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Excited state intramolecular proton transfer (ESIPT) has been demonstrated in new intramoleculary hydrogen bonded (IHB) polymers of interest as photostabilizers, triplet quenchers, photochromic materials, laser dyes and electroluminescent materials. The new IHB polymers containing the 2-(2-hydroxyphenyl)benzoxazole moiety in the main chain were used to explore the effects of polymer structure, extended conjugation and competition with excimer formation on the ESIPT process. It was found that polymer structure, and particularly extent of conjugation, affects an IHB polymer's ability to exhibit ESIPT.

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EXCITED-STATE INTRAMOLECULAR PROTON TRANSFER IN POLYMERS

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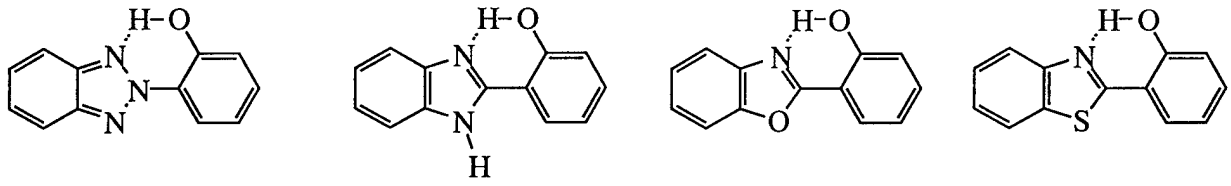
ABSTRACT

Excited state intramolecular proton transfer (ESIPT) has been demonstrated in new intramoleculary hydrogen bonded (IHB) polymers of interest as photostabilizers, triplet quenchers, photochromic materials, laser dyes and electroluminescent materials. The new IHB polymers containing the 2-(2-hydroxyphenyl)benzoxazole moiety in the main chain were used to explore the effects of polymer structure, extended conjugation and competition with excimer formation on the ESIPT process. It was found that polymer structure, and particularly extent of conjugation, affects an IHB polymer's ability to exhibit ESIPT.

INTRODUCTION

Several small dissymmetric aromatic molecules which contain an intramolecular hydrogen bond (IHB) as part of a 6-membered ring are used as photostabilizers of polymers. Examples include 2-(2-hydroxyphenyl)benzotriazole (HPB),[1] 2-(2-hydroxyphenyl)benzimidazole (HBI),[2] 2-(2-hydroxyphenyl)benzoxazole (HBO)[3] and 2-(2-hydroxyphenyl)benzothiazole (HBT).[4]



HPB HBI HBO HBT

The mechanism by which these molecules dissipate absorbed energy and thereby protect the polymer from photochemical degradation (e.g. yellowing when exposed to sunlight) is commonly believed to be excited state intramolecular proton transfer (ESIPT, Figure 1).[5,6] Derivatives of HPB are the most important polymer photostabilizers because the entire ESIPT cycle occurs in the subpicosecond time regime and deactivation of the excited keto state occurs essentially in a nonradiative manner.[1] Vogl and coworkers[7] have developed methods for covalent attachment of HPB derivatives into many flexible polymers to prevent leaching of the photostabilizer from the polymer. Scott and coworkers[8] have investigated energy transfer in these side-chain systems and were the first to show ESIPT as the operating mechanism for photostabilization.

Another important consequence of ESIPT is that a population inversion occurs since the keto tautomer does not exist in the ground state. After the suggestion of Khan and Kasha,[9] the ESIPT process has been exploited for use in proton transfer laser dyes such as salicylamide, sodium salicylate, 3-hydroxyflavone and HPB.[6,10] Incorporation of HPB into polymers has been investigated by Acuna and coworkers[11,12] with the purpose of developing solid state proton transfer laser materials. Their investigations have shown that HPB can lase either when doped into poly(methylmethacrylate) (PMMA)[11] or when it is covalently attached as a side chain in copolymers of PMMA.[12]

We have been interested in the solid state properties,[13] such as electroluminescence,[14] of conjugated rigid (and semi-rigid) chain polymers. One of the major prerequisites for commercial development of polymer LED devices[15] is resistance of the polymer to degradation. It occurred to us that incorporating HBO and related moieties into the main chain of rigid chain polymers might lead to robust electroluminescent materials, provided that they (1) exhibit ESIPT and (2) fluoresce.

