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On the photosensitivity of poly(acryloylacetone) in solution

I. Petkov [a], S. Masuda [b], N. Sertova [a], L. Grigorov [a]

[a] *University of Sofia, Department of Organic Chemistry, 1 James Bourchier Avenue, 1126 Sofia, Bulgaria*

[b] *Department of Applied Chemistry, Technical College, The University of Tokoshima, Tokoshima 770, Japan*

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Abstract

The influence of UV irradiation on the keto-enol ratio of poly(acryloylacetone) (PAA) in solution was examined. The tautomeric equilibrium is strongly displaced to the keto form. Important differences in the photosensitivity of the monomeric β-diketone (acetylacetone) (AA) and PAA were established depending on the structural features. The polymeric structure of PAA is an important parameter in the process. A possible route for the formation of the keto form is discussed.

Keywords: Photosensitivity; Poly(acryloylacetone); UV irradiation; Keto-enol ratio

1. Introduction

The light-induced transformations of enolizable β-dicarbonyl compounds (β-DCC), their derivatives and analogues have been the subject of recent extensive study [1-4]. On UV irradiation, photoinduced proton transfer takes place. As a result, the photoactive tautomer (enol form) undergoes transformation into the keto form.

We are interested in the influence of structural features and the nature of irradiation on the mechanism of the photoketonization process. Polymeric β-DCC is an attractive model for investigation for the following reasons.

(1) The photoreactivity of the enol and keto units.
(2) The possibility of chemical modification of the enol or diketo units to receive many functional polymers, e.g. metal complexes, S and N derivatives, pyrasolones, etc.
(3) The presence of the β-DCC moiety as a structural element in many biologically important polymers permits the influence of radiation (UV light, γ ray, X-ray) on their behaviour to be investigated and conclusions to be drawn about many biological processes.
(4) Excited state proton transfer. Enol to keto tautomerization has been employed as a mechanistic tool and in technological applications in photolithography, as a probe of the environment around proteins, micelles, β-cyclodextrins and films and in chemical lasers, energy storage devices at a molecular level, high-energy radiation detectors and polymer stabilizers [5].

In Ref. [6], we showed that there are certain specific peculiarities of the photoketonization of poly(ethylacryloylacetate) in solution in contrast with its structural analogue, the monomeric β-DCC acetoacetic ester.

The basic objective of this study was to investigate the photochemical behaviour of poly(acrlyoylacetone) (PAA), the structural analogue of acetylacetone (AA), in solution.

2. Results

The absorption spectra of PAA in different solvents show an intense band in the 270-276 nm region. According to Morton et al. [7], the high intensity band at 274 nm is associated with the n-π^* transition in the CO conjugated ethylene system (enol form). The type of solvent does not influence the position of this band. The keto-enol ratio of the AA unit in the polymer is not always equal to that of the monomer. The enolic fraction in the polymer was measured in a ^{1}H NMR spectrometer and found to be 96% ($CDCl_3$) (in AA monomer, 81% enol ($CDCl_3$)). The enolic fraction in the polymer is approximately equal in different solvents [8]. Three tautomers of PAA are theoretically possible: one keto and two enol forms. ^{1}H NMR spectral data revealed that PAA was entirely in the enol form, in which the carbonyl group is adjacent to the methyl group [9]. By analogy with the structure of the monomer, the structure of PAA is shown below.

