

# Photoinduced Pyridine Cleavage-Closure in Viscous Polymer Solutions

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We have found that photoinduced pyridine ring cleavage-closure occurs in polymeric viscous solution, because in certain polymer solutions, pyridine can serve as a photo-modulated crosslinker. We suggest this reaction as a way to control a polymer's optical properties. Irradiation of the system: poly(4-vinyl pyridine)/pyridine/water with 250-nm wavelength range leads to the appearance of a new absorption band centered at 360 nm, new red-shifted emission, and HOMO-LUMO band gap changes. The subsequent irradiation with 360 nm (the new absorption band maximum) leads to reversion almost to the initial stage. A main active product of the photoreaction is aldehyde enamine, which has two active groups: primary amine and aldehyde, which can associate with the polymer molecules to form a physical crosslinked supramolecular structure. We evaluated the activation energy of the pyridine ring cleavage and back reaction depending on the polymer/pyridine/water ratio and by changing the polymer structure. The activation energy of pyridine's ring cleavage in viscous polymeric solutions is in the range of 0.6–3.2 Kcal/mol. The activation energy of the back reaction is significantly lower and is in the range of 0.05–0.15 Kcal/mole.

**KEY WORDS:** Pyridine; Dewar pyridine; photochemistry; physical crosslinking; poly(4-vinyl pyridine).

## INTRODUCTION

The pyridine molecule has well-known photosensitive properties [1,2]. Under UV-irradiation at 250 nm (main absorption band) pyridine initially transforms to Dewar isomer (Fig. 1). Then, upon photohydration, a cleave reaction takes place and DP turns to the aldehyde enamine. The aldehyde enamine is unstable, and in a time scale of the minutes at room temperature reverts to pyridine. The formation and rearomatization of the aldehyde enamine is easily observed spectrophotometrically [1–3]. Aldehyde enamine has an intense absorption band at 366 nm maximum. Conversely, the absorption

spectrum of DP at room temperature was never observed. Investigation of the stabilized DP at 0°C showed absorption at 400 nm. Expanded study of DP was done by matrix isolation infrared spectroscopy [4,5] and DFT calculation [6].

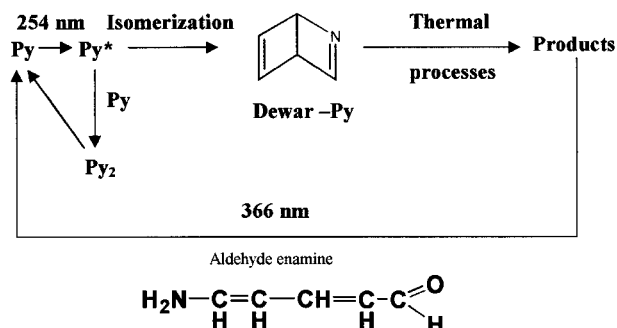
In the present contribution we show that photoinduced cleavage-closure reactions of pyridine take place also in the polymer viscous solution and we show how these photoinduced cleavage-closure reactions can control the optical properties of the polymer.

Since the first examples of reversible photochemical reactions in polymers were reported [7,8], extensive efforts were devoted to investigation photochemistry in the polymeric media. Photochemical reactions in a polymeric media were shown to be reversible depending on the wavelength of irradiation [9–12]. The importance of this topic is the possibility of controlling polymer's optical properties [13]. Recently we demonstrated a new photosensitive system based on pyridine, which also

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**Fig. 1.** Scheme of the photoinduced processes: Py: Pyridine in the ground state. Py\*: Pyridine in the excited state. Another possibility is the  $\text{Py}_2$  formation as a product of the bimolecular reaction between  $\text{Py}^*$  and Py.

exhibits the potential ability of photoinduced optical property control [14]. Under UV-irradiation, a viscous solution of poly(4-vinyl pyridine)/pyridine turns to gel. The photoinduced conformational change leads to a corresponding electronic property change of the polymer. New emitting centers appear in the gel. The photoinduced changes can be stored in the material over a month; however, mechanical perturbation or heating can convert the gel back to the solution with consequent emission property changes.

