

The Effect of Active Azodyes on the Polycapromamide Photo-Oxidation Kinetics

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Synopsis

Investigations were carried out on polycapromamide films (PCA) at room temperature in air. Samples were dyed with oxyethylsulfonic and monochlorotriaminic active dyes. Irradiation was carried out with a low-pressure Hg lamp ($\lambda = 254$ nm, intensity equals 1.5×10^{15} sm⁻² sec⁻¹). During irradiation, ESR spectra of five poorly resolved lines of superfine structure were observed for all samples. Analysis of ESR spectra shows that quintet belongs to radicals $\sim\text{CONH}\dot{\text{C}}\text{HCH}_2\sim$. The initial accumulation rate of radicals was measured on linear parts of radical accumulation curves. Similarly, accumulation of PCA carboxyl groups kinetics was measured. The initial accumulation rates of radicals and carboxyl groups are linear functions of absorbed radiation on polymer and dye. There is a tendency of increasing carboxyl group yields with radical yields for different dyes. One can assume that it follows from this correlation that radicals are precursors of carboxyl groups. Luminescence spectra measured for PCA with salt and covalent bonded dyes are located near 425 nm. The data allow the conjecture that PCA luminescence is connected with centers bonded with PCA macromolecules.

It is known that carboxyl groups are one the endproducts of polyamide photo-oxidation.¹⁻⁵ It is assumed that photo-oxidation mechanism of polyamides is radical. But measurement of radical and carboxyl group yields with or without dyes was not carried out. Radicals were registered only at -196°C .^{6,7}

Investigations were carried out on polycapromamide films (PCA) ($M_n = 14,000$; $M_w = 25700$; $d = 1.13$; thickness, $80 \mu\text{m}$). The following active dyes were introduced into the PCA: β -oxyethylsulfonic red and yellow (OESR, OESY); monochlorotriaminic red and yellow (MCTR, MCTY). Depending on the method of introduction, the dyes form either salts or covalent bonds with polymer.⁸ Photo-oxidation was investigated at room temperature in air. Samples were irradiated with a low-pressure Hg lamp ($\lambda = 254$ nm). Intensity measured by ferryxalate actinometry equals 1.5×10^{15} sm⁻² sec⁻¹. Concentration of radicals in samples was measured by comparing of ESR spectra of the radicals and standard (double integrals of ESR signals were compared). As a standard, a single crystal of synthetic ruby was used. One of the lines of the Cr³⁺ spectrum is situated at 1800 gs and not hidden by polymer radical spectra.

Sample and standard spectra were registered at unchanged regulation of the ESR spectrometer.

ESR spectra were measured by a "Rubin" spectrometer with high-frequency modulation (100 kilocycles/sec) of magnetic field and equipped with a reflecting

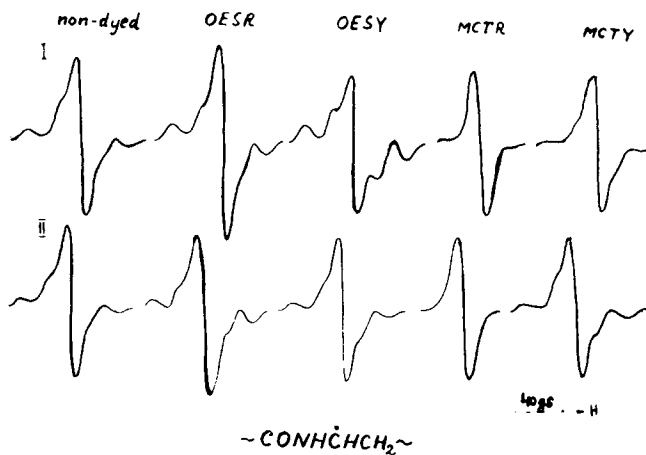


Fig. 1. ESR spectra of PCA radicals: I, salt bond; II, covalent bond.

cavity. Sensitivity of the apparatus at full SHF power is about 5×10^{10} spins/gauss. PCA carboxyl endgroups were measured by potentiometric titration of PCA solutions in hot benzyl alcohol. Dye photodegradation kinetics in PCA was measured spectrophotometrically. Luminescence characteristics of PCA were measured with a phase fluorometer and a special fluorimeter.

