

# Photoinduced Structural Changes in Poly(4-Vinyl Pyridine): A Luminescence Study

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In the present work we show a way of controlling photoluminescence (PL) properties through photoinduced quasi-crystal formation in a system based on poly(4-vinyl pyridine) (P4VPy). Under UV irradiation at 380 nm, concentrated solutions of P4VPy in pyridine turn into gel. This phase transition results in changes in the optical properties of this polymer. The position of the PL maximum can be changed continuously from 440 to 480 nm during irradiation. After several minutes of UV irradiation a new red-shifted PL at 492 nm appears upon excitation by light of a wavelength corresponding to that of the initial PL maximum, which is also red-shifted during irradiation. Solutions of P4VPy in pyrimidine show similar behavior, but those in pyridazine do not exhibit such behavior. We have found that the reason for the observed changes in the electronic properties is a photoinduced directional ordering of polymer molecules in a special quasi-crystal formation. The process originates from a structural change in the side chain of P4VPy, namely, protonation of the polymeric pyridine after solvation. During irradiation, the polymeric pyridinium ion interacts with neutral polymeric pyridine molecules. Interchain interaction through hydrogen bonds lead to an electronic property change. We observed that the process of photoinduced sol-gel transformation is reversible. Mechanical perturbation or heating can convert the gel back to a fluid solution. The red-shifted PL is not observed, and the initial PL is blue-shifted to 450 nm and stays there.

**KEY WORDS:** Structural changes; poly(4-vinyl pyridine); photoinduced ordering; luminescence; quasi-crystal formation.

## INTRODUCTION

Polymers with tunable optical properties that may be varied in predictable ways are of great interest both for a fundamental understanding of their electronic properties and for practical applications, e.g., in optical data storage and retrieval devices [1–3]. Numerous studies have focused on how such optical properties depend on polymer chemical structure [4–6]. Materials that exhibit tunable photoluminescence (PL) [7–9] have been syn-

thesized. The synthetic approach encompasses a wide range of investigation and is discussed elsewhere. An obvious application for these polymers is their potential use in light-emitting diodes in display technology.

One way to vary the optical properties of a polymer is to change its chain packing order [10,11]. In many cases the dependence of PL properties on the structural ordering of polymers has been shown [12–15]. The PL of pyridine-containing polymers, poly(*p*-pyridine) and poly(*p*-pyridil-vinylene), was red-shifted in thin film compared to that in solution [13]. In the film, interchain interactions lead to the distribution of electrons over wider parts of the molecule than occurs in the solution. Such delocalization causes a reduction of the band gap and consequently the red shift of the PL. These results show

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the usefulness of varying electronic properties through control of polymer chain packing.

Recently, reversible and tunable optical properties of bipyridine-containing poly(*p*-phenylene-vinylene) thin films were found that depended on a protonation–deprotonation processes [16]. A red shift of 0.2 eV in the PL maximum was observed upon full protonation of a free-base film. Since no covalent bond reorganization in a pyridine-containing conjugated polymer is expected to occur during protonation–deprotonation processes, order changing of the packed arrangement was suggested to explain this phenomenon.

The effect of the molecular-level arrangement (polymer molecule conformation) on the optical properties of a polymer was shown in poly(phenylene-vinylene) (PPV) derivatives [17]. It was found that increasing the size of the side chains increases the intrinsic persistence length of the PPV backbone and that this change in stiffness has dramatic effects on the PL. With increasing intrinsic stiffness of the polymer backbone, the peak absorption is shifted to the red, the Stokes shifts are reduced, and the quantum yield of the PL is greatly enhanced.

Polymer chain conformation is well known to be dependent on environmental parameters such as solvent composition, pH, temperature, and ionic strength [18]. In addition, UV–vis irradiation causes changes in polymer chain conformation [19]. Thus, a possible approach to controlling optical properties of these polymers is to find a method of controlling their conformational changes. Also, this indicates the possibility of using a photochemical method, which would be preferable because such methods are fast, reversible, and easy.

In the present work we report a way of controlling PL properties through photoinduced quasi-crystal formation, which can be specified as a “soft crystal,” in a system based on poly(4-vinyl pyridine) (P4VPy). Under UV irradiation at 380 nm, a concentrated solution of P4VPy in pyridine turns to gel. This phase transition results in changes in the optical properties of this polymer. In the absorption spectrum, a new absorption appears in the visible range, and the position of the PL maximum can be changed continuously from 440 to 480 nm during irradiation. After several minutes of UV irradiation a new red-shifted PL appears upon excitation by light of a wavelength corresponding to that of the initial PL maximum, which is also red-shifted during irradiation. Solutions of P4VPy in pyrimidine show similar behavior, but those in pyridazine do not exhibit such behavior.