Water addition to this system exhibits easily available back-and-forth reactions via photoinduced cleavage-closure of the interstitial pyridine molecule.

The effect can be useful in memory devices. Via photoinduced pyridine cleavage-closure reactions, different phases in the polymer solution can be formed precisely depending on the irradiated beam location.

## EXPERIMENTAL

For this work, poly(4-vinyl pyridine) (P4VPy) with a molecular weight of 50.000, poly(2-vinyl pyridine) with a molecular weight of 40.000 (Polyscience Corporation) were used. Polymers were carefully dried in the vacuum oven ( $10^{-3}$  torr) at  $90^\circ\text{C}$  for 1 week before use. The pyridine was anhydrous (water  $< 0.003\%$ ) obtained from Aldrich. The water used was triply distilled with pH = 7.0. Aniline (Aldrich) was used in 1:1 molar ratio with free molecules. Systems (I): P4VPy/pyridine/water with molar ratios of 1:1:1; between the P4VPy repeating unit, pyridine and water molecules were studied with UV-VIS, photoluminescence, aniline quenching experiments, Raman spectroscopy, evaluation of the activation energy. System (II): P4VPy/pyridine/water with molar ratios of 2:1:1 between the P4VPy repeating unit, pyridine, and water molecules was studied with UV-VIS spectroscopy.

System (III): poly(2-vinyl pyridine)/pyridine/water (molar ratio 1:1:1); between polymer repeating units, pyridine, and water molecules was used for the evaluation of the energy activation of the photoinduced forth and back reaction. Also for the energy activation evaluation the ratios between free solvent, polymer-bonded molecules, and water in systems I and III varied over a wide range. At the initial stage, all systems were highly viscous, homogeneous, and transparent solutions. The solutions (I–III) were colorless. The spectroscopic measurements were done immediately after preparation.

Absorption spectra were recorded on a Shimadzu UV-3101PC scanning spectrophotometer. The samples were prepared by sandwiching the polymer solutions between flat quartz slides (Chemglass, Inc.) separated by 10–20  $\mu\text{M}$ . Excitation and PL spectra were taken on a Shimadzu RF-5301PC spectrofluorimeter. Samples were contained in a 2.5-mm quartz cuvette (Starna), and data were collected at right angles to the excitation beam. UV-irradiation at 250 nm ( $0.6 \text{ mW}/\text{cm}^2$ ) and 360 nm ( $2.3 \text{ mW}/\text{cm}^2$ ) was accomplished by a Xenon short-arc lamp (Ushio) inside the Shimadzu RF-5301PC. An irradiated area approximately 2 mm diameter in size ensured that the sample irradiation, photoluminescence, and excitation occurred in exactly the same area, in case of the emission properties investigation, and 1 cm in diameter for the quartz slides, in the case of the UV-VIS measurements. Periodically, the irradiation was interrupted and UV-VIS photoluminescence measurements were performed. The resolution of the emission and excitation spectra was 1 nm; the resolution of the absorption spectra was 2 nm.

The gelation was evaluated visually, depending on the ability of the solution to flow.

Raman spectra before and after UV irradiation were recorded using a Renishaw System 1000 (excitation wavelength at 514 nm, power at the sample location 3 mW).

The activation energy of the photoinduced processes has been determined according the Arrhenius equation [15]. The period of time required for attaining the certain optical density at 360 nm has been chosen as the parameter of the reaction. Irradiation and the absorption spectra registration were done at the same temperature. The temperature range was 10– $60^\circ\text{C}$ . The temperature cell (model SCT, Shimadzu) and TCC Controller (Shimadzu) were used for UV-irradiation and absorption spectra recording, respectively.

