Photostabilization of Cellulose Acetate by Macrocyclic Dyes as a New Class of Polymer Light Stabilizers

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Macrocyclic dyes based on aromatic diamines and phathalodinitrile have been found to be effective light stabilizers of cellulose acetate. They act by the mechanisms of UV screening and photosensitization. Its effectiveness depends on the structure of compound.

KEY WORDS Photostabilization, cellulose acetate, macrocyclic dyes.

1. INTRODUCTION

Despite the fact that a large number of cellulose acetate light stabilizers are presently known, in particular stabilizers of triazole series,[1] carboxysulphonamides[2] and others, the search for new effective photostabilizers appears to be a very active field. Recently, several new macroheterocyclic compounds (HC) have been obtained by the interaction of aromatic diamines with phathalodinitrile.[3] An important property of these compounds is their ability to dye textile materials into yellow-red-brown colors, depending on the nature and the amount of compound. Another important property is their very high thermal stabiity (up to 350°C). They have a developed conjugate chain and high photostability. Recently two of them have been proposed as polymer light stabilizers.[4] No information is available about light protective action of other compounds from this class of macrocyclic compounds.

The aim of the present work is to examine the light stabilizing efficiency of macrocyclic compounds obtained by interaction of aromatic diamines with phathalodinitrile, search for more effective light stabilizers, and elucidate the mechanism of light stabilization.

2. MATERIALS AND METHODS

HC were obtained by the interaction of aromatic diamines with phathalodinitrile according to previously described procedures.[3,5]

Cellulose acetate (CA) of 56.8% degree of acetylation was purified by precipi-

tation. Transparent films of 10–15 μ thickness were cast out of 5% CA and HC solution in acetone.

The films were irradiated with unfiltered light of a medium pressure mercury lamp in air at a distance of 30 cm for 24 to 48 h. The irradiated film was dissolved in acetone, and the viscosity of 0.5% solution was measured.

Film photolysis and photooxidation studies were carried out at 254 nm in vacuum and in air respectively at 25°C. The incident light intensity was estimated by potassium ferrioxalate actinometry and was controlled by photoelement. Oxygen absorption by the films during irradiation was determined manometrically.[6] The quantity of acetic acid formed upon CA photodestruction was determined by titrating its aqueous solution with sodium hydroxide. Total amounts of volatile products were measured manometrically. Acetic acid has been found to be the main (more than 90% total) gas product of CA photolysis.

3. RESULTS AND DISCUSSION

Chemical structures of the chosen HC are differentiated by the degree of conjugation and planarity (Scheme 1). For example: HC based on phathalodinitrile and *p*-phenylene diamine (HC-1) has a conjugated nonplanar system.[7] HC based on phathalodinitrile and 9,9-bis(4-dianiline)fluorene (HC-2) is unconjugated.
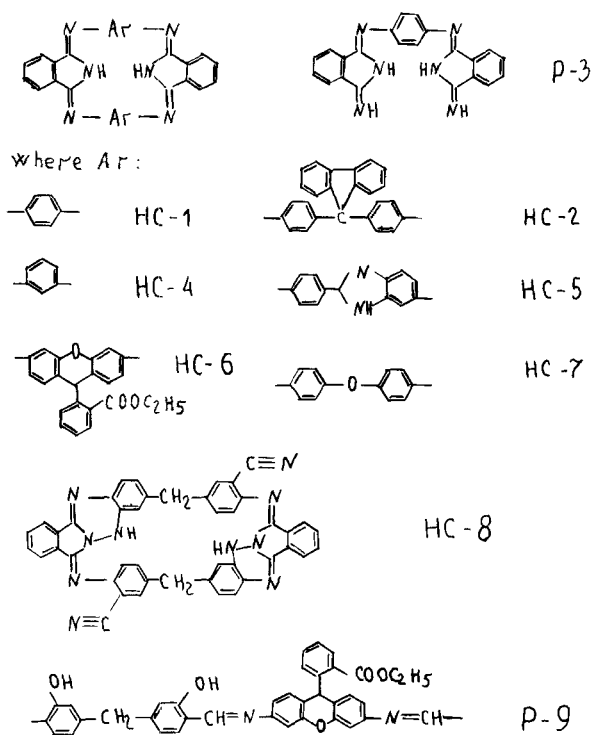
SCHEME 1

To ascertain the effect of the structure of macrocyclic stabilizer on its properties we also investigated the product of liner condensation of phathalodinitrile and p-phenylene diamine (P-3) and liner polymeric product (P-9).[3]

Photolysis. Figure 1 shows the kinetic curves of acetic acid formation under irradiation of CA unstabilized and stabilized films at 254 nm. In all cases the plots of acid concentration against the irradiation time are represented by straight lines.