We observed that the process of photo-induced sol-gel transformation is reversible. Mechanical perturbation or heating can convert the gel back to a fluid solution.

The red-shifted PL is not observed, and the initial PL is blue-shifted to 450 nm and stays there.

We have found that the reason for the observed changes in electronic properties is a photoinduced solution arrangement in a special quasi-crystalline order. The process originates from short-range interaction between the solvent molecule and the side-chain group of the polymer after solvation. Most likely, a structural change in the side chain of (P4VPy), namely, protonation of the polymeric pyridine, takes place. During irradiation, at the conformational level a photoinduced orientation of the polymer molecules occurs, with a concomitant reduction of disorder. The driving force that causes these changes in electronic properties is a process that reduces the disorder in the system, photoinduced “dimerization” between polymeric charged side-chain pyridine groups and free pyridine or between charged and noncharged polymeric groups. The latter causes interchain interaction and aggregate formation. Most probably, the first part of the process, namely, protonation of polymeric pyridine molecules, is irreversible. The next stage—gel formation—is reversible. To help explain the observed behavior and to give a more complete understanding of the physical properties of this polymeric system, in addition to the PL data, we obtained IR and X-ray diffraction data for this material, and we measured the intensity of its second harmonic generation (SHG). In this paper we present these data and show how they explain the observed photo-induced ordering phenomena.

## EXPERIMENTAL

For this work, P4VPy with a molecular weight of 50,000 (Polyscience) was used.  $^1\text{H-NMR}$  and EPR investigations of the P4VPy showed that it has less than 0.1% monomer impurity and has no residues of initiator or any other impurity. (Additional experiments with purified P4VPy from the monomer residue show no influence of the latter on the photoinduced processes in P4VPy.) P4VPy was dissolved in three solvents with different hydrogen-bond basicities: pyrimidine (Pm),  $pK_{\text{HB}} = 1.37$ ; pyridine (Py),  $pK_{\text{HB}} = 1.86$ ; and pyridazine (Pz),  $pK_{\text{HB}} = 1.95$  [20]. The pyridine was anhydrous (<0.003% water) and obtained from Aldrich. Pz and Pm were also obtained from Aldrich. The ratio between free solvent and side-chain Py groups was 1:1 in all three solutions. Solutions were homogeneous and transparent. The solutions were colorless in Pm and Py and yellowish in Pz. The spectroscopic measurements were done immediately after preparation.

Absorption spectra were recorded on a Shimadzu UV-3101PC scanning spectrophotometer. Excitation and PL spectra were taken on a Shimadzu RF-5301PC spectrofluorimeter. Samples were contained in a 2.5-mm quartz cuvette, and data were collected at right angles to the excitation beam. UV irradiation at 380 nm ( $5.3 \text{ mW/cm}^2$ ) was accomplished with a xenon short arc lamp (Ushio) inside the Shimadzu RF-5301PC. A polarization cell attachment was used to investigate the influence of the polarization of the incident light on the photoinduced ordering processes. We observed that the photoinduced solution conversion into a gel does not depend on the excitation beam polarization, but only on its energy. All of the experiments were made with an excitation beam power of  $5.3 \text{ mW/cm}^2$ .

A  $2.5 \times 2.5\text{-mm}^2$  quartz cuvette was used, where the irradiated area size of approximately 2 mm in diameter ensured that the sample irradiation and PL excitation occurred in exactly the same area. The excitation wavelength was chosen to give the maximum PL intensity. Periodically, the irradiation was interrupted and PL measurements were performed. The resolution of the emission and excitation spectra was 1 nm.

Photo registration of PL changes was also done. For that investigation, the solution was kept in a  $1 \times 1\text{-cm}^2$  quartz cuvette and was irradiated through the mask. Afterward the mask was removed and a picture of the PL solution in the irradiated and nonirradiated area was taken. IR spectra of liquid and solid films were recorded in a  $\text{CaF}_2$  cell (0.01 mm) by means of a Bruker IFS-113v spectrometer. The polymer film was prepared by heating the powder at  $250^\circ\text{C}$  between  $\text{CaF}_2$  plates.