## RESULTS

Figure 2 presents the absorption spectra of a thin film of P4VPy composition (I) placed between two quartz

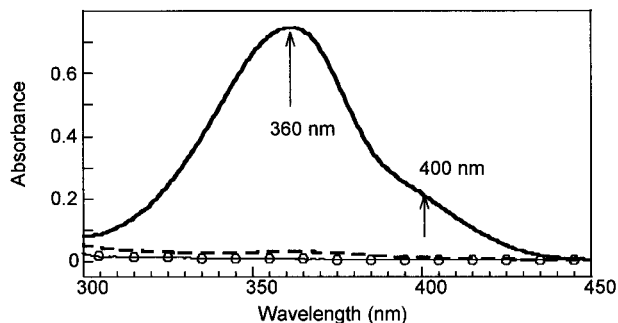


Fig. 2. UV-absorption spectra of the P4VPy/pyridine/water thin film (composition [I]) before (thin solid line with open circles) and after UV irradiation at 250 nm for 60 min (solid line); followed by irradiation at 360 nm for 180 min (dashed line) at room temperature.

slides before and after UV irradiation for 1 h at 250 nm with an additional UV-irradiation at 360 nm for 3 h.

An intense absorption band centered at 360 nm with a shoulder at 400 nm appears in the polymer composition under irradiation at 250 nm. The intensity of the new absorption band is reversible. By following the irradiation at 360 nm, we observed that the intensity decreases approximately to the initial value (Fig. 2, dashed line). It is noteworthy that complete reversal to the initial values was never observed. If the content of solvents (pyridine, water) is conserved in the system, the process is repeatable not less than 10 cycles.

Figure 3 shows photoinduced changes in the emission (right curves) and excitation spectra (left curves) with the same polymer composition before (solid lines with closed circles) and after UV irradiation at 250 nm (solid lines) and then restored (dashed lines) after subsequent irradiation at 360 nm. Before irradiation the initial polymer solution has comparatively high emission inten-

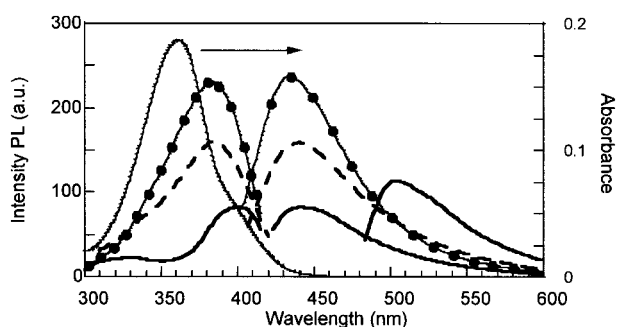


Fig. 3. Emission (right traces) and excitation (left traces) spectra composition (I) before (thin solid line with closed circles) and after UV irradiation at 250 nm for 10 min (solid lines), followed by irradiation at 360 nm for 15 min (dashed lines). Spectra excitation of the emission at 504 nm is not shown. For comparison, the absorption spectra after the first irradiation at 250 nm (left curve, thin solid line) is presented.

sity with a maximum at 435 nm (quantum yield 0.17) by excitation at 380-nm wavelength [14]. Upon irradiation at 250 nm the intensity of the emission drops (quantum yield 0.043), with significant changes of the excitation spectra. In the excitation spectrum, instead of the maximum at 380 nm, two new maxima at 315 nm and 400 nm appeared. Simultaneously with blue emission intensity decreasing, a new emission at 504 nm maximum appears under excitation at 470 nm (excitation spectrum is not shown; the properties of the new emitting centers will be discussed elsewhere [16]).

After irradiation at 360 nm the reinstated emission and excitation spectra reproduced the initial emission and excitation spectra character features with a lower quantum yield (0.13). The long-wavelength emission at 504 nm disappeared. This process also is repeatable.