During irradiation, ESR spectra of five poorly resolved lines of superfine structure with splitting 22 ± 1 gauss were observed for all samples (Fig. 1). The central line intensity considerably depends on the nature of the dye and the type of dye bonding with PCA. The differences in lineshape of the various ESR spectra are dependent on the ratio of quintet and singlet signals (see below).

Registration temperature and exposition time are of little importance for the signal form. The ESR signal is considerably saturated with increase of SHF power, which is typical of polymer radicals. Spectrum extreme components are less saturated than the central one. But the dependence of the general intensity of the signal on SHF power practically does not alter with the change in nature and concentration of the dye, its type of bonding with the polymer, and stabilized radical concentration.

While storing previously irradiated PCA samples at room temperature in darkness, a decrease in general concentration of stabilized radicals was observed. Simultaneously, the form of the ESR signal changed, the intensity of extreme components decreased more considerably than the central one, and for a sufficiently prolonged time of storage, only a single line ($g = 2.006 \pm 0.002$; width, 13 ± 1 gauss) remains in the spectrum (about 10% of the initial signal).

Obtained data show that stable polymer radicals are formed upon irradiation of both the dyed and nondyed PCA, the ESR signal being a superposition of singlet and quintet.

Analysis of ESR spectra shows that quintet belongs to radicals $\sim\text{CONH}\dot{\text{C}}\text{HCH}_2\sim$ (I).⁹ A detailed analysis of the quintet has been performed in an earlier paper.⁹ This analysis is based on assignment of ESR spectra for radicals formed in deuterated PCA samples.¹⁰ Identification of radical responsible for singlet has failed so far. However, at room temperature "singlet"

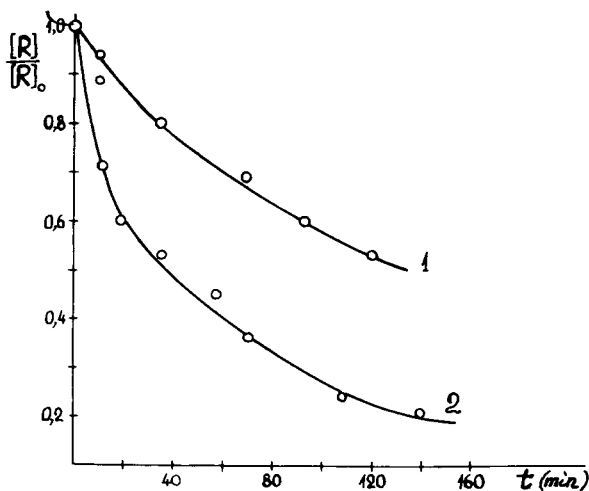


Fig. 2. PCA radical death kinetics in dark, room temperature: 1, UV exposure 120 min; 2, UV exposure 10 min.

radicals are about an order more stable than “quintet” radicals and formed at more prolonged exposures. Maximum intensity of the singlet is about 10% of the integral signal (average). Therefore, it was suggested that the singlet did not significantly disturb calculation of initial rate of “quintet” radical formation.

On the basis of presented results, one can draw the conclusion that radical I is one of basically important radicals for photoconversion of PCA. It follows, then, that elementary reactions with the participation of this radical, as suggested in the hypothetical scheme of photochemical conversion of polyamides,¹ can in principle actually take place. As radical I dies with visible speed (Fig. 2), it is evident that it can play a sufficiently active role in the photoconversion of PCA.

