IV	B		600	110–115	253; 372	84.0
V	B		100	90–95	263; 368	
VI	B		1200	210–215	258; 372	77.0
VII	B		1680	103–105	277; 315	79.8

AROYLENEBENZIMIDAZOLES AS DYES AND STABILIZERS OF POLYCAPROAMIDE AND POLYETHYLENTEREPHTALATE

Thermoplastic fiber-forming polymers such as polycaproamide (PCA) and polyethyleneterephtalate (PETP) are converted into fibers from melts. Hence, the most ecologically clean method is to impart the dye to the fiber by means of bulk dyeing. This in turn demands high thermostability of the dyeing agents. Benzimidazole derivatives are known as stabilizing agents for polymers. We were attracted by thermostable aroylenebenzimidazols (ABI) which act as dyeing materials.

The general method of their synthesis is based on bicyclic bis-(*o*-nitroanilines) and the corresponding anhydrides of tetracarbonic acids of naphthalene.[6] Characteristics of the investigated naphthoylenebenzimidazoles are presented in Table III.

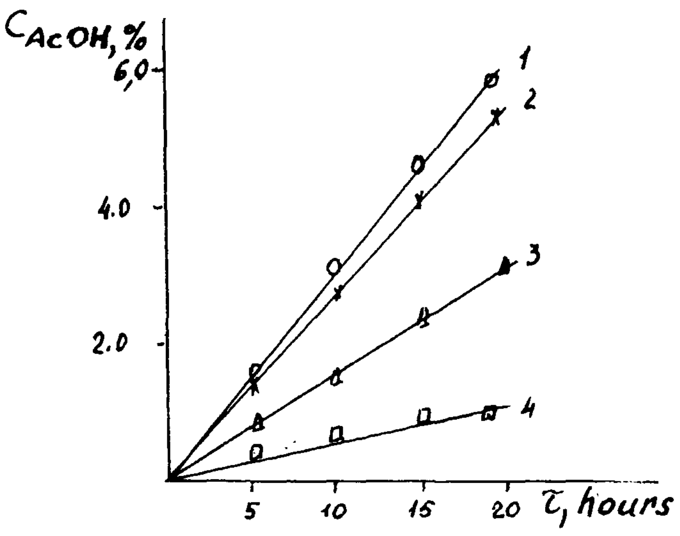


FIGURE 2 The dependence of acetic acid yield from the UV-irradiation dyed CDA films time. 1—initial CDA; 2—dyed by PAC-I; 3—dyed by PAC-IV; 4—dyed by PAC-V.

The data on the molecular weight and retention of physical mechanical properties for dyed and undyed PCA fiber prior to and after the UV-irradiation (Table IV) show a significant increase in photo-oxidative stability of the dyed PCA fibers. At the same time physical mechanical factors are independent of the way the additive is introduced to the fiber. Fiber containing 0.6% by weight ABI-III were obtained using a polymer concentrate of the dyeing agent synthesized by means of polyamidation, whereas other compounds were obtained using conventional techniques, i.e., by introducing ABI to the polymer melt.

With the aim of investigating the changes in PCA fiber amorphous-crystalline structure an X-ray study of the initial and dyed by ABI-VI PCA-fibers was carried out.

High angle X-rayogram data are shown in Table V.

The analysis reveals the identity of diffraction maxima which is evidence for the constant character of the 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 increase in the crystallinity on UV-irradiation is associated with the adjustment of the inhibitor to polymer crystallites (the contraction) as well as with a possible "burn-out" of the amorphous portion of the polymer resulting in packing of the structure.

The small angle meridianal measurement results indicate the absence of small angle diffraction maxima testifying to the absence of high-pèriodic structure, i.e., in this case there is no regular alteration to the crystalline and amorphous regions along the fiber axis. The presence of small angle diffusion dispersion indicates submicroemptiness (SME) in fiber. The results of small angle X-ray measurements are shown in Table VI, which shows that the large SME have sizes 260–290 Å and fine SME 60–80 Å with a concentration of 10^{14} and 10^{15} cm^{-3}, respectively.