To investigate the photoproduct, Raman spectroscopy of the material before and after irradiation was applied. Figure 4 presents the Raman spectra of the polymer composition before and after UV irradiation at 250 nm during 6 h. Raman spectra of the polymer composition after irradiation (gel) contrasted significantly with the initial state (viscous solution) (see Fig. 3). The notable decrease of the intensity of the absorptions in the range of the aromatic ring stretching vibrations at 1597, 1452, 1557 $\text{cm}^{-1}$ , and the appearance of new ones in the C-O bending vibration range (1121  $\text{cm}^{-1}$ ), two kinds of absorption in the range of cumulative double bonds (2102 and 2165  $\text{cm}^{-1}$ ) were observed after UV irradiation. These results clearly show pyridine ring conversion during irradiation at 250 nm.

As was mentioned above, upon irradiation at 254 nm, pyridine in the presence of water undergoes photoin-

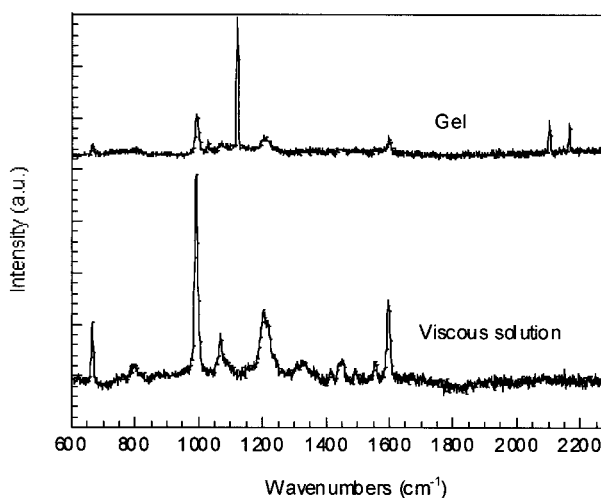


Fig. 4. Raman spectra of the composition (I) before (viscous solution) and after (gel) UV irradiation at 250 nm for 6 h at room temperature.

duced cleavage [1,2]. The first step is photoisomerization to DP, and the second step is hydrolysis to aldehyde enamine. The photoproduct has absorption at 366 nm with an extinction coefficient of  $4 \times 10^4$ . The quantum yield of the reaction is low  $\sim 0.004$  [1,2].

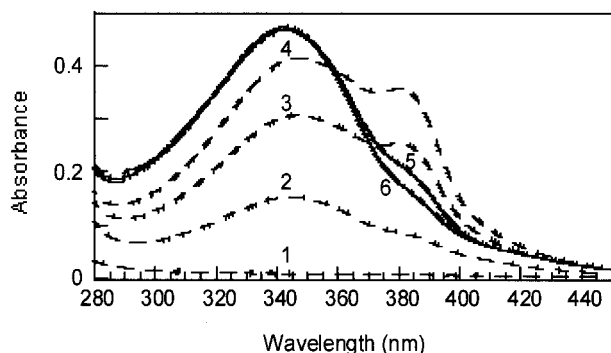
In the viscous polymer solution the new absorption band has similar properties. The notable difference is in stability and back reaction. The photoproduct in pyridine/water solution is unstable and in a time scale of minutes spontaneously reverts to pyridine with water elimination [1,2]. In the viscous solution the intensity of the new absorption at 220–440 centered at 360 nm preserves the same value over 1 month, then slowly decreases.

The back reaction can be induced by irradiation from the absorption maximum at 360 nm (see Fig. 2). The process is repeatable, and the described composition can be repeated described processes not less than 10 cycles.

An additional absorption at 390–400 nm (see Fig. 2) is an essential feature of the photoreaction in the viscous polymer solution, compared with the pyridine/water solution. The intensity of the absorption at 390–400 nm depends on the concentration ratio of polymer/solvent and is higher with increased polymer concentration.

To clarify the essential feature of the absorption in this wavelength range, the thermal stability of the irradiated samples was investigated. The irradiated polymer composition was kept at 60°C for 2 hours. Periodically, the absorption spectrum was registered. During this time, the absorption at 390–400 nm decreased constantly and reached 0.2 of the initial value. However, at the same time the intensity of the absorption at 360 nm did not change or even increased slightly (data not shown).