It can be observed from kinetics curves that the speed of radical accumulation decreases with increase in exposure time (Fig. 3). Investigation of radical death

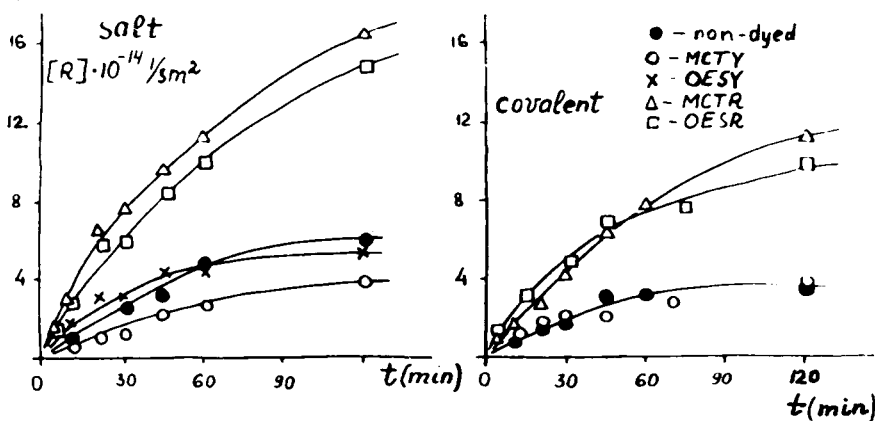


Fig. 3. PCA radical accumulation curves: (●) nondyed; (○) MCTY (4.3 mmole/kg); (×) OESY (15.4 mmole/kg); (□) OESR (16.7 mmole/kg); (Δ) MCTR (7.0 mmole/kg).

TABLE I
Initial Accumulation Rate of Radicals and Quantum Yields of Radical Formation

Type of bond of dye with polymer	Initial optical density of dye	Initial concentration of dye $C_0 \times 10^3$, mole/kg	Initial accumulation rate of radicals $W_R \times 10^{-11}$, $\text{sm}^{-2} \text{sec}^{-1}$	Quantum yields radical formation $\gamma_k^R \times 10^4$
OESR salt	0.52	8.7	3.7	5.7
	0.92	15.4	4.7	5.5
	1.35	22.5	5.8	5.8
	1.60	26.8	6.6	6.0
OESR covalent	0.50	8.4	3.1	4.9
	1.05	17.5	4.3	4.5
	1.30	21.7	4.8	4.7
MCTR salt	0.26	1.35	2.34	2.5
	0.30	1.60	2.38	2.4
	0.57	3.00	3.51	3.1
	0.60	3.20	3.32	2.8
	1.25	6.75	4.90	3.7
	1.4	7.5	5.55	4.1
MCTR covalent	0.35	1.85	2.10	1.9
	0.37	2.00	2.30	2.2
	0.60	3.20	2.68	2.1
	0.67	3.60	2.85	2.4
	1.30	7.00	2.72	2.0
	1.37	7.10	2.95	2.0
OESY salt	0.33	4.3	1.48	0.9
	0.93	11.9	1.80	1.2
	1.13	14.4	1.89	1.2
	1.6	20.0	1.78	1.1
OESY covalent	1.0	12.9	0.97	0.2
MCTY salt and covalent	0.3-1.3	2.5-10	1.32	0.7 ± 0.1
PCA (nondyed)			$W_R^0 = 1.20 \times 10^{11}$	$\gamma_R^0 = (1.7 \pm 0.3) \times 10^{-4}$

kinetics of PCA samples containing different dyes has shown that the kinetics practically do not depend on the type of dye and the character of its bonding with the polymer. Investigation of the death kinetic of radicals I suggests that radicals I recombine with the formation of crosslinks. But detection of crosslinks has failed because recombination of all accumulated radicals results in one crosslink against about 10^9 macromolecules (viscosimetric data).

The decrease in radical accumulation rate for long exposures is assumed to be mainly due to the recombination of radicals. The decrease in radical accumulation rate in dyed polymers could not be fully explained by the decrease in dye concentration, not exceeding 5-10% for OESY and MCTY and 20-30% for OESR and MCTR at 120 min of exposure, whereas radical accumulation rate becomes several times lower.