This approach is to combine the high thermal stability of rigid-rod polymers with the photochemical stability and resistance to degradation by free radicals of IHB moieties. Additionally, the presence of heteroatoms in the main chain of these polymers should make them soluble in organic solvents using the Lewis acid complexation technique.[16] This allows for relatively facile device fabrication. Another potential use for these polymers is as solid state laser materials: IHB rigid and semi-rigid chain polymers are expected to inherit the excellent thermal stability of the parent rigid chain polymers.[17]

The goals of this study, which represents a first step in the development of novel electroluminescent polymers, were thus to prepare rigid (and semi-rigid) chain polymers containing IHB moieties in the main chain, and to investigate the ESIPT process in these polymers.

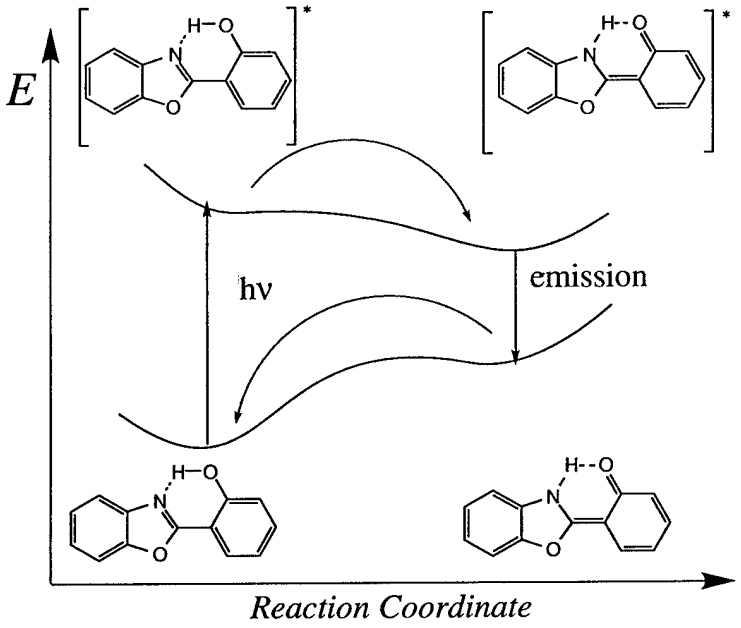


Figure 1: Schematic representation of the ESIPT process for HBO. The molecule exists as the enol form in the ground state, but tautomerizes to the keto form in the excited state. After deactivation of the excited keto state, the proton transfer is reversed and the enol starting geometry is regenerated.

EXPERIMENTAL SECTION

Materials. The polymers mHPBO and pHPBO shown in Figure 2 were synthesized by condensation in polyphosphoric acid of 4,6-diamino-1,3-benzenediol (DABDO) with 4-hydroxyisophthalic acid (Fluka, > 99%) and 2-hydroxyterephthalic acid[18] respectively. DABDO was prepared by reducing 4,6-dinitro-1,3-benzenediol[19] with Sn/HCl in EtOH/H_2O,[20] which was precipitated as its dihydrochloride salt in 10 M HCl. DABDO was recrystallized from 3M HCl prior to use. The polymers mH6FPBO and pH6FPBO (Figure 2) were synthesized by condensation in polyphosphoric acid of 2-*bis*-(3-amino-4-hydroxyphenyl) hexafluoropropane (TCI, > 98 %) with 4-hydroxyisophthalic acid (Fluka, > 99%) and 2-hydroxyterephthalic acid, respectively.[21]

Characterization. Thin films of good optical quality were prepared by spin coating of polymer solutions in either formic acid/trifluoroacetic acid/methane sulfonic acid (40/10/1), or nitromethane/$GaCl_3$ solution as previously described.[22,23] Optical absorption spectra were recorded with a Perkin-Elmer Model Lambda 9 UV-Vis-nir spectrophotometer. Steady state photoluminescence spectra were recorded by using a Spex Fluorolog-2 spectrofluorometer equipped with a Spex DM3000f spectroscopy computer. The polymer films were positioned such that emission was detected at 23° from the incident radiation beam.