Figure 5 presents the absorption spectra of the polymer composition (II) irradiated by 250 nm during different periods of time (1–0 min, 2–15 min, 3–30 min, 4–45 min) followed by the irradiation at 360 nm (curves 5–30 min, 6–45 min).



**Fig. 5.** Absorption spectra of composition (II) before (1), during irradiation at 250 nm (2), after 15 min (3), after 30 min (4), after 45 min (dashed lines), and after irradiation at 360 nm (5–30 min, 6–45 min, solid lines).

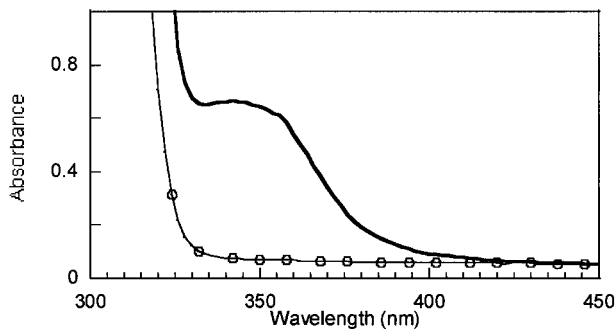
min, 6–45 min). The growth of the absorption at 390 nm coincides with the growth of the absorption at 345 nm (Fig. 5, curves 2,3,4). Nevertheless, the significant decrease of the absorption at 390 nm caused by the following irradiation at 360 nm does not coincide with the behavior of the absorption maximum, which even increased slightly (Fig. 5, curves 5,6).

The principal difference between centers, responsible for the photoinduced absorption at 360 nm and 390–400 nm was confirmed by the doping experiments of composition (I) with aniline (Fig. 6). In the presence of aniline the absorption at 360 nm appears. However, an absorption at 390–400 nm does not form.

## DISCUSSION

Upon UV irradiation at 250 nm (pyridine's main absorption band) the intense wide absorption in the 290–440 nm wavelength range centered at 360 nm appeared in the polymer viscous solution (see Fig. 2). The properties of the new absorption (appearance upon the irradiation at 250 nm, the peak position at 360 nm, extinction coefficient of  $3.4 \times 10^4$ ) coincide with the properties of the absorption resulting from photoinduced cleavage reaction of pyridine in pyridine/water solution [1,2]. That means that in polymer viscous solutions, pyridine also has the ability of this cleavage reaction with the formation of the aldehyde enamine structure. The Raman spectra (see Fig. 4) confirmed ring-opening photoreaction.

However, compared with pyridine/water solution, the photoinduced absorption spectrum in the viscous polymer solution is significantly stable. During 1 month of storage of the irradiated sample at room temperature, the photoinduced absorption spectrum practically does not change. The reason for this is the interaction between strong aldehyde enamine dipole (extinction coefficient of



**Fig. 6.** Absorption spectra of the composition (I) doped with aniline before (thin solid line with open circles) and after UV irradiation at 250 nm for 60 min at room temperature (thick solid line).

$3.4 \times 10^4$ ) with another dipole: pyridine's sidechain of the polymer. Charge distribution on the polymer side-chain group was discussed recently [17]. This interaction leads to physical crosslinking. The wider range of the electron density distribution is followed by the crosslinking. The latter results in the electronic property change. A long-wavelength shifted emission at 504 nm is shown in the emission spectra (see Fig. 3) of the irradiated composition. In the case of the aniline doped system, neither emission at 504 nm nor gelation were detected. During irradiation, the active group of the photoproduct, most probably the aldehyde group, interacts with the aniline preserved crosslinking formation. It is important to note that at the same time, absorption at 390–400 nm does not appear.

At the present stage we have no unequivocal prove for the origin of the absorption at 390–400 nm. One explanation can be found in the bimolecular reactions such as  $2 + 2$  or  $2 + 4$  cycloadditions forming dimers of the pyridine (see Fig. 1), causing a creation of the peak at 390–400 nm.