The initial accumulation rate of radicals was determined (measured) on linear parts (up to 30 min of exposure) of radical accumulation curves. Table I presents values of these radicals. Initial rate of radical formation in dyed polymer can

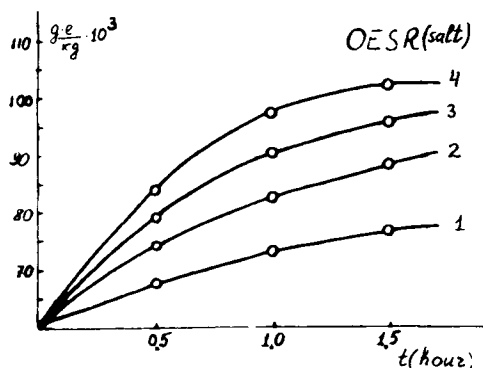


Fig. 4. PCA carboxyl accumulation curves, OESR dye (salt). Initial dye concentration 1, nondyed; 2, 5.8 mmole/kg; 3, 11.7 mmole/kg; 4, 20.0 mmole/kg.

be expressed as (assuming that influence of degradation products on UV absorption is negligible)

$$W_R = \gamma_R \cdot \Phi_n + \gamma_k^R \cdot \Phi_k$$

where Φ_n and Φ_k are numbers of quanta absorbed in unit time respectively on polymer and dye; γ_R and γ_k^R are respective quantum yields of radical formation.

It follows from the equation that

$$W_R/\Phi_n = \gamma_R + \gamma_k^R \cdot \Phi_k/\Phi_n$$

i.e., the W_R/Φ_n value must linearly rise with increase in Φ_k/Φ_n if γ_R and γ_k^R do not depend on dye concentration.

Mapping of dependence has shown that in OESR, OESY, and MCTR (covalent bonding) it is linear for all concentrations investigated ($\gamma_k^R = \text{const}$). In case of MCTR (salt bond), considerable deviation from linear dependence has been observed (γ_k^R increases as dye concentration increases). But for all cases, curves are extrapolated for the same value $\gamma_R = 1.5 \times 10^{-4}$ at $\Phi_k/\Phi_n = 0$. This agrees well with the γ_R^0 value directly measured for undyed polymer (Table I). Therefore, γ_k^R was calculated for each dye concentration by

$$\gamma_k^R = (W_R - \gamma_R^0 \cdot \Phi_n)/\Phi_k$$

Table I summarizes γ_k^R values for all investigated dyes. Assuming a single-quantum process and the absence of self-quenching, the quantum yield of radical formation γ_k^R (Table I) should not depend on dye concentration. This is correct for OESY (salt bond), OESR (salt and covalent bonds), and MCTR (covalent bond). Because ESR operates at sensitivity limits, one can assume this is correct only approximately for MCTY (salt and covalent bonds).

In case of MCTR (salt bond), γ_k^R value increase from 2.5×10^{-4} up to 4.0×10^{-4} at a dye concentration change from 1.3×10^{-3} up to 7.5×10^{-3} mole/kg. From Table I one can see that in case of dye salt bonding with PCA, γ_k^R is higher than in the case of covalent bonding, i.e., PCA photodestruction in case of salt bonding with the investigated dyes is bigger than in case of covalent bonding, and in both cases is bigger than PCA photodestruction without dyes.

TABLE II
Initial Accumulation Rate of Carboxyl Groups and Quantum Yields of Carboxyl
Groups Formation

Type of bond of dye with polymer	Initial optical density of dye	Initial accumulation rate of		Quantum yields carboxyl groups formation $\gamma_k^n \times 10^2$
		Initial concentration of dye $C_0 \times 10^3$, mole/kg	carboxyl groups $W_n \times 10^3$, g·e·g./kg·he	
OESR salt	0.35	5.8	31.8	6.8
	0.70	11.7	44.0	6.8
	1.20	20.0	64.0	6.9
MCTR salt	0.50	2.7	27.8	2.8
	0.85	4.6	27.8	2.6
	1.20	6.5	27.8	2.5
OESY salt	1.50	8.1	27.8	2.6
	0.33	4.3	19.2	2.3
	0.60	7.8	20.6	2.1
MCTY salt	1.30	16.8	22.6	2.2
	0.70	5.6	12.0	0.8
	1.30	10.3	19.0	1.8
PCA (nondyed)		0	16.2	$\gamma_n^0 = (2.9 \pm 0.1) \times 10^{-2}$

Accelerating influence of dyes on radical formation can be determined in principle by two processes: by the dye absorbed energy transfer on polymer (sensitization) and by the formation in the initial photochemical act of dye particles capable to react with polymer (initiation).