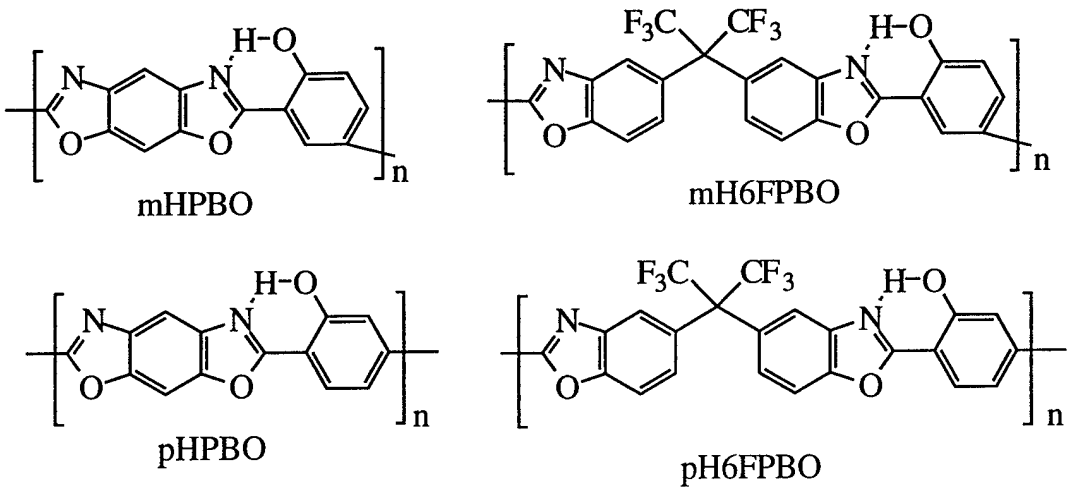


Figure 2: Structures of mHPBO, pHPBO, mH6FPBO and pH6FPBO.

RESULTS AND DISCUSSION

One of the principal challenges of this work was to distinguish between the various pathways of emission. We have already demonstrated that in the solid state, rigid rod polymers can emit *via* an excimer (excited state dimer) pathway, the signature of which is a broad, featureless emission with a significant Stokes shift.[13a] Emission from an ESIPT pathway, in which the keto form is the emitting species, is also characterized by broad and featureless emission with a significant Stokes shift.[6] We resolved this problem by exploiting the fact that the excimer emission is concentration dependent whereas emission from the keto form (ESIPT pathway) is not. The chains of the photoactive polymer were thus isolated from one another by diluting them in a thin solid film of an inert polymer host, preventing excimer formation. The effect of this dilution on the emission spectrum was then determined. If the emission band progressively shifted to higher energy with decreasing concentration and the shape of the band became more structured, the emission was judged to be from the absorbing species, indicating that ESIPT did not occur. On the other hand, if the emission band did not show a concentration dependence, ESIPT was determined to have occurred. The choice of inert polymeric host (PMMA or poly (vinylacetate) (PVAc)) was dictated by solubility of the active polymer and the inert host in the solvent and the ability to prepare optical quality films from a given solution. Phase separation was ruled out by control experiments (results not shown): dilution of the non-hydroxylated analogues of pHPBO, mH6FPBO and pH6FPBO in all cases caused the emission band to shift to higher energies as expected for excimer emission.[13a]

Figure 3 shows the UV spectrum of a pHPBO thin solid film on fused silica, together with the emission spectra of pHPBO as a pure polymer and when diluted in PMMA. The emission from the pure polymer is broad and featureless with a significant Stokes shift. However, the emission band exhibits a blue shift when diluted in PMMA. The fact that the emission band is concentration dependent indicates that emission cannot arise from an ESIPT pathway, suggesting that excimer formation occurs while ESIPT does not.

Figure 4 shows the UV spectrum of a thin solid film mHPBO on fused silica, together with the emission spectra of the polymer when pure and when diluted in PVAc. The UV spectrum shows λ_{max} to be approximately 70 nm blue shifted relative to pHPBO (360 nm vs. 427 nm), as is expected due to the differences in conjugation. Nevertheless, the emission band is red shifted relative to that of pHPBO. More importantly, the emission spectra are not concentration dependent. These results indicates that mHPBO does in fact exhibit ESIPT.

