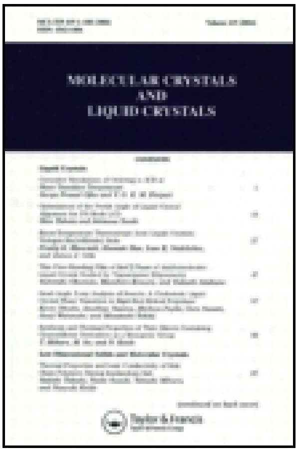

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Polymer-Mediated Proton Transfers of 7-Azaindole Embedded in Poly(2-hydroxylethyl methacrylate) Matrix

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Host-guest interactions including polymer-mediated proton transfer dynamics are investigated for 7-azaindole embedded in poly(2-hydroxyethyl methacrylate) matrix using time-resolved fluorescence and transient absorption spectroscopy. Upon absorption of a photon the dye molecule having cyclic H-bonds with a polymeric group undergoes excited-state double proton transfer in 100 ps to form its tautomer, while the molecule without an H-bond bridge does not experience the proton transfer within the lifetime of 1200 ps. The reverse proton transfer takes place on the time scale of 60 μs in the ground state.

Keywords 7-azaindole; poly(2-hydroxyethyl methacrylate); photoluminescence; excited-state proton transfer; reverse proton transfer

INTRODUCTION

There has been extensive research in 7-azaindole (7AI) because it is the chromophore of 7-azatryptophan, a promising alternative optical probe of proteins, and its dimer is regarded as a DNA model base pair.[1,2] While the dimer undergoes stepwise or asynchronous concerted proton transfer within 10 ps,[1] the monomer forms a cyclically H-bonded 1:1 complex with an alcoholic molecule and goes through an excited-state double proton transfer (EDPT) in 100–200 ps to give birth to the tautomeric species (T).[2] Specific interactions between guest and host molecules have been found to alter the optical properties of dyes embedded in macromolecules.[3,4] The interactions are of great interest due to their implications for dye lasers, LEDs, nonlinear optical devices, and photostimulated biological switches.[5]

Here we report fluorescence and transient absorption kinetic profiles together with absorption and emission spectra to reveal the polymer-mediated EDPT and the following ground-state reverse double proton transfer (GRDPT) of 7AI embedded in solid poly(2-hydroxyethyl methacrylate) (PHEMA) having alcoholic groups.

METHODS, RESULTS, AND DISCUSSION

Purified 7AI was added to purified 2-hydroxyethyl methacrylate to be 0.1 mM before adding AIBN as an initiator. The solution was transferred to 1-cm rectangular cells and kept at 50℃ in the dark for a week. All the optical measurements, the details of which are described elsewhere,[4-6] were carried out using cell-removed bare polymeric samples at room temperature.

Figure 1 shows that excitation at 290 nm yields the normal fluorescence mainly while excitation at 400 nm gives birth to the tautomeric fluorescence. However, excitation at 320 nm shows a spectrum having the dual fluorescence bands. Tentatively we consider that only the 7AI molecule having cyclic H-bonds with an alcoholic

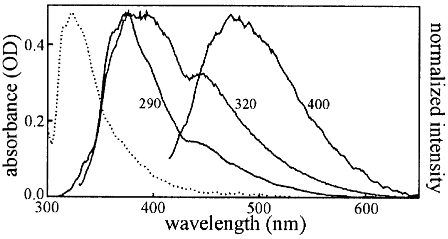

FIGURE 1 Absorption (dotted) and emission (solid, $\lambda_{\text{excitation}}$ in nm shown inside) spectra of 7AI in PHEMA.

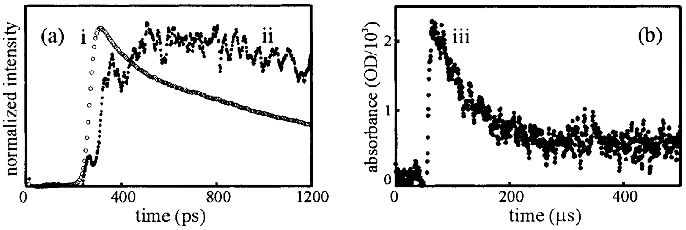

FIGURE 2 Fluorescence (a) and transient absorption (b) kinetic profiles of 7AI in PHEMA with excitation at 266 nm. **i**, **ii**, and **iii** were monitored at 360±10, 540+, and 420±10 nm, respectively.

group at the moment of excitation undergoes EDPT to form a T* molecule.[2] It is interesting to note that T in PHEMA is energetically stable enough to exist in the ground state. It is known[7] that T does not exist to be detectable in alcoholic solvents.

While the normal fluorescence shows two decay components of 100 and 1200 ps, the tautomeric fluorescence rises in 100 ps and decays in 2500 ps (Figure 2, Table 1). Thus we assert that 100 ps is the EDPT time of 7AI having a cyclic H-bond complex with an alcoholic group in PHEMA. The slow 7AI* decay component indicates that the molecule without the H-bond bridge at the moment of excitation cannot form the bridge within the lifetime of 1200 ps because of the rigidity of the solid matrix. On the other hand, the transient absorption reveals two decay times of 60 and 10000 μs, which are attributed to the time of GRDPT and the lowest triplet-state decay time of 7AI, respectively. It is noteworthy that GRDPT in PHEMA is extremely slow compared with GRDPT in solvents, which is too fast to measure the rate.[7]

The proposed mechanism for the EDPT and following GRDPT of

TABLE 1 Fluorescence and transient absorption kinetic functions of 7AI in PHEMA, deconvoluted from Figure 2.

profile	λ_{monitor} (nm)	deconvoluted kinetic function
i	360±10	$0.2\exp\{-t/(100\text{ ps})\} + 0.8\exp\{-t/(1200\text{ ps})\}$
ii	540+	$[1 - \exp\{-t/(100\text{ ps})\}]\exp\{-t/(2500\text{ ps})\}$
iii	420±10	$0.8\exp\{-t/(60\ \mu\text{s})\} + 0.2\exp\{-t/(10000\ \mu\text{s})\}$

7AI mediated by PHEMA matrix is described in Figure 3. The dye molecule having the H-bridge with an alcoholic group at the ground state undergoes EDPT in 100 ps upon excitation and subsequent GRDPT in 60 μs. However, the molecule without the bridge is unable to form the bridge, which is prerequisite for EDPT, within the lifetime of 1200 ps. The rigid polymeric host slows proton transfers and stabilizes the photochromic isomer of the guest dye.

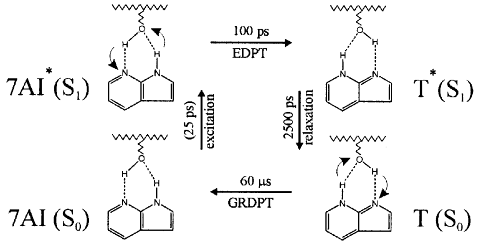

FIGURE 3 Schematic double proton transfer mechanism of 7AI in PHEMA. 7AI without an H-bond bridge upon excitation cannot undergo EDPT within the lifetime of 1200 ps.

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