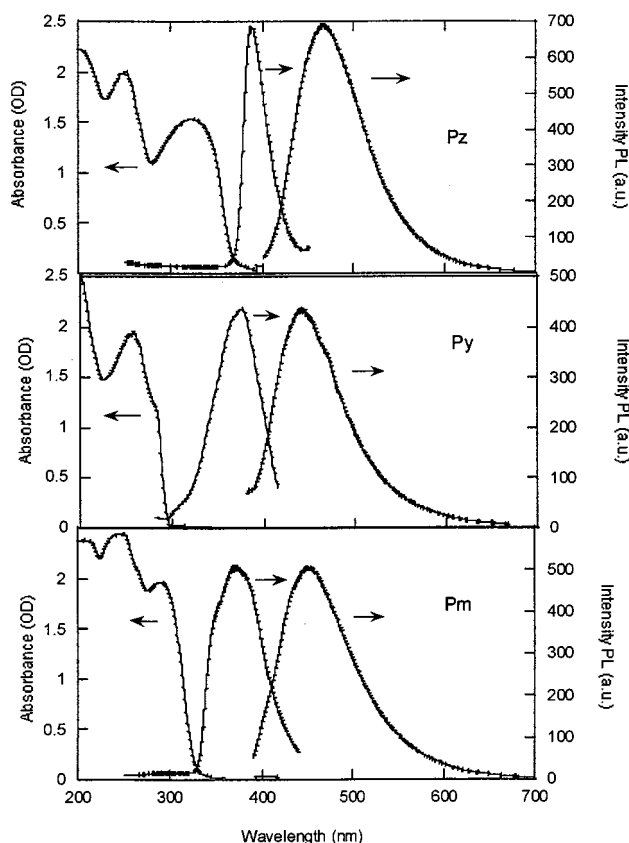
X-ray measurements were made using a Searle low-angle camera operating with Ni-filtered  $\text{Cu-K}_\alpha$  radiation (average wavelength,  $1.54 \text{ \AA}$ ) [14]. Samples were held in 1.5-mm quartz X-ray capillaries, which were flame-sealed to prevent solvent evaporation.

To investigate the material structure we also applied the method of second harmonic generation (SHG). A Q-switched Nd:YAG laser (Surelite) operating at a 1064-nm fundamental wavelength, 10-Hz repetition frequency, and 7-ns pulse duration was used. The sample was placed at the focus of a lens having a 1.5-m focal length, which produced a spot  $400 \mu\text{m}$  in diameter. The laser energy at the sample was 12 mJ per pulse, with a peak power of  $1.5 \text{ GW/cm}^2$ . The second harmonic (SH) signal generated by the sample was observed through a 532-nm interference filter by means of a photomultiplier. The sample was placed at the focus of a lens having a 1.5-m focal length, which produced a spot  $400 \mu\text{m}$  in diameter. The laser energy at the sample was 12 mJ per pulse, with a peak power of  $1.5 \text{ GW/cm}^2$ . The SH signal generated by

the sample was observed through a 532-nm interference filter by means of a photomultiplier. For SHG measurement, the sample was irradiated for 75 min with 380-nm UV through a mask whose shape is shown in the inset in Fig. 8. Afterward, the mask was removed, and a 1064-nm beam was swept across the sample, passing first through a region that had been exposed to UV light, then through an unirradiated region, and, finally, through a second region that had been irradiated with UV. A quartz plate was used as an intensity reference. The PL measurements were made immediately after UV irradiation of the sample, and then the SHG experiment was performed.

## RESULTS

Figure 1 shows the initial absorption spectrum (left traces), excitation spectrum (middle traces), and PL spectrum (right traces) of P4VPy in Pm, in Py, and in Pz. The absorption spectrum shows a major peak at 252 nm,



**Fig. 1.** The initial absorption spectrum (left traces), excitation spectrum (middle traces), and PL spectrum (right traces) of P4VPy in Pm, in Py, and in Pz. The ratio between free solvent molecules and side-chain Py groups was 1:1 in all three solutions.

with a shoulder at 270 nm, in Py; two peaks, at 243 and 298 nm, in Pm; and two peaks, at 252 and 324 nm, in Pz. We also observe a shorter-wavelength absorption at 200 nm, whose presence is indicated in all three panels, Pm, Py, and Pz.