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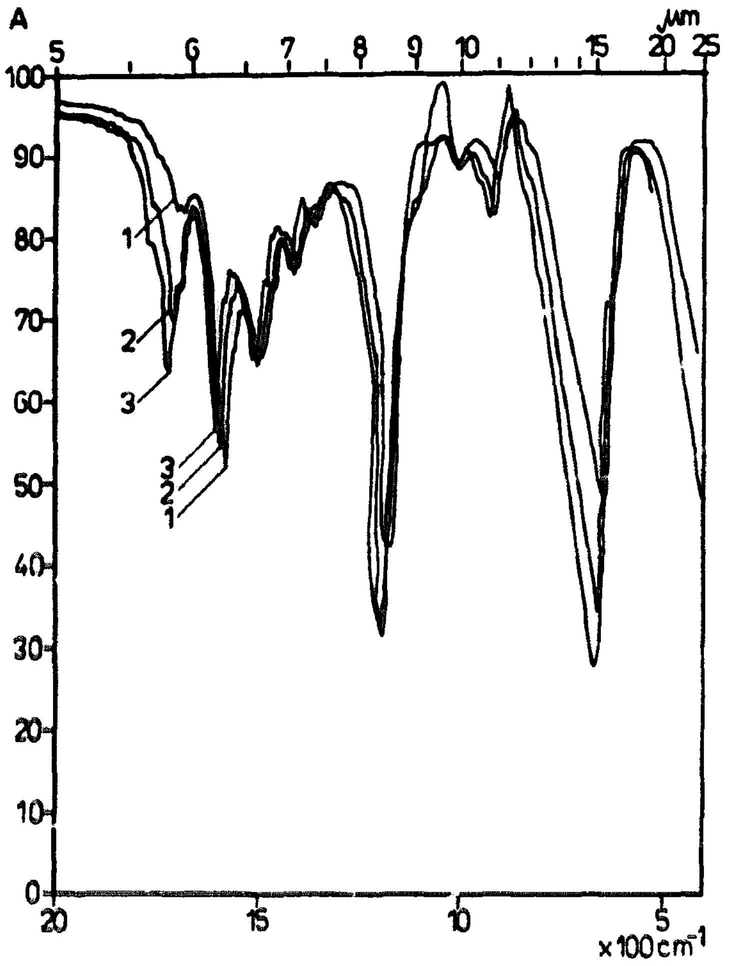
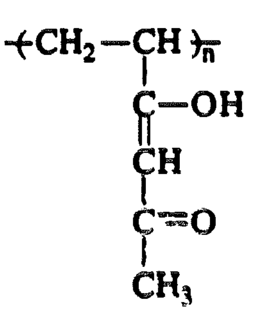


Fig. 1. Changes in the IR spectrum of PAA in CHCl$_3$ ($C = 1 \times 10^{-2}$ g l^{-1}): 1, unirradiated; 2, 60 min irradiated; 3, 120 min irradiated.



$$-\!\left(CH_2-\underset{\substack{|\\ C-OH\\ \|\\ CH\\ |\\ C=O\\ |\\ CH_3}}{CH}\right)_n\!-$$

There is a change in the keto–enol equilibrium on going from monomeric AA to PAA. This is associated with the closeness of the tautomeric units in PAA due to hydrogen bonds within the units and between different units. These conclusions are in agreement with the IR spectral data (Fig. 1). The strong absorption at 1605 cm^{-1} (enol form) and very weak absorption at 1720 cm^{-1} (keto form) are characteristic of a high degree of enolization; the *cis*-chelate form is dominant. There is no direct evidence for the presence of the *trans*-enol form.

2.1. Photochemical experiments

The UV irradiation of PAA in CH$_3$CN, CH$_2$Cl$_2$, (CH$_3$)$_2$Cl$_2$ and CHCl$_3$ at 254 nm resulted in changes in the absorption spectra (Figs. 1 and 2). The light-induced spectral changes are clearly due to enol → keto conversion. In PAA, the extinction coefficient of the keto form is very small and therefore only changes in the concentration of the enol form could be followed spectrophotometrically. In contrast with polymeric β-ketoesters [6], the spectral picture after irradiation was stopped (dark reaction) was very different. In the UV spec-