The data of Table VI shows that the sizes and volume of a large SME upon the

TABLE III

Structure and properties of the bis-aroylenebenzimidazol derivatives

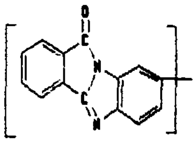
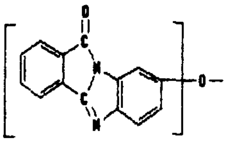
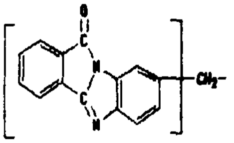
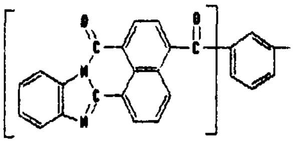
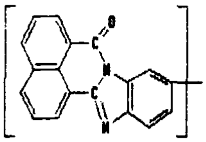
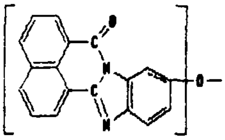
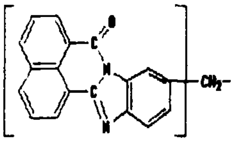
ABI	Structure	T melt., °C	T decomp., °C	MM	λ max. in DMFA
I		435	454	442	282
II		336	395	458	325
III		294	370	456	355
IV		303	386	639	430
V		435	588	538	425
VI		335	395	554	418
VII		295	370	552	415

TABLE III (*Continued*)

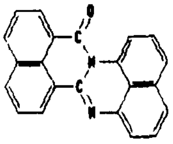
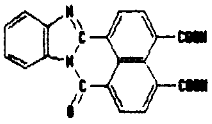
ABI	Structure	T melt., °C	T decomp., °C	MM	λ max. in DMFA
VIII		—	358	324	460
IX		—	320	342	420

TABLE IV

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

PCA with additive	Retention, %		
	MM	Tension	Elongation
Initial	42.7	47.60	70.5
ABI-I	91.7	91.17	89.6
ABI-II	94.3	92.80	91.4
ABI-III	89.4	87.80	90.0

TABLE V

X-rayogramms data of dyed by ABI-VI and initial PCA-fibers

The structural characteristics	PCA-fiber	
	Dyed	Initial
Intensity of diffraction maxima (relative units)	40	59
Scattering angle 2θ	10 30′	10 40′
The crystallites disorientation middle angle $\Delta\varphi$ meas.	150	130
The rate of crystallinity, %	61	85
Sizes of the crystallites:		
longitudinal h_k, Å	85	102
cross D_k, Å	50	52

dyeing of fiber decreases. This testifies that the molecules of dye are incorporated into the SME pores. The dye is incorporated into the fine SME with a decrease of the fine SME concentration for industrial fiber by 20 times and for the laboratory sample by 5 fold.

TABLE VI

The results of small angle X-ray measurements of initial and dyed by ABI-VI PCA fibers

	Large SME			Fine SME		
PCA-fiber	SME size, Å	SME vol., sm^{-3} 10^{17}	SME conc., sm^{-3} 10^{14}	SME size, Å	SME vol., sm^{-2} 10^{19}	SME conc., sm^{-3} 10^{15}
Industrial	282	1.18	3.14	61	1.24	47.70
Initial dyed	264	0.96	3.50	69	1.73	2.23
Laboratorial	288	1.25	2.26	79	2.58	11.30
Initial dyed	260	0.93	3.38	69	1.73	2.23

TABLE VII

The physical mechanical properties of dyed and initial PCA-fiber before and after 24 hours UV-irradiation

		Breaking tensity MPa		Breaking elongation %		Retention %	
PCA-fiber	Conc. of ABI-VI, %	Before irrad.	After irrad.	Before irrad.	After irrad.	Tensity	Elongat.
Initial	—	325.68	154.99	122	86	47.6	70.5
Dyed by	0.5	240.76	285.69	130	98	83.8	75.4
ABI-VI	1.0	341.73	317.12	116	106	92.8	91.4

TABLE VIII

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

		Spec. viscosity		
Irradiation source	PCA-fiber	Before irrad.	After irrad.	Retention of η_{sp}., %
Daylight lamp	Initial	2.16	1.15	53.24
	Dyed by ABI-VIII	2.18	1.69	77.52
LDC-60	Dyed by ABI-VI	2.17	0.88	39.36
UV-mercury-quartz lamp	Initial	2.16	0.93	43.18
	Dyed by ABI-VIII	2.18	1.22	55.96
PRK-2	Dyed by ABI-VI	2.17	2.04	94.30

At the same time the dye is incorporated into the fine SME, filling in pores and promoting fiber strengthening, it also influences photo-oxidative stability of the PCA-fibers. These data are confirmed by the results of physical mechanical investigations (Table VII) showing that dyed fibers have a best photo-oxidative stability than the undyed ones.

The dye molecules filling the SME space are linked with the macromolecules by the physical chemical forces. Therefore, at the loading of the dyed fiber, the load distribution on the fiber is equal along the cross-section. That causes the fiber to be strengthened. The data of Table VII show that the introduction to PCA of the dye ABI-VI in a concentration of 0.5–1.0 wt% leads to an essential increase of the fiber tensile strength and that is displayed following UV-irradiation.