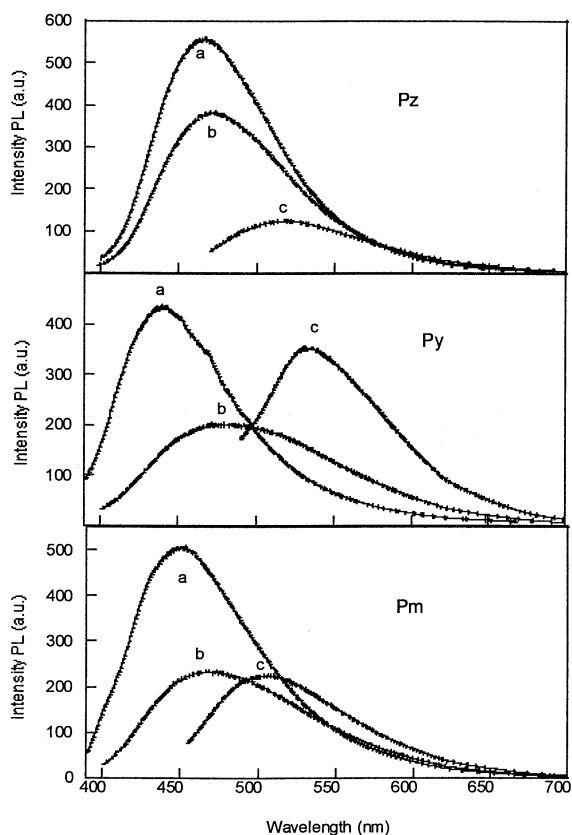
The initial PL spectra of P4VPy were blue, with different emission maxima of 435, 440, and 460 nm, in Pm ( $pK_{HB}$  5 1.37), Py ( $pK_{HB}$  5 1.86), and Pz ( $pK_{HB}$  5 1.95), respectively. The intensity of the PL spectra was approximately the same in Pm and Py and comparatively higher in Pz. (The ratio between free solvent and side-chain Py groups was 1:1 in all three solutions.) The maxima of the excitation spectra in Pm and Py lie at 370 and 375 nm, respectively, and are red-shifted in Pz to 385 nm. The excitation spectrum, in all three solutions, does not overlap with the main absorption band but overlaps with the tail of the absorption spectrum. In Pz, however, the overlap of the excitation and absorption spectra is more pronounced than in Pm and, especially, in Py. It is important to note that the full width at half-maximum (FWHM) of the excitation spectrum in Pz is half that in

Py and Pm, changing from 0.72eV in Py and Pm to 0.36eV in Pz. The narrowing of the excitation spectra of P4VPy in Pz originates from a stabilization of the orientation of the polymeric side-chain groups. The stabilization occurs by hydrogen-bond interaction with solvent molecules. On the other hand, this indicates that the PL and excitation spectra show a strong dependence on the hydrogen-bond aggregate formation.

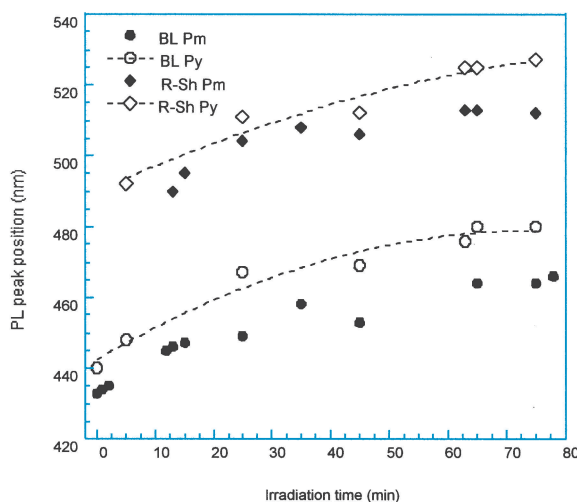
Upon UV irradiation (5.3 mW) for 75 min, different PLs of P4VPy/solvent were observed under excitation at the appropriate wavelengths. As shown in Fig. 2, in Pm, emission maxima occurred at 468 and 512 nm (panel Pm; b and c, respectively); in Py, at 480 and 527 nm (panel Py; b and c, respectively); and in Pz, at 470 nm (panel Pz; b). Furthermore, the <sup>TM</sup>internal red-shifted PL at 517 nm, which was completely overlapped by the blue luminescence, peaks in Pz. To compare the PL intensity change before and after irradiation, initial PL spectra are also shown in Fig. 2. The PL spectra labeled <sup>TM</sup>a in all three panels are the initial PL spectra obtained in sealed cuvettes before UV irradiation.

An increase in the viscosity of the solutions accompanied the shift and tunability of the PL. We observed that the refractive index of the solution increased upon the transformation of the solution to a gel. This increase was approximately 0.09 at 400 nm, or from about 1.48 to 1.57. The solution in Pz becomes a gel immediately after preparation without irradiation.