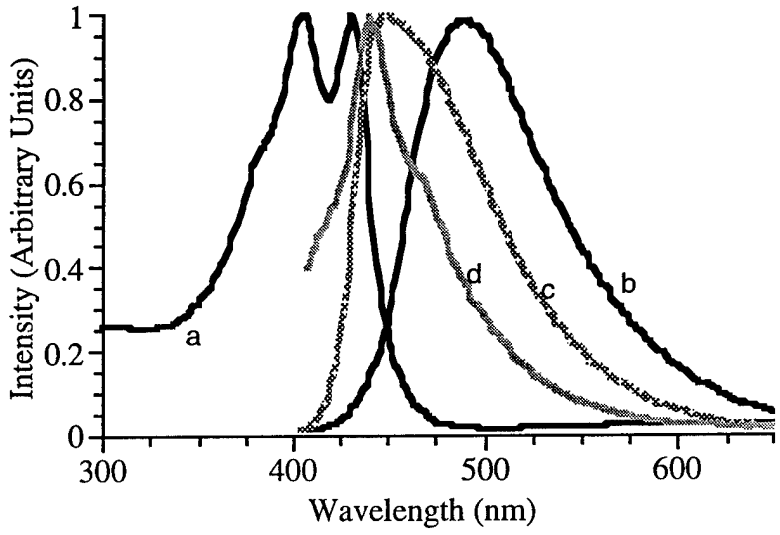


Figure 3: UV and fluorescence spectra of pHPBO.
UV (pure polymer) (curve a)
Emission
pure polymer (curve b)
1% in PMMA (curve c)
0.1 % in PMMA (curve d)

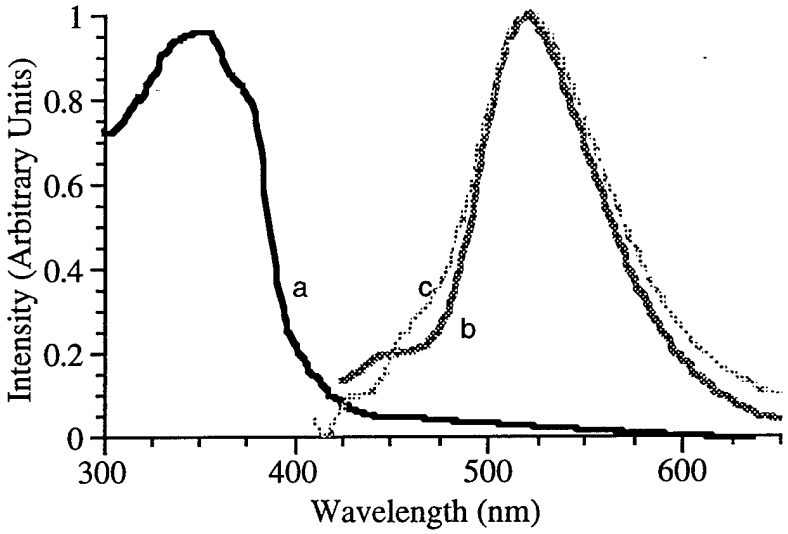


Figure 4: UV and fluorescence spectra of mHPBO.
UV (pure polymer) (curve a)
Emission
pure polymer (curve b)
1% in PVAc (curve c)

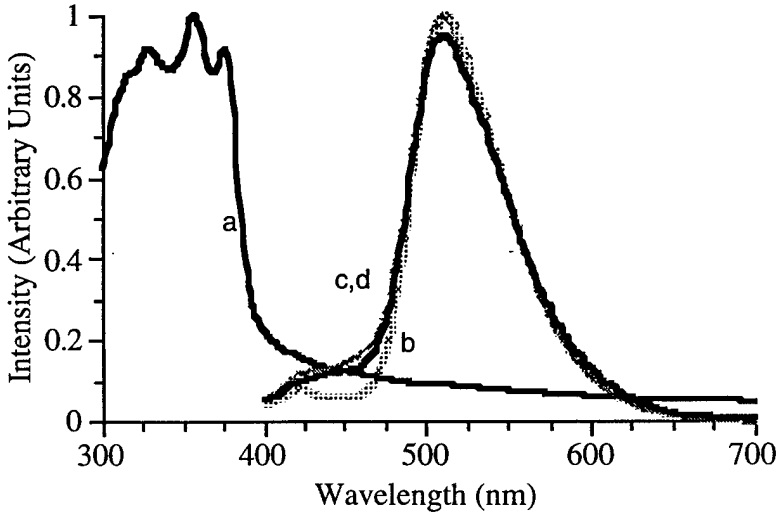
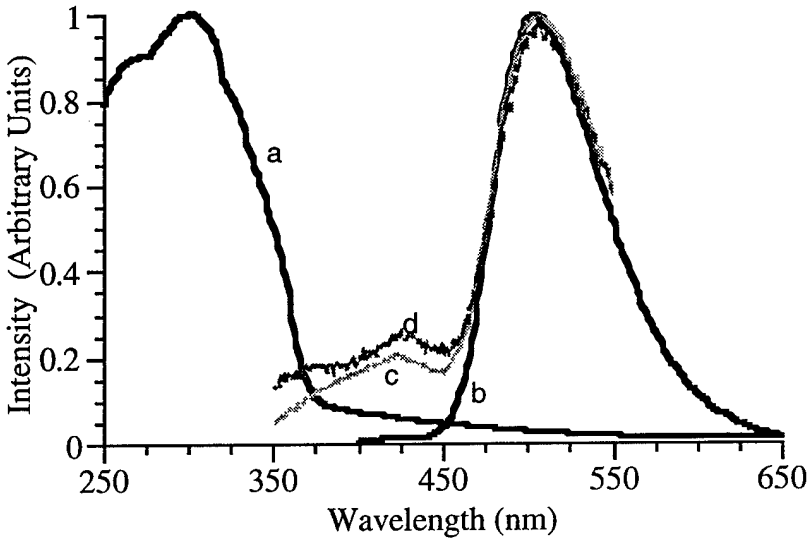