As shown by Figure 1, the HC stabilizers exhibit a large protective effect on the rate of the photodestruction of CA films. The efficiency of the light stabilizer action was characterized by the value of W_0/W_{st}, where W_0 and W_{st} are the rates of acid formation in CA with a stabilizer and in the presence of a stabilizer.

The light stabilizer introduced into the polymer can simultaneously act by several mechanisms, the principal ones being UV-screening, inhibition and photosensitization. The contribution of stabilizer UV-screening to the total efficiency of the stabilizer was calculated by Equation (1).[8]

$$i_f = \frac{D_{p+st}}{D_p} \frac{1-10^{-D_p}}{1-10^{-D_{p+st}}} \tag{1}$$

where D_p and D_{p+st} are the absorbtivities of unstabilized and stabilized films. The coefficient i_f shows the factor by which the stabilizer decreases the light absorption of the polymer. If the stabilizer acts only as a UV absorber the photodestruction rate must decrease by a factor of i_f in accordance with the amount of light absorbed by the polymer. With the coefficient i_f taken into account, the stabilizer efficiency, A, was determined by Equation (2):

$$A = \frac{W_0}{W_{st} \cdot i_f} \tag{2}$$

Unde the experimental conditions the value of i_f remained constant within the error of measurement (10%). The measured values of A for stabilizers are listed in Table I. It is seen from Table I that $A < 1$ for all investigated light stabilizers. So we conclude that the given stabilizers act not only as UV absorbers but also as photosensitizers. Table I also shows that the most effective light stabilizers are HC-1–HC-4, for which the values of A are the highest.

Photodestruction. The light stabilizing activity of HC-1 and HC-4 is confirmed
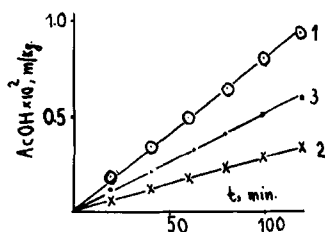

FIGURE 1   The kinetic curves of acetic acid formation under irradiation of CA unstabilized (1), stabilized by 0.08 M HC-1 (3) and HC-4 (2) in vacuum at 25°C.

TABLE I

Dependence of the stabilizer efficiency on the structure of the stabilizer[a]

Stabilizer	$A = W_0/W_{st}/i_f$	Stabilizer	$A = W_0/W_{st}/i_f$
HC-1	0.15	HC-6	0.08
HC-2	0.20	HC-7	0.09
P-3	0.16	HC-8	0.12
HC-4	0.34	P-9	0.15
HC-5	0.14		

[a]Concentration of the stabilizer in CA 5 mass %.

TABLE II

Comparative data on the light stability of CA films

Stabilizer	Concentration, mass %	Retention of reduced viscosity of 0.5% CA solutions after irradiation time t, %	
		$t = 24$ h	$t = 48$ h
—	0.0	13	7
TSC	0.5	25	
	2.0	79	
	5.0	70	
HC-1	0.5	79	
	2.0	92	
	3.0	94	66
	5.0	93	58
HC-4	0.5		31
	2.0		74
	3.0	96	80
	5.0		91

by the data (Table II) on the loss of reduced viscosity of CA solution in acetone after the UV irradiation of films stabilized with HC-1, HC-4 and one of the most effective known stabilizers (5,10,12-trisulphonamide carbasole (TSC)).

The light stabilizing activity of HC-1 is substantially higher than that of TSC and the light protective effect of HC-4 is even higher. Protective effects of HC-1 and HC-4 become manifest at relatively low concentrations (0.5%). Noteworthy is the high stabilizing effect of HC-1 and HC-4 in prolonged irradiation.