Figure 3 shows the dependence of the PL's peak position on the irradiation time. As one can see, the peak position of the blue PL in Py (BL Py), and also in Pm (BL Pm), is red-shifted as the sample is irradiated. After 5 and 12 min (Py and Pm, respectively) of UV irradiation,



**Fig. 2.** Emission spectra before UV irradiation (a) and after UV irradiation at 380 nm ( $5.3 \text{ mW/cm}^2$ ) in Pm (b, c), in Py (b, c), and in Pz (b, c). Blue and red-shifted PL after irradiation—b and c, respectively.



**Fig. 3.** Peak position of blue (BL) and red-shifted (R-Sh) PL of P4VPy in pyrimidine (Pm) and pyridine (Py) versus time of irradiation.

a new red-shifted PL appears. The solution of P4VPy in Pz does not exhibit such behavior. The wavelength of excitation of the new red-shifted PL corresponds to that of the blue PL maximum. The peak positions of these new PL emissions are further red-shifted during irradiation. The blue- and red-shifted PL in Pm are saturated at 460 nm (blue PL) and 512 nm (red-shifted PL). The blue PL in Py is continuously red-shifted during irradiation, until it reaches 480 nm, where it remains. The red-shifted PL in Py can reach 570 nm by excitation at 480 nm, as shown in Fig. 4. The area irradiated through the mask glows with yellow PL, as opposed to the remaining nonirradiated area, which exhibits no PL under the chosen excitation wavelength (480 nm). The blue scattered light in the remaining area is of the same wavelength as the excitation wavelength of 480 nm.

We analyzed the data presented in Fig. 3 and found that for the Py solution the transition energy of the green PL depends on the transition energy of the blue PL according to the following empirical equation (1):

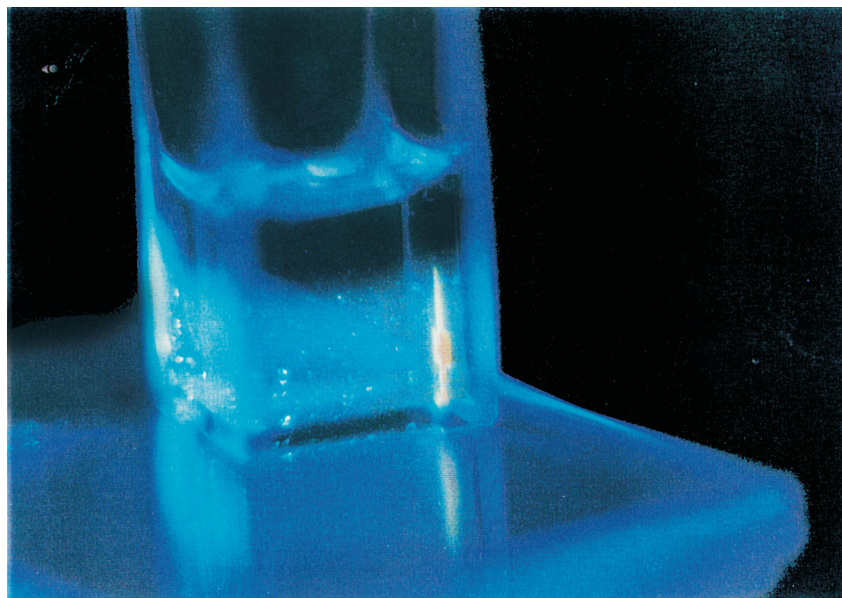
$$E_G^{PL} = 5 E_B^{PL} - 2 D_B/2 + 1 C \text{ (eV)} \quad (1)$$

where  $E_B^{PL}$  is the energy of blue PL (eV),  $E_G^{PL}$  is the energy of green PL (eV),  $D_B$  denotes the Stokes losses of the blue PL (eV), and  $C$  is the constant in the first approximation. (Note that  $C$  is a function of the molecular rearrangement in the excited and ground states over the range  $0.05 \pm 0.015$  eV.)

This equation is a classical characterization of an energy transition in a dimer complex [21]. Creation of dimers, as shown by Kasha *et al.* [22], results in splitting the singlet exciton state into two states. Based on this, we can conclude that the appearance of the new red-shifted PL may originate from a similar process in our polymeric system. The complex is based on the  $^{TM}$ monomer, which is the blue emitting center. The  $^{TM}$ dimer in our system is apparently a molecular complex between polymeric pyridine (or a pyridinium ion) and a free solvent molecule. In the work of E. Lifshitz and coauthors [21] it was shown that the molecular arrangement head-to-tail results in a red shift of the singlet±singlet absorption band. This, probably,  $^{TM}$ dimer structure in our system is a polymeric pyridinium ion-free solvent molecule. The influence of interaction of solvent molecules on the PL change is demonstrated in Fig. 2.