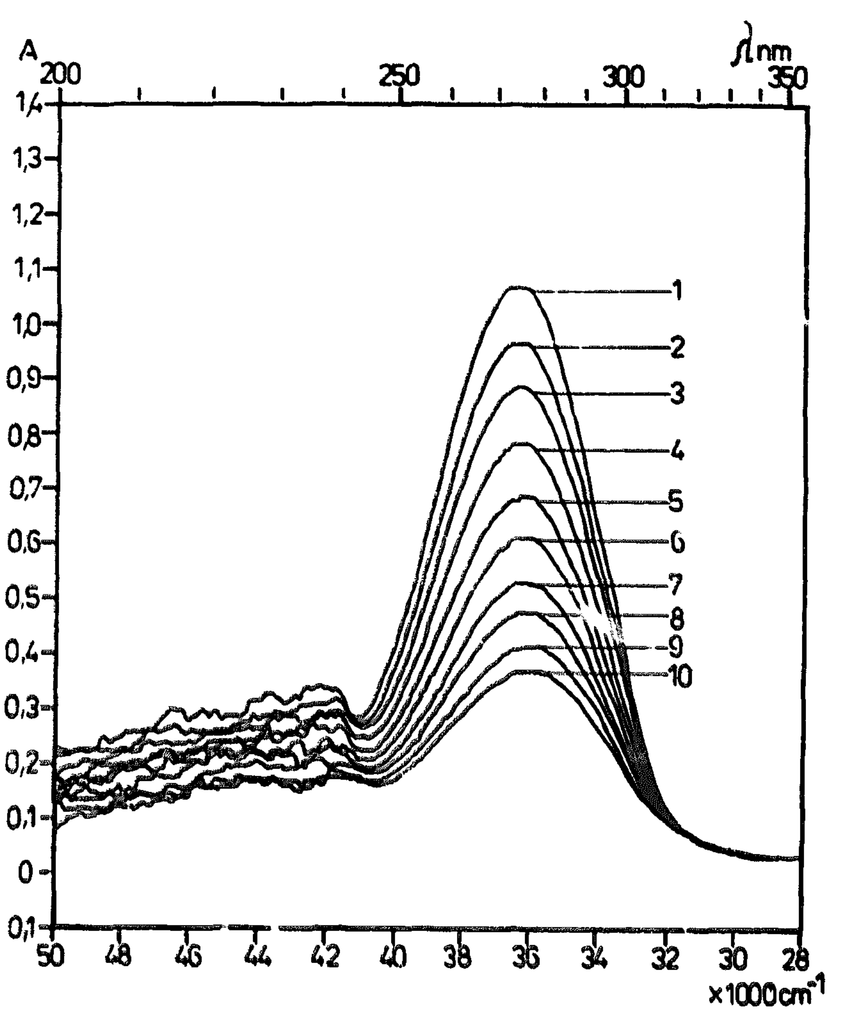


Fig. 2. UV spectra of PAA in CHCl$_3$ ($C = 1 \times 10^{-4}$ g l^{-1}) measured at different times (during 15 s) after the start of irradiation: 1, unirradiated; 2–10, irradiated.