Photooxidation. In order to obtain additional data on the light stabilizing action of HC the investigation of CA photooxidation was undertaken. Figure 2a shows the plot of the concentration of oxygen absorbed, $[O_2]$, against irradiation time in the photooxidation of three CA samples, viz., unstabilized film (curve 1), CA film stabilized by HC-1 (curve 2) and 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl (nitroxyl radical) (curve 3).

As seen from Figure 2a, HC-1 decreases the rate of CA photooxidation. On the other hand the nitroxyl radical exhibits no inhibitor effect in a photoreaction. This is due to its action as a photosensitizer. In the dark reaction after irradiation the
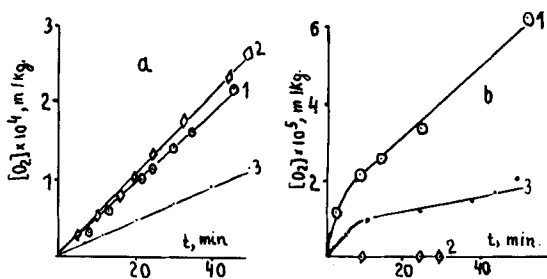
FIGURE 2 Kinetic curves of oxygen absorption under irradiation with light of wavelength of 254 nm (a) and after irradiation in darkness (b) for CA unstabilized (1) and in the presence of 0.01 mole/kg nitroxyl radical (2) or 0.016 mole/kg HC-1 (3) at 25°C.

photosensitization effect is absent and the nitroxyl radical exhibits its inhibition action, so the post-irradiation oxidation does not occur (Figure 2b, curve 2).

All free radicals formed by light are presented in polymer at initial stages of dark reaction after irradiation. This affords development of a new approach to estimate the inhibitory activity of stabilizer by means of analysis of the post-irradiation kinetics. It is important to note that HC-1 does not prevent the post-irradiation oxidation of CA even though the concentration of HC-1 is 1.6 times higher than that of the nitroxyl radical. The kinetics of the post-irradiation oxidation is given by Equation (3)[6]

$$[O_2] = \frac{k_p[PH]}{k_t} \cdot \ln \frac{1 + \xi th(t/\tau)}{1 + th(t/\tau)} + W_\infty \cdot t \tag{3}$$

where k_p and k_t are the rate constants of chain propagation and termination under oxidation of CA; [PH] is the concentration of CA units, τ is the lifetime of the free radicals at the steady-state conditions, $\xi = W_p/W_\infty$, where W_p and W_∞ are the oxidation rates at time $t = 0$ (when light is switched off) and at steady-state mode of the post-irradiation oxidation respectively. Equation 3 has been used to determine the oxidation kinetic parameter $k_p[RH]/k_t$. The estimated value of $k_p[RH]/k_t = 0.5 \cdot 10^{-5}$ mole/kg for CA in the presence of HC-1 is close to value of $k_p[RH]/k_t = 1.0 \cdot 10^{-5}$ mole/kg for unstabilized CA. Thus we can conclude that HC-1 is not an inhibitor of CA radical chain photooxidation.

If a dye is not an inhibitor and acts only as UV absorber and a photosensitizer, the the dependence of photooxidation quantum yield ϕ_{O_2} on light intensity τ_0 under the conditions of strong light absorption must be described by Equation 4[9]:

$$\phi_{O_2} = \alpha\phi_i + \frac{k_p[RH]}{k_t} \sqrt{\phi_i \cdot 10^{-3}} \frac{1}{\sqrt{\tau_0 \varepsilon C}} \tag{4}$$

where ϕ_i is the photoinitiation quantum yield due to the photosensitization by a dye, α is the number of oxygen molecules absorbed in a non-chain oxidation process per free radical formed, ε and C are the extinction coefficient and concentration of a dye.

Figure 3 shows tht the experimental dependence of ϕ_{O_2} on light intensity τ_0 under the photooxidation of CA in the presence of HC-1 is in agreement with the theoretical prediction (Equation 4).

The value of ϕ_i is 0.004. These data show that HC-1 introduced into CA is not an inhibitor; it acts as UV absorber and photosensitizes the oxidation of CA by a radical mechanism.