Absorption spectrum changes in all three solutions are displayed in Fig. 5. In all three solutions, Pz, Py, and Pm, narrowing of the absorption bands is observed. In Py it is most apparent; in Pm a prolonged tail of absorption in the visible range appears.

IR spectra in the range near  $3300 \pm 3500 \text{ cm}^{-1}$  (the range of proton vibration) of liquid pyridine, solid P4VPy film, and a solution of P4VPy in Py before irradiation are presented in Fig. 6. An intense, wide absorption band appears at  $3400 \text{ cm}^{-1}$  in the P4VPy solution spectrum, while no such band is observed in liquid Py and solid



**Fig. 4.** A solution of P4VPy in Py after UV irradiation through a mask (yellow image). The area which was irradiated by UV light is yellow colored for PL compared to the remaining nonirradiated volume. The optical image of the irradiated area can be preserved for 1 month.

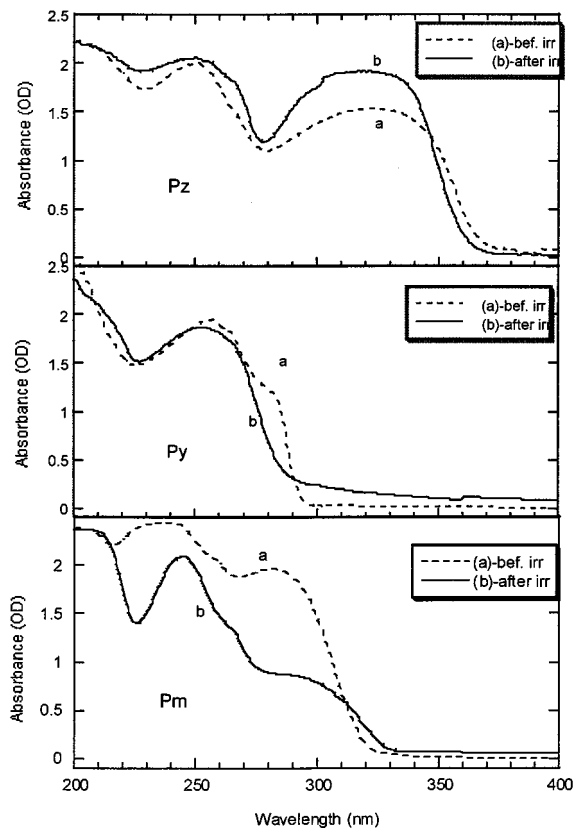


Fig. 5. Absorption spectra before (bef.) (b) and after (a) UV irradiation in Pm, Py, and Pz.

P4VPy. Apparently this absorption appears as the result of the polymer–solvent interaction. This new band at  $3400\text{ cm}^{-1}$  most likely can be assigned to the stretching proton vibration of the  $\text{N}^+\text{–H}$  bond of the pyridinium ion ( $\text{Py}^+\text{H}$ ). (A corresponding band of a neutral NH group H-bound to Py appears at  $3150\text{ cm}^{-1}$  [23].) The molar intensity of this band is 10 times larger than that estimated for free pyridinium [24] and is, on average,  $13 \cdot 10^{-4}\text{ cm} \cdot \text{mmol}^{-1}$  per pyridinium ion. Also, the intensity of this band rises as the polymer concentration is increased. The rather high frequency indicates that  $\text{Py}^+\text{H}$  H-bonding with the pyridine molecule is quite weak (4–8 kJ/mol) [24]. An analogous intense absorption band also appears at  $3400\text{ cm}^{-1}$  in Pm and Pz solutions of P4VPy. With UV irradiation, the intensity of that band decreases, and at the same time an increasing wide absorption in the range below  $3100\text{ cm}^{-1}$  is observed.

X-ray data on P4VPy/Py solutions before and after irradiation are reproduced in Fig. 7. The initial solution shows two diffraction peaks with different intensities: with a low intensity at  $8.5\text{ \AA}$  and with a much higher intensity at  $4.3\text{ \AA}$ . The low-intensity peak at  $8.5\text{ \AA}$  shows

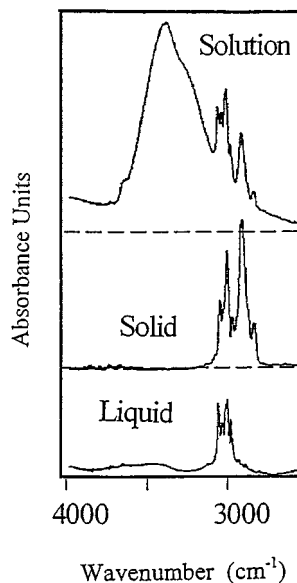


Fig. 6. IR spectra of liquid pyridine, a thin solid film of poly(4-vinyl pyridine), and a solution of P4VPy in pyridine.

that some ordering exists in the initial solution. Most probably that ordering is induced by the high concentration of the polymer in the solution. After irradiation redistribution of the peak intensity occurs. The intensity at  $4.3\text{ \AA}$  decreases, and at the same time the intensity at  $8.5\text{ \AA}$  increases.