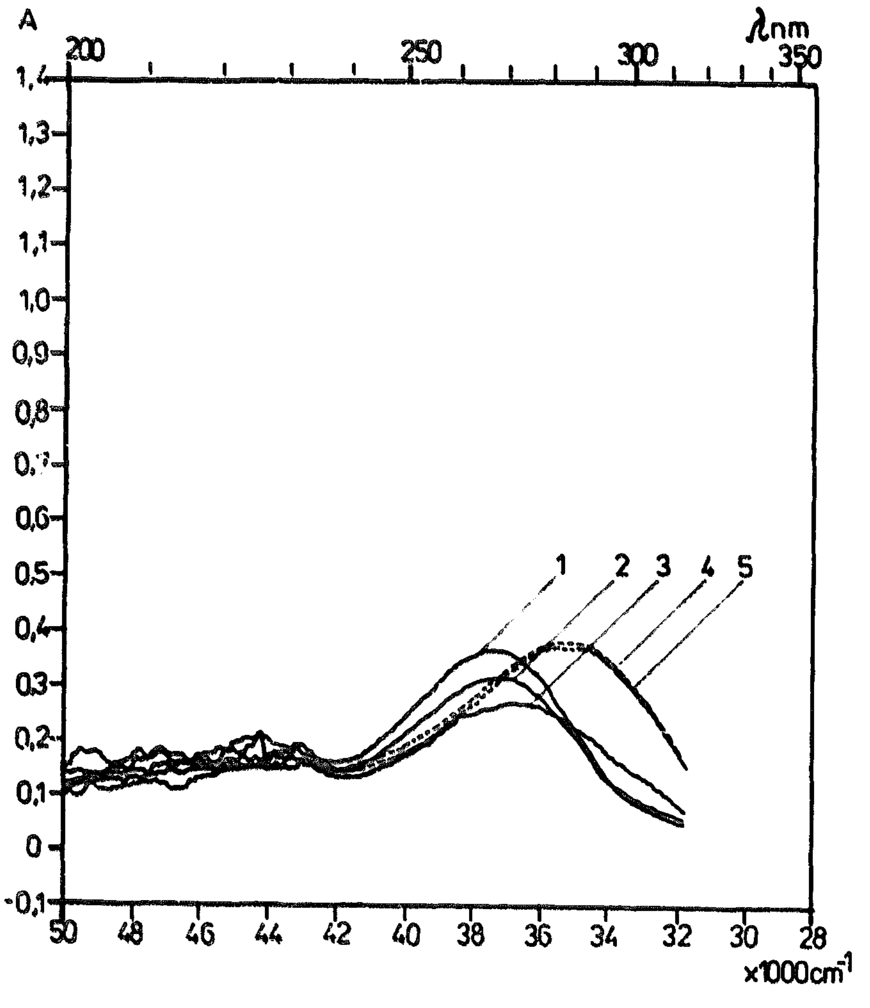


Fig. 3. UV spectra of PAA in CHCl$_3$ ($C = 1 \times 10^{-4}$ g l^{-1}) measured at different times after the cessation of irradiation: 1, 35 s irradiated; 2, 10 min after irradiation; 3, 60 min after irradiation; 4, 10 h after irradiation; 5, 30 h after irradiation.

Table 1
Observed change in the absorbance of a PAA solution during UV light irradiation

τ_{irr} (s)	Absorbance	τ_{irr} (s)	Absorbance
0	0.70 ± 0.01	75	0.48 ± 0.013
15	0.64 ± 0.01	90	0.45 ± 0.01
30	0.59 ± 0.013	105	0.43 ± 0.013
45	0.55 ± 0.02	120	0.40 ± 0.013
60	0.51 ± 0.013		

Table 2
Results of the fitting of the experimental data using the kinetic model with the absence of the *trans*-enol form

