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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE November 16, 1998	3. REPORT TYPE AND DATES COVERED Technical Report # 32		
4. TITLE AND SUBTITLE Electroluminescent Proton Transfer Polymers		5. FUNDING NUMBERS N00014-94-1-0540 Kenneth J. Wynne R & T Code 3132111		
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9. SPONSORING / MONITORING AGENCY NAMES(S) AND ADDRESS(ES) Office of Naval Research 800 North Quincy Street Arlington, VA 22217-5000		10. SPONSORING / MONITORING AGENCY REPORT NUMBER 19981120 170		
11. SUPPLEMENTARY NOTES <i>Polymer Preprints</i> , 38,(1), 347-348(1997).				
a. DISTRIBUTION / AVAILABILITY STATEMENT Reproduction in whole or in part is permitted for any purpose of the United States Government. This document has been approved for public release and sale; its distribution is unlimited.		12. DISTRIBUTION CODE		
13. ABSTRACT (Maximum 200 words) Effects of molecular size, extended conformation, and excimer formation on excited state intramolecular proton transfer (ESIPT) in main chain polymers were investigated in a series of homopolymers and copolymers. Several polymers were shown to exhibit both photoinduced and electrically induced ESIPT luminescence, demonstrating proton transfer electroluminescence. The observed electrically induced population inversion and stimulated emission imply that electrically pumped organic diode lasers may be feasible. Reproduced From Best Available Copy				
14. SUBJECT TERMS Proton transfer electroluminescence; intramolecular proton transfer; electroluminescent polymers; polymer lasers.		15. NUMBER OF PAGES 2		
		16. PRICE CODE		
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Unlimited	

OFFICE OF NAVAL RESEARCH

GRANT NO: N00014-94-1-0540

R&T Code 3132111
Kenneth J. Wynne

Technical Report NO. 32

Electroluminescent Proton Transfer Polymers

By

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Prepared for Publication

in

Polymer Preprints

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November 16, 1998

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ELECTROLUMINESCENT PROTON TRANSFER POLYMERS

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Molecular materials, such as 2-(2-hydroxyphenyl)benzoxazole (HBO) and 2-(2-hydroxyphenyl)benzothiazole (HBT), which contain intramolecular hydrogen bonds are known to undergo excited state intramolecular proton transfer (ESIPT) upon photoexcitation (2-5). Such materials that undergo photoinduced structural changes are of practical interests for applications as diverse as photostabilizers for polymers, laser dyes, triplet quenchers, photochromic materials, optical data storage, and optical switching devices (2-8). Extensive studies of the fundamental photophysics and photochemistry of these materials have been reported (2-5). Our interest centers on the incorporation of proton transfer molecules, such as HBO and HBT (Figure 1), into main-chain and side-chain polymers, understanding of the photophysics and photochemistry of such polymers, and exploration of their applications in solid state devices (6-8). For example, we recently discovered that electroluminescence can occur in polymers containing HBO and HBT moieties as a result of *electrically generated intramolecular proton transfer* (EGIPT) (7).

Although the ESIPT process is well established to occur in small discrete molecules such as HBO and HBT, as illustrated in Figure 2, or when they are covalent attached to side-chain polymers, it is not clear *a priori* whether ESIPT would occur in the stiff-chain polymers of Figure 1. Potential complications arise from consideration of effects of molecular size, extended conjugation, concentration quenching, and competition of ESIPT with intermolecular excited state complex (excimer) formation. Intermolecular excimers and exciplexes have previously been observed in conjugated polymers such as poly(*p*-phenylene benzobisazoles) (PBO and PBZT, Figure 1) (10). We have thus used the model compounds and the series of polymers in Figure 1 to explore the effects of molecular size, extent of conjugation, concentration quenching, and competition with excimer formation on intramolecular proton transfer as well as on the electroluminescent device potential of the materials. The details of these studies are reported elsewhere (6-9).

EXPERIMENTAL SECTION

2,5-Diamino-1,4-benzenedithiol (DABDT) (Daychem or TCI) was purified by recrystallization from aqueous HCl as previously reported (11). Hydroxyterephthalic acid was prepared by the method reported by Miura *et al.* (12). Terephthalic acid (Fluka, > 99%), 1,10-decanedicarboxylic acid (Aldrich, 99%), 1,4-phenylene diacrylic acid (Aldrich, 97%), and 2,6-naphthalene dicarboxylic acid (Aldrich, 95%) were used as received. Poly(phosphoric acid) (PPA) and 85% phosphoric acid (ACS reagent grade, Aldrich) were used to prepare 77% PPA, which was used as the polymerization medium. Phosphorus pentoxide (Fluka) was used as received. The copolymers 2 were synthesized by condensation copolymerization in polyphosphoric acid of the tetrafunctional monomer, DABDT, with aromatic and aliphatic diacids, as previously described (9). The total molar quantity of the diacid was set to be equal to that of the DABDT, as required for high molecular weight copolymers. In the case of the intramolecularly hydrogen bonded copolymers 2, the molar quantity of the rod-like moiety was varied between 1 and 100%. Copolymers 2 with mol% HPBT include: 2a (1%), 2b (5%), 2c (10%), 2d (15%), and 2e (40%). Polymer yields were quantitative in all cases.

Optical absorption spectra of thin films were obtained with a Perkin-Elmer Model Lambda 9 UV/Vis/NIR Spectrophotometer and steady state photoluminescence (PL) studies were performed by using a Spex Fluorolog-2 Spectrofluorometer equipped with Spex DM3000f Spectroscopy computer. The polymer films were positioned such that emission was