Figure 8 shows the dependence of the SH signal intensity on the position of the  $1064\text{-nm}$  beam. We observed that with the resolution of the focused  $1064\text{-nm}$  beam, the profile of the intensity of the SH signal

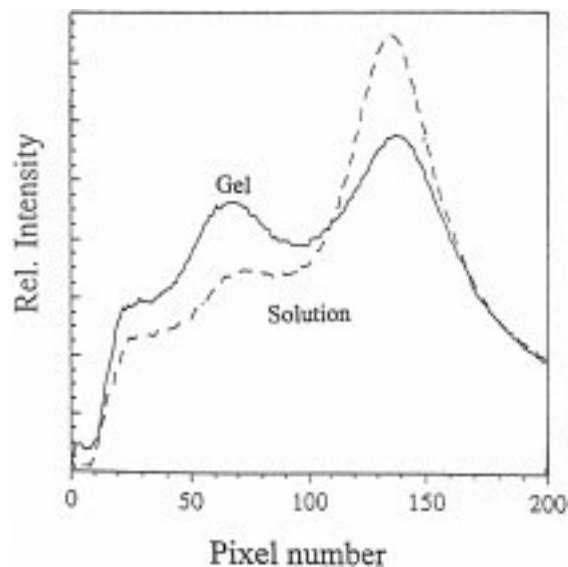


Fig. 7. X-ray diffraction measurements in solution and gel.

repeats the shape of the mask openings. The regions that were not UV-irradiated did not give any SH signal, while the UV-irradiated region did. Another important observation is the dependence of the SH signal intensity on the fundamental laser beam polarization. The SHG signal was observed with S-polarization of the fundamental laser beam and was not observed at all with P-polarization of the laser beam.

## DISCUSSION

In this contribution we showed that poly(4-vinyl pyridine) dissolved in Py at 1:1 molar ratio between solvent and polymeric side groups forms extremely light-sensitive material (Figs. 1–4). Under UV irradiation at 380 nm, this photosensitive system exhibits tunable PL properties, where the PL changes are dependent on the amount of light that is absorbed by the system (Fig. 3). P4VPy exhibits similar properties in Pm and is practically non-light-sensitive in Pz.

Under UV irradiation at 380 nm the solution turns to a gel. The analysis of photoinduced processes by optical spectroscopy, X-ray, and IR measurements first indicates the transformation of one species to another. The intensity of an initially blue PL decreases at the same time that that of a new red-shifted PL increases (Fig. 2). The intensity of the X-ray diffraction peak at 4.3 Å decreases and the intensity at 8.5 Å increases (Fig. 6). IR data reveal an increase in the wide absorption in the range below 3100

$\text{cm}^{-1}$  and a decrease in the  $3400\text{-cm}^{-1}$  absorption during UV irradiation. Investigation of the dependence of the transition energy of the new red-shifted PL on the transition energy of the blue PL indicates that the photoinduced transformation of one species to another is similar to photoinduced dimerization. The “dimer” arrangement between free solvent and the side-chain pyridine group (or pyridinium ion) creates a new emitting center of the red-shifted emission. The empirical equation (1) shows that an exchange of excitation energy between molecules that formed the “dimer” is about half of the Stokes losses in blue PL. This value reveals a unique property of the “dimer.” Both molecules mainly preserve their electronic structure, and their mutual interactions may be considered an additional perturbation [21]. The energy of this interaction in the ground and excited state ranges from 0.015 to 0.05 eV, which corresponds to the energy change that occurs in weak hydrogen bonding. Interaction between charged and neutral pyridine side-chain groups forms another kind of “dimer,” which is responsible for interchain interaction. Wide absorbancy below  $3100\text{ cm}^{-1}$  can be modeled by the formation of interchain quasi-symmetrical H bonds ( $\text{Py-H-Py}$ ), which are quite strong ( $\sim 50\text{ kJ/mol}$ ) and are well known for pyridine [23].

