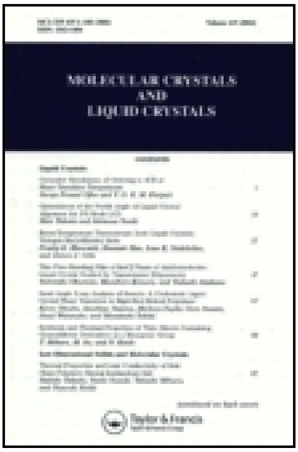

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Cyclic Intramolecular Proton Transfer Dynamics of Polyquinoline

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Cyclic Intramolecular Proton Transfer Dynamics of Polyquinoline

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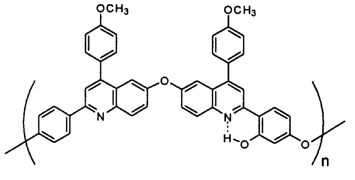
The excited-state intramolecular proton transfer and following reverse ground-state proton transfer of photoluminescent polyquinoline are investigated by measuring temperature-dependent fluorescence and transient absorption kinetic profiles. The transfer at the lowest excited singlet state takes place within 6 ps via a preexisting intramolecular hydrogen bond with a negligibly small activation energy. On the other hand, the reverse transfer at the ground state occurs in the time scale of 10 μs. The rapid proton transfer cycle of the polymer is of great interest due to its implications for optoelectronic devices such as dye lasers.

Keywords: polyquinoline; excited-state proton transfer; reverse ground-state proton transfer; photoluminescence; transient absorption

INTRODUCTION

Great interest is currently focused on the exploration and development of new photoluminescent and electroluminescent materials useful to information and telecommunication media. In particular, electroluminescent polymers have various advantages such as easy-processiblity, variable colors, low drive voltage, good flexibility compared with inorganic materials. Thus there have been extensive attempts to improve optical, nonlinear, electroluminescent, semiconducting, and photoluminescent properties of π-conjugated polymers for their applications in light emitting diodes, solar cells, nonlinear materials, and lasers.[1-3] However, organic polymers have problems such as low luminescence quantum efficiency, short lastingness, and poor thermal stability. Intramolecularly H-bonded moieties within such a polymer backbone can play an important role due to their photochemical stability, thermal resistance, and low self-absorption by offering an adiabatic proton transfer or an efficient deactivation path.[2-4]

Thus we have investigated the cyclic intramolecular proton transfer dynamics of polyquinoline (PQH) by using time-resolved absorption and emission spectroscopy to shed light on the applicability of the polymer for electronics and photonics.



Polyquinoline (PQH)

METHODS, RESULTS, AND DISSCUSION

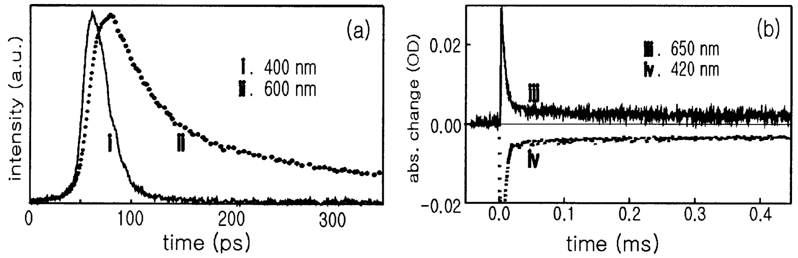


FIGURE 1 Fluorescence (a, excited at 290 nm) and transient absorption (b, excited at 355 nm) kinetic profiles at shown monitored wavelengths of PQH in TCE.

The procedures of PQH synthesis[3] and the measurement details of picosecond photoluminescence kinetics[4] and transient absorption kinetic profiles[5] are described elsewhere. Sample temperature was controlled using a closed-cycle He cryostat (Jannis, CCS-100).

PQH in tetrachloroethane (TCE) shows dual blue and red fluorescence bands. While the blue band decays in 6 ps, the red one rises in 6 ps and decays with two time constants of 30 and 400 ps (Figure 1 and Table 1). While 6 ps is ascribed to the excited-state intramolecular proton transfer (EIPT) of the normal enol chromophore (N_E), 30 ps and 400 ps are attributed to the vibrational and electronic relaxation times of the photogenerated excited tautomeric keto chromophore (T_K), respectively. Both the transient absorption and bleach recovery kinetic profiles show a biphasic exponential kinetics of 0.01 ms and 8 ms, which are attributed to the decay times of the ground and lowest-excited triplet states of T_K. Thus 10 μs corresponds to the reverse ground-state intramolecular proton transfer (RGIPT) of PQH.

TABLE 1 Kinetic functions deconvoluted from Figure 1.

profile	deconvoluted kinetic function
I	exp[-t/(6 ps)]
ii	{1-exp[-t/(6 ps)]}{0.8 exp[-t/(30 ps)] + 0.2exp[-t/(400 ps)]}
iii	0.9 exp[-t/(0.01 ms)] + 0.1 exp[-t/(8 ms)]
iv	– 0.88 exp[-t/(0.01 ms)] – 0.12 exp[-t/(8 ms)]

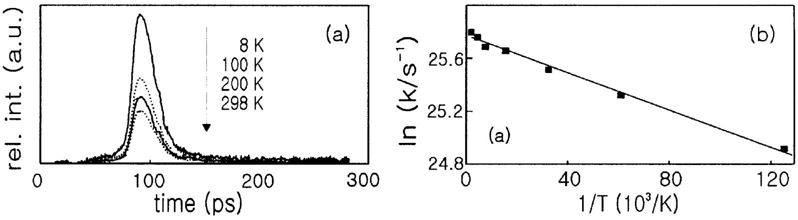


FIGURE 2 The variation of the normal fluorescence decay kinetics with temperature (a) and the Arrhenius plot of the EIPT rate (b). The activation energy (**E$_a$**) and the preexponential factor (**A**) were estimated to be 0.06 kJ mol^{-1} and 2×10^{11} s^{-1}, respectively.

To avoid the liquid-solid phase transition of a solution, we have used the film instead of the solution to study the temperature dependence of the EIPT. The decay kinetics of the normal fluorescence does not change noticeably with the extreme variation of sample temperature (Figure 2). However, the initial fluorescence amplitude decreases with temperature increment. These indicate that the real EIPT time is shorter than our temporal resolution. Because the integrated intensity of the same fluorescence is proportional to the lifetime (that is the EIPT time), we can determine lifetimes at various temperatures to plot the Arrhenius relation. It is noteworthy that the $\mathbf{E_a}$ of 0.06 kJ mol^{-1} is negligibly small and that the collisional frequency (the **A** of 2×10^{11} s^{-1}) between the proton donor and the acceptor is extremely high. Because real polymers are more-or-less rigid, H-bonds are more likely to be frozen. This makes the EIPT extremely fast via tunneling through a preexisting H-bond bridge.[6,7] It is known[8,9] that the H-bond between an OH group and a nitrogen atom is the strongest and that its proton transfer barrier is the smallest. These also support the extremely fast EIPT of PQH having a negligibly small $\mathbf{E_a}$.

The EIPT of PQH takes place within 6 ps with a negligibly small $\mathbf{E_a}$ of 0.06 kJ mol^{-1} while its following RGIPT takes 10 μs. The preexisting H-bond between the proton donor and the acceptor is suggested to be very strong and rigid. This makes the proton transfer of the polymer extremely fast with an extremely small $\mathbf{E_a}$. The rapid and efficient proton transfer cycle may be helpful for the polymer to be utilized in dye lasers, optoelectronics, and photostabilizers.

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