TABLE IX

The retention of specific viscosity and the sorption constants of the irradiated PETP-fibers

			Unirradiated fiber		Irradiated fiber	
ABI	Concentration, % mass	Retention η_{sp}., %	*a*, %	*E*, kJ/mol	*a*, %	*E*, kJ/mol
—	0.0	71.3	1.41	1.60	—	—
IV	1.0	82.6	2.98	2.40	1.34	1.59
VI	3.0	—	3.74	2.60	0.97	2.38
VII	3.0	—	2.70	1.53	1.54	3.53
IX	0.5	79.9	—	—	—	—
	1.0	83.4	—	—	—	—
	3.0	90.5	—	—	—	—

Thus, the addition of bis-aroylenbenzimidaoles provides an improvement to supermolecular arrangements of PCA products which, in turn, improve the photooxidative stability thereof.

Hence, the investigated ABI-stabilizers protect the PCA not by a screening mechanism only. Bis-aroylenimidazoles fluoresce similar to some other benzimidazole derivatives effected by UV-irradiation, resulting in the possibility of quenching of the polymer excited states.[7]

The dye ABI-VI displays both stabilizing and sensitizing properties depending on the light wavelength. On irradiation of the dyed PCA fiber with the full spectrum of a daylight lamp it is found that for an increase in the exposure time there results a decrease in the absorption intensity of ABI-VI at λ = 420 nm, and the dye is completely consumed within 8 days under irradiation.

On the basis of the above facts it can be concluded that the total effect of quenching, screening and sensitization is exhibited in the UV-region. The aroylenebenzimidazoles act as sensitizers outside its own absorption spectrum, where screening and quenching effects are not exhibited. The latter conclusion was confirmed during a comparative study of the effects of additives ABI-VI and ABI-VIII, which are similar to each other by structural features except for the fact that the absorption of the ABI-VIII occurs in the longer wavelength region with λ = 460–569 nm.

It can be seen from Table VIII that for long wavelength irradiation (daylight lamp LCD-80) of the PCA fiber dyed by ABI-VI, a stabilizing action is observed whereas this factor is twice as low for a sample dyed by ABI-VIII.

The obtained method of dyeing and stabilizing the thermoplastic polymers by aroylenebenzimidazoles derivatives turned out to be universal. This conclusion is based on the investigation results of the properties of the polymer composition based on PETP and ABI-IV, VI, VII and IX (Table IX).

The sorption constants of both irradiated and non-irradiated dyed PETP fiber calculated from sorption isotherms for water (Table IX) are shown to be higher compared to the initial ones for almost all dyed samples. This may be associated with the plastifying action of the additive. The maximum sorption of the irradiated fiber is significantly lower which may be caused by either packing of the polymer structure during irradiation, similar to the packing during heat treatment, or by the structuring which occurs during irradiation by hard rays similar to the structuring in other polymers, polystyrene in particular.

An investigation of the dependence of dielectric characteristics on frequency showed the maximum of dielectric losses of the initial PETP to lie in the range of 1 kHz, while that of unmodified samples is shifted insignificantly towards higher frequencies and decreased in absolute value. The maximum of the dielectric loss tangent related to the dipole-symmetry mobility for the initial PETP is observed at 115°C. The position of this maximum along the temperature axis doesn't change on introduction of 0.1% of aroylenebenzimidazole whereas its absolute value is decreased by 1.5. A subsequent increase of the ABI concentration up to 0.5% and 3% results in a sudden increase of tg and a shift of the maximum by 10°C and 25°C, respectively towards lower temperatures revealing the plactifying action.

A significant increase in the stability of modified PETP films is also explained by the plastifying action of the additive. The latter favors an even distribution of stresses and orientational hardening of the polymer.[8]

The observed dependence of incident light on the total effect of stabilization for PCA in the case of PETP wasn't observed. This provides a conclusion about the effect of the polymer environment on the type of stabilizer action.

Thus, the prospects for the utilization of naphthoylenebenzimidazole derivatives as thermostable dyes both for PCA and the PETP are demonstrated.

CONCLUSION

Based on the scientific concept of increasing the light stability of heterochain polymers the possibility for simultaneously dyeing and increasing the light stability of polymers by means of the introduction to their structures of additives with bifunctional action was shown. The light stabilizing action of the derivatives of hexazocyclanes, aroylenebenzimidazols, polyazomethynes has been systematically studied. It was shown that their stabilizing effect is independent of the type of substituents on the aromatic rings and is determined by the length of the conjugated chain. Their stabilizing mechanism depends on such properties as UV-absorption, inhibition, quenching and sensitization of the excited states.

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