Photoinduced “dimerization” leads to self-organization of the system in quasi-crystal order. Since SHG is originated from noncentrosymmetric macroscopic order [27], our observation of SHG provides evidence for such a structure. Dependence of the intensity of the SHG signal on laser beam polarization shows that the photoinduced

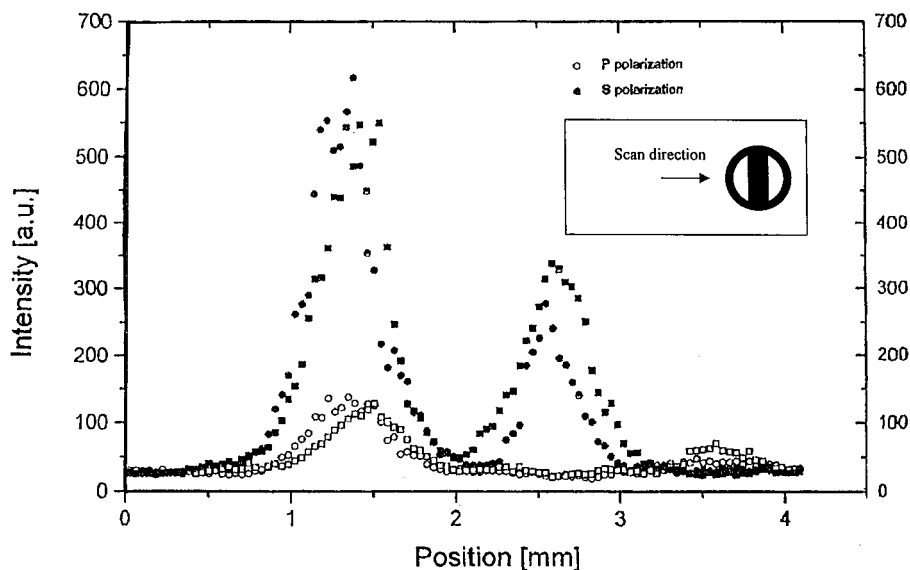


Fig. 8. SHG signal intensity dependence on the position of the 1064-nm beam across the irradiated and nonirradiated area. Inset: The mask for solution irradiation.

structure formation has directional order (Fig. 8). X-ray data, together with the SGH indicate a quasi-crystal order of the system with two parameters: 4.3 and 8.5 Å (Fig. 7).

The process of photoinduced dimerization depends on the solvent properties, as shown in Figs. 1–4. We examined this process in solvents whose hydrogen bond basicity ranges from  $pK_{\text{HB}} = 1.37$  to  $pK_{\text{HB}} = 1.95$ . As mentioned above, the system is most responsive to light in the case of Py, where  $pK_{\text{HB}} = 1.85$ ; much less responsive in Pm, whose  $pK_{\text{HB}}$  is 1.37; and practically insensitive to light in Pz, which has a  $pK_{\text{HB}}$  of 1.95. The red shift of the blue PL increases with increasing hydrogen-bond basicity of a solvent (Fig. 1). The narrowing of the excitation spectra of P4VPy in Pz originates from the homogeneous energy distribution in the ground state. The homogeneous energy distribution obviously stems from the stabilization of the polymer side-chain group orientation by hydrogen-bond interaction with solvent molecules. Based on X-ray and SHG data, the following conclusions can be made: a red shift of the blue emission is initiated by a particular orientation of the side-chain group, which is due to their hydrogen bond interaction with a solvent; this orientation introduces the order to the initial P4VPy solution.

The IR data (Fig. 6), which show an intense  $\text{N}^+ - \text{H}$  stretching band in the unirradiated solution, suggested that the first step in this process, before the photoinduced rearrangement, is the protonation of the polymeric pyridine group upon solvation. Detailed investigation of this protonation will be discussed in our forthcoming publication [25].

## CONCLUSIONS

Concentrated solutions of poly(4-vinyl pyridine) in Py and in Pm with a 1:1 ratio between free solvent molecules and side-chain groups are photosensitive systems that exhibit tunable PL properties as a response to UV irradiation. Under UV irradiation at 380 nm, photoinduced “dimerization” takes place. Interchain interactions occur and the solution converts to a gel with a quasi-crystal structural order and, through multiple hydrogen bonds, gives rise an electronic structure change of the emitting centers. An important system property is the reversibility of induced structure changes. Mechanical perturbation or heating can convert the gel back to the solution. Upon such conversion, the red-shifted PL is not observed, and the initial PL is blue-shifted to 450 nm and stays there. The photoinduced gelation can then be repeated, and the conversion cycle performed again, more than at least five times. The magnitude of the photoin-

duced changes depends in a predictable way on the amount of light with which the system is irradiated

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