Figure 5: UV and fluorescence spectra of pH6FPBO.
UV (pure polymer) (curve a)
Emission
pure polymer (curve b)
1% in PVAc (curve c)
0.1 % in PVAc (curve d)

Figure 6: UV and fluorescence spectra of mH6FPBO.
UV (pure polymer) (curve a)
Emission
pure polymer (curve b)
1% in PVAc (curve c)
0.1 % in PVAc (curve d)



Figures 5 and 6 show the UV and fluorescence spectra for pH6FPBO and mH6FPBO, respectively. Comparison of the UV spectra shows that λ_{max} for pH6FPBO is red shifted relative to mH6FPBO, as expected from differences in the conjugation. On the other hand, the emission of the pure films of these polymers occurs at ~515 nm in both cases. Additionally, the 515 nm emission band is independent of concentration. The independence of the emission band on concentration rules out excimer emission and indicates that both pH6FPBO and mH6FPBO emit by ESIPT.

In several studies of small molecules which exhibit ESIPT, a small shoulder on the blue edge of the keto emission was reported. The origin of this band is controversial. Explanations of the origin of the shoulder include multiple ground state conformations[24] and the conjugate base.[25] Some of these spectra show a blue shoulder as well. Control experiments indicate that in the case of the diluted polymers, this band is an artifact arising from trace impurities in the inert polymer host.

The results of these experiments indicate that despite the presence of HBO in the backbone of a polymer, ESIPT may not occur. The reason that pHPBO does not exhibit ESIPT whereas mHPBO, mH6FPBO and pH6FPBO all do may have to do with conjugation. All of the polymers which exhibit ESIPT have conjugation in the backbone disrupted either by meta linkages or by an sp^3 carbon. The effect of conjugation on the ESIPT pathway can be explained by considering the effect of increasing conjugation on the relative energy levels of the species depicted in Figure 1. All of the polymers which exhibit ESIPT emit at ~ 515 nm (Figures 4, 5 and 6) suggesting that the relative energy levels of the keto states are not sensitive to structural perturbations on the periphery of the HBO moiety. On the other hand, examination of the corresponding UV spectra shows that λ_{max}, the band edge and the shape of the UV spectra of the enol form are all quite sensitive to structural perturbation. The effect of increasing the conjugation length is to decrease (red shift) the energy gap between ground state and excited state of the enol forms. The overall effect is that the energy of the excited state of the enol form decreases relative to the energy level of the excited state of the keto form. There is an increase in the energy barrier between the two states in accord with Hammond's postulate.[26] In the case of polymers with extended conjugation, the barrier is sufficiently high to block the ESIPT channel completely.

CONCLUSIONS

We have synthesized new rigid chain polymers containing intramolecular hydrogen bonds in the main chain, some of which exhibit ESIPT. There are a number conclusions that can be drawn concerning ESIPT in these polymers. Incorporation of HBO moiety in main chain polymers does not inhibit ESIPT per se; however, extended conjugation of a polymer does have a detrimental effect on ESIPT. Also, we find that either ESIPT emission is exhibited or excimer emission is seen in these polymers.

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