However, based on the literature data [1,2], as well as the properties of the absorption such as maximum position, low thermal, and photoinduced stability, we cannot exclude the possibility that DP also can be responsible for that absorption. Probably, isomerization of the polymer side-chain group can lead to DP formation.

At any time, for the period of storage, the intensity of the absorption can be decreased by the irradiation of the samples with UV light at 360 nm (maximum of the new absorption band) almost to the initial value (see Figs. 2 and 5). The process is reversible (see Fig. 3).

The reverse process occurs in the excited state of the free pyridine photoproduct. In the excited state (by irradiation at 360 nm), the electrostatic strength repulsion lessens the interaction between the pyridine photoproducts and polymeric side-chain groups. The absorption centered at 390–400 nm decreases. The emission at 504 nm disappears. Upon of the continuation of the irradiation, the absorption at 360 nm decreases almost to the initial value. The closure of pyridine's open form takes place.

The physical crosslinking nature of the interchain interaction was confirmed by evaluation of the energy activation of the cleavage-closure reactions depending on the polymer structure and polymer/pyridine/water ratio. The activation energy of the pyridine cleavage and closure of system (I) were 3.2 Kcal/mol and 0.15 Kcal/mol, respectively. With increasing free pyridine concentration, activation energy of the pyridine ring cleavage lowers to 0.6 Kcal/mol. The concentration of water has no significant influence on the activation energy of the pyridine

ring cleavage. However, it decreases the activation energy of the closure to 0.05 Kcal/mol. We compare this effect with photoinduced reaction of the pyridine cleavage-closure in the poly(2-vinyl pyridine) solution (III). If the activation energy of the cleavage was comparative, in a range of 5.4–8.2 Kcal/mol, depending on the pyridine concentration, however, energy activation of the back reaction was significantly larger and photoinduced crosslinking practically irreversible. That means that reversibility of the crosslinking is based on the interaction between the unshared electron pair of the pyridine and the aldehyde group of the photoproduct.

The interaction between the polymer side-chain group and the photoproduct is irreversible when the electronegative charge of nitrogen is shielded.

## CONCLUSION

Pyridine is well known to undergo photocleavage in the pyridine-water solution. An essential feature of the process is the spontaneous back reaction. In the present contribution we showed that pyridine in the polymer solution, in the presence of water, can serve as a photomodulated crosslinker.

Irradiation of the system with 250 nm leads to the appearance of a new absorption band centered at 360 nm with a shoulder at 400 nm, new red-shifted emission at 504 nm, and decrease of the intensity of the initial blue emission, HOMO-LUMO band gap change, and gelation.

The photoinduced reaction includes not less than three main stages. The first one is pyridine isomerization, the second one is the cleavage of the free pyridine molecule with aldehyde enamine formation, and the third one is the photoproduct interactions with the side-chain groups of the polymer. The Dewar pyridine-unstable photoproduct of the first stage probably reveals itself in the formation of the absorption at 390–400 nm [1], and the absorption maximum at 360 nm belongs to the resulting photoproduct; both of them stabilized by means of the interaction with the side-chain groups of the polymer.

The subsequent irradiation with 360 nm leads to the transformation of the system almost to the initial stage. The back reaction is based on the physical crosslinking and then on the closure of the free pyridine molecule.

We have evaluated the activation energy of the pyridine ring cleavage and back reaction as a function of the polymer/pyridine/water ratio. Activation energy of the pyridine ring cleavage in viscous polymeric solutions is in the range of 0.6–4.0 Kcal/mol, depending on the pyridine concentration. The value is lowered with increase of pyridine concentration. Activation energy of the back reaction

is significantly lower, in the range of 0.05–0.15 Kcal/mole.

Potential use of the findings is in the memory devices. By photoinduced pyridine cleavage-closure reaction, different phases in the polymer solution can be formed precisely, depending on the beam location.

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