It seems that radical accumulation rate increase with increase in dye photo-destruction rate decides in favor of an initiation mechanism. But it will be also correct to assume that the increase in dye destruction rate and the increase in energy transfer from dye to polymer can occur simultaneously with a change in dye structure. Accumulation of PCA carboxyl groups kinetics was measured for salt and covalent bonding depending on dye concentration (Fig. 4).

Quantum yields of carboxyl group formation γ_k^n for samples with covalently bonded dyes are negligible small and accumulation of carboxyl groups depends on polymer only.

Accumulation of PCA carboxyl groups kinetics is not described by equations of zero, first, and second orders. Initial accumulation rates of carboxyl groups were determined on linear parts of kinetics curves (exposure time up to 30–45 min.). Initial accumulation rates of carboxyl groups are summarized in Table II. The initial accumulation rate of carboxyl groups can be shown as in the case of radicals:

$$W_n = \gamma_n \cdot \Phi_n + \gamma_k^n \cdot \Phi_k$$

where Φ_n and Φ_k are the same as in the case of radicals; and γ_n and γ_k^n are the respective quantum yields of carboxyl groups formation. Table II summarizes the values of γ_k^n .

As radical I interaction with oxygen results ultimately in carboxyl group formation, it is natural to assume that the influence of the dyes on the rate of for-

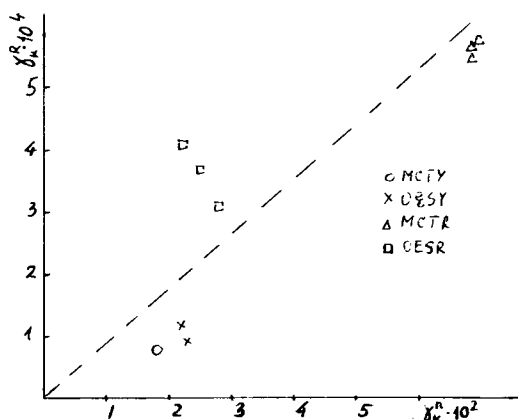


Fig. 5 Correlation of PCA radical and carboxyl quantum yields for different dyes.

mation of carboxyl groups must be the same nature as the formation of radicals I. Comparison of data in Tables I and II confirms that carboxyl group formation rate at UV irradiation of PCA in the presence of active dyes is as a rule higher than the formation of these groups in undyed polymer. The fact that γ_k^n for carboxyl group formation is higher than that for radical formation is evident; radicals are active intermediate particles, and carboxyl groups are endproducts.

It is interesting to point out that there is a tendency of increasing carboxyl group yields with radical yields for different dyes (Fig. 5). One can assume that it follows from this correlation that radicals are precursors of carboxyl groups.

Luminescence spectra for salt and covalent bond of PCA with dyes are located near 425 nm. The shape and intensity of PCA film luminescence spectra do not change when well-known polymer purification procedures, such as prolonged soaking in polar and nonpolar solvents (ethyl and benzyl alcohols, heptane, hexane, ether). Soxhlet extraction with ethanol, and polymer precipitation from concentrated HCl, are employed. Luminescence intensity increases after extraction of monomer and low molecular fraction from PCA film by boiling it in distilled water.

The above allows the conjecture that PCA luminescence is connected with the centers included in PCA macromolecules. It should be noted that similar results have been obtained for PCA films from Japan (film thickness 30 μm). The short lifetime ($\tau \sim 10^{-9}$ sec) of excited states confirms that the PCA emission appears in fact to be fluorescence. The decrease of the luminescence quantum efficiency φ and τ with increase in dye concentration points to the energy transfer from the excited states of PCA emission centers to the dye molecules.

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