The obtained results help explain the dependence of HC efficiency, A, on its concentration (Figure 4). At low HC concentration (0–1.5%), where the photoinitiation rate due to HC is much lower than the photoinitiation rate due to pure CA, the photosensitization effect is absent and HC acts ony as UV absorber. Within this range of concentrations $A = 1$ and the polymer light stability increases by a factor of i_f (see Equation 1). The photosensitization becomes noticeable ($A < 1$) only at high concentrations of HC.

Problem of the photosensitization.   As follows from the data presented here, the decrease in the photosensitizing action of HC stabilizers must improve their light protective efficiency. Therefore the effect of the structure of HC stabilizers on their photosensitizing activity is of great importance. All the investigated stabilizers (Scheme 1) have a $>C{=}N{-}$ group. The photochemical reactions of the $>C{=}N{-}$ group are similar to that of a carbonyl group.[10] So it may be assumed that the primary photochemical reaction of HC stabilizers is to abstract an H atom from the substrate by a $>C{=}N{-}$ group.

In the case of HC-6 and P-9 (see Table I) an additional path of photosensitization may be due to a rhodamine fragment introduced in the structure of HC. But the values of A for HC-6 ($A = 0.08$) and P-9 ($A = 0.15$) are of the same order of magnitude as for the other HC compounds studied. Therefore the rhodamine
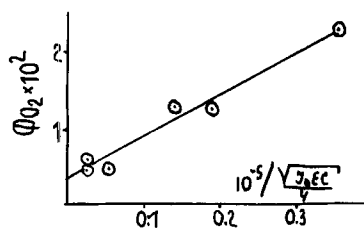

FIGURE 3   Dependence of quantum yield of oxygen absorption on light intensity and concentration of HC-1 during photooxidaton of CA.
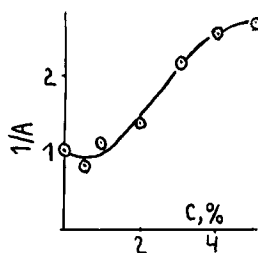

FIGURE 4   Dependence of the reciprocal value of A on the concentration of HC-1.
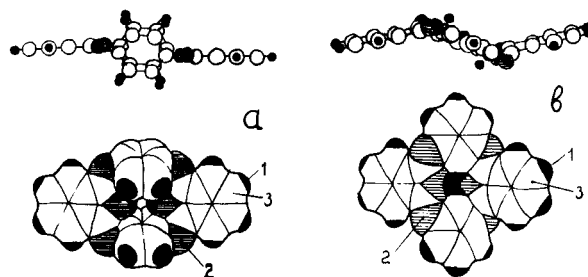
FIGURE 5 Views of HC-1 (a) and HC-4 (b) structures from one side and from above. The values of 1, 2 and 3 point out H, N and C atoms respectively.

fragment appears to have no effect on the photosensitization. It should be noticed that the intramolecular transfer of a hydroxyl proton is possible in the excited state of $>C=N-$ group of P-9 via a six-membered cycle.[11] The intramolecular transfer of a proton suppresses the photoinitiation reaction[8] and should lead to the higher value of A in the case of P-9. The experimental results, however, do not agree with this supposition: the value of $A = 0.15$ for P-9 is less than the value of $A = 0.34$ for HC-4. Thus the rate of deactivation of the excited states for all the investigated HC stabilizers is much higher than the rate of the intramolecular proton transfer.

The aggregation of molecules and the degree of conjugation of a $>C=N-$ group with aromatic rings may have a reasonable effect on the reactivity of HC stabilizers. This assumption is supported by the large difference between the values of A for para- and meta-isomers of hexazocyclane, HC-1, and HC-4 respectively. The computer models of the geometrical structures of HC-1 and HC-4 (Figure 5) shows that the structure of HC-4 is closer to planar than that of HC-1. The planar structure of HC-4 is favorable to aggregation of HC molecues that could lead to efficient quenching of the excited states of HC. In addition, the degree of conjugation of HC-4 is much higher than that of HC-1, so the reactivity of HC-4 must be lower than that of HC-1.

The obtained results give reason to believe that the search for new effective photostabilizers should be conducted among macrocyclic aromatic compounds having a structure approaching the planar one.

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