Sample	C_0	A_k	a_k	R^2
PAA	0.70	0.44	0.00927	0.9994

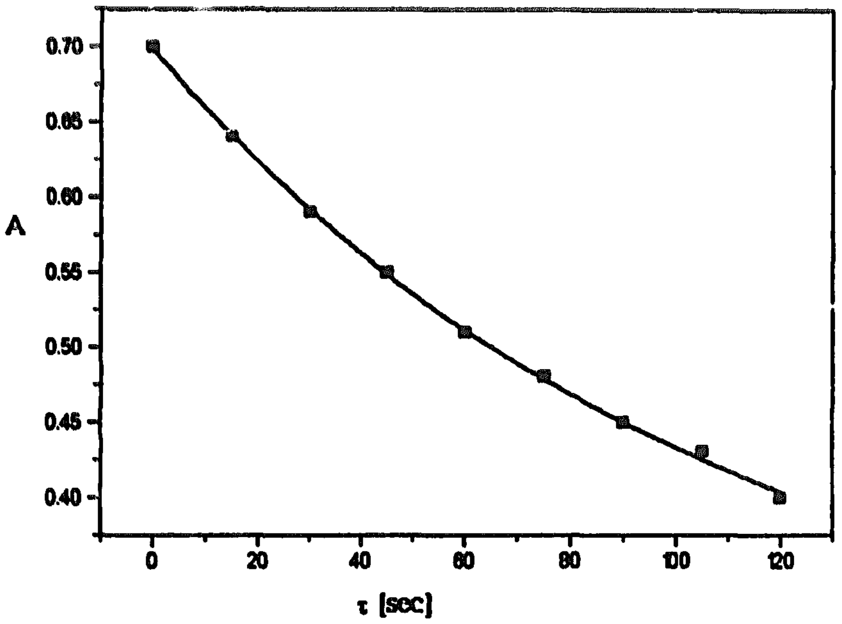


Fig 4. Results of the experimental data fitting using the kinetic model with the absence of the *trans*-enol form.

trum of PAA, a new maximum appears at 295 nm (Fig. 3) after 150 s of irradiation, and the enol peak is small. For shorter times (less than 150 s), a peak at 270 nm (*cis*-enol form) is observed.

2.2. *Kinetic experiments*

The changes in absorbance of the PAA solution on UV light irradiation are presented in Table 1.

A kinetic model was applied to the absorbance of the PAA solution and a mathematical simulation is presented to explain the photoreaction of *cis*-enol to the diketo form and its dependence on the photoisomerization of *cis*-enol to *trans*-enol. In the equations, the concentrations of *cis*-enol (C_c), *trans*-enol (C_t) and the diketo form (C_k) in latent form are in accordance with the Beer–Lambert law, $A = \epsilon cl$, where A is the absorption of the *cis*-enol form, ϵ is the molar extinction coefficient, c is the concentration of the absorbing form and l is the path length of the solution.

The analysis using a kinetic model with the participation of the *trans*-enol form, proposed in Ref. [6], is not applicable. Therefore a simple model with the absence of the *trans*-enol form was used [6]

$$E \longrightarrow K$$

The kinetic model can be represented by

$$C_c + C_k = C_0$$

$$C_c = C_{c0} - A_k[1 - \exp(-a_k t)]$$

$$C_k = C_{k0} + A_k[1 - \exp(-a_k t)]$$

where

$$a_k = k_{kc} + k_{ck}$$

$$A_k = C_0\left(\frac{k_{ck}}{k_{kc} + k_{ck}} - \frac{C_{k0}}{C_0}\right)$$

and k_{ck} and k_{kc} are the kinetic constants of the forward and reverse reactions.

The results of the experimental data fitting are presented in Table 2 and Fig. 4. The large value of the correlation coefficient R supports the validity of the model with the absence of photoisomerization of *cis*-enol to *trans*-enol.

3. Discussion

The experimental data indicate that, in PAA on UV irradiation, ketonization occurs. As can be seen from the kinetic measurements, the formation of the diketo tautomeric form in PAA during irradiation is very fast. In contrast with monomeric AA, where photoketonization of the chelated enol takes place with low yields (10^{-3}) [10], in PAA the quantum yield ($\phi = 0.15$) of the process is comparable with that observed for β-ketoesters. The second important fact is that with regard to the two possible models of formation of the diketo form, i.e. direct *cis*-enol → diketo or via a transient (*trans*-enol form), the kinetic measurements are in accordance with a direct mechanism. As can be seen from the experimental results, the reversible dark process diketo → *cis*-enol occurs. This is shown by the appearance of a maximum at 300 nm after irradiation is stopped. This absorption maximum appears in PAA solution several hours after irradiation (Fig. 3).

Previous investigations of the photochemistry of β-DCC [1–4] and polymeric β-DCC [6], the results of Vierov et al. [10] and the present results for PAA allow three conclusions to be drawn about the photochemical behaviour of PAA in solution:

(1) in contrast with monomeric AA, UV irradiation of PAA leads to fast, effective photoketonization: *cis*-enol → diketo;
(2) after irradiation, there is a partial reversible process: diketo → *cis*-enol;
(3) in CH_3CN and $CHCl_3$, a new absorption maximum is observed at 300 nm with or without irradiation.

The reason for the low quantum yields of photoketonization of the chelated enol of monomeric AA is the high degree of symmetry of AA. UV irradiation causes fast, effective enol–enol conversion (Scheme 1).

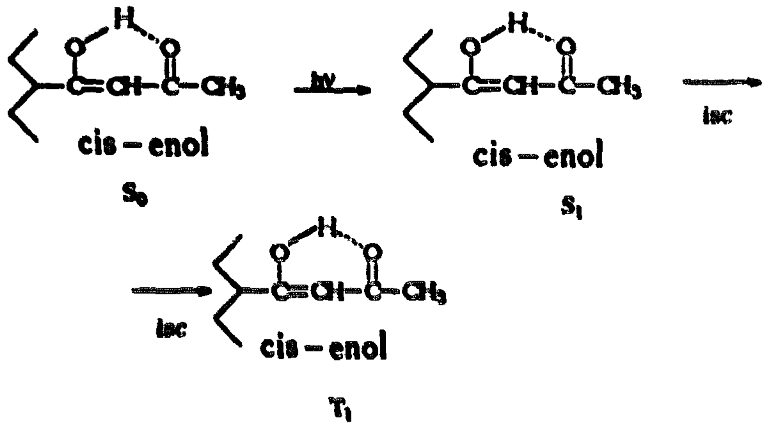
The enol → diketo process is insignificant. The large polymer chain in PAA is an important structural factor: the symmetry is disturbed and the process of photoketonization is effective. Our results are in accordance with the conclusions of Vierov et al. [10] on the influence of oxygen. The presence of oxygen favours the direct path *cis*-enol → diketo.

One possibility is that photoketonization takes place in the singlet state

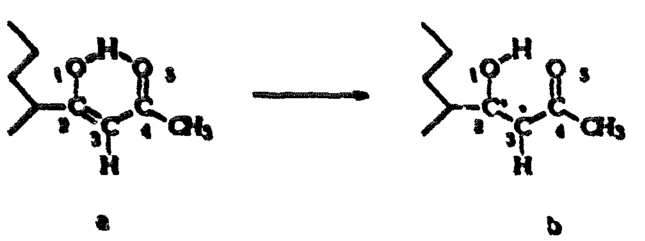
$$\text{PAA-}cis\text{-enol} \longrightarrow [\text{PAA-}cis\text{-enol}]^* \longrightarrow [\text{PAA-diketo}]^* \longrightarrow \text{PAA-diketo}$$

The partial reversible process also takes place in the singlet excited state S_1.

Enol ⇌ enol photoisomerization involves intersystem crossing to the triplet excited state T_1, which may be expected to be very efficient (Scheme 2)



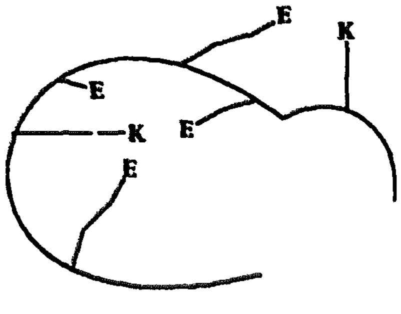
When the molecule is in the S_1 state, the 2–3 bond order decreases, reaching nearly the same magnitude as that of the 3–4 bond. This means that rotation around the 2–3 bond is highly probable (Scheme 3)



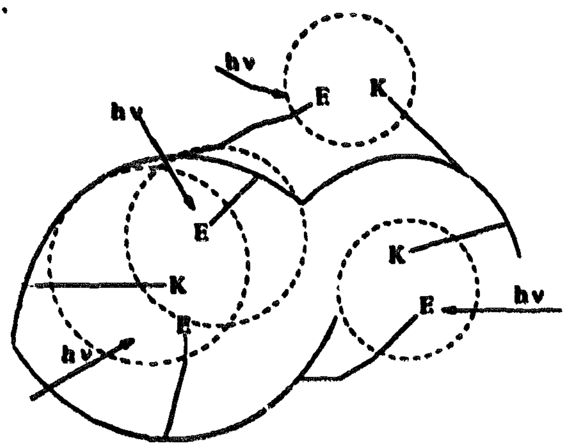
Quantum chemical calculations [11] of the energies of the S_1 and T_1 states indicate that these energies become equal at 90° rotation around the 2–3 bond (b).

Because of this there is fast intersystem crossing $S_1 \rightarrow T_1$. Arguments for the formation of an orthogonal triplet (b) of ethyl acetoacetate (enol form) have been presented by Kittel et al. [12]. The polymer chain plays a very important role. The processes of rotation and the formation of a transient are difficult. In PAA, the photoketonization of *cis*-enol units takes place in a specific environment created from the polymer chain. In contrast with poly(ethylacryloylacetate) (enol = 30%), in PAA, the enolization of β-dicarbonyl units is very high (enol = 96%). Therefore the presence of structures with alternating enol and keto fragments is insignificant and the possibility of cascade proton transfer is low [6].

The fast process of photoketonization in PAA, in contrast with monomeric AA, can be explained by unequal disorder around the enol and diketo chromophores



In such a situation, the *cis*-enol units can perform the role of antenna in polymer molecules. The enol units are very effective light-absorbing species. Changes in the electron structure of the excited enol form [10,11] will facilitate energy transfer between the keto and enol forms. Usually polymer sensitizers are based on chemically modified polymers with ketone groups [13]. However, in the excited state, carbonyl groups are very effective proton acceptors. This will favour the process of energy transfer as well as chemical reactions in the matrix. The hard polymer matrix is a determining factor of the longer life of the excited species in PAA than in monomeric AA.



A conceptual illustration of energy transfer in an antenna polymer.

The formation of an orthogonal triplet of the enol form in the excited state (diradical) plays a very important role. It is known that the acetone structure has E_t = 78–92 kcal mol^{-1}. In this respect, it should be noted that E_t = 78 kcal mol^{-1} is necessary for photosensitized ketonization [12]. The photoinduced ketonization of PAA can therefore be described as follows

$$\begin{tikzcd}
\begin{matrix} cis\text{-enol units} \\ S_0 \end{matrix} \arrow[r, "h\nu"] & \begin{matrix} cis\text{-enol units}^* \\ S_1 \end{matrix} \arrow[r, "\text{antenna}", "\text{effect}"'] \arrow[d, "\text{isc}"] & \begin{matrix} \text{diketo units}^* \\ S_1 \end{matrix} \arrow[d, "\text{isc}"] \\
& \begin{matrix} \text{enol units}^* \\ T_1 \end{matrix} & \begin{matrix} \text{diketo units}^* \\ T_1 \end{matrix} \arrow[l, "\text{sensibilization}"'] \arrow[d] \\
& & \begin{matrix} \text{diketo units} \\ S_0 \end{matrix}
\end{tikzcd}$$

The analysis of the electronic spectra of PAA indicates that the change in intensity of the absorption band associated with the chelated enolic units is connected with an additional change in the 290–300 nm region after the cessation of irradiation. It should be noted that a similar low intensity band can be observed in the UV spectrum of PAA without UV light after a long period of time (dark process). It is probable that these observations reflect an n–π* transition in the keto group which is completely masked by the high intensity band of the enolic form. According to Morton et al. [7], the β-diketo form is characterized by a low intensity absorption band at 310 nm. In contrast with monomeric AA, in PAA after photoketonization, there are many diketo units associated with the polymer chain. They can form a long system and ε will have higher values. The polymer chain permits β-diketone units to be ordered in sandwich structures. Such complexes have been demonstrated for monomeric β-DCC [14]. It is possible that such ordered structures are energetically stable and move the keto–enol equilibrium to the keto form. Further investigations in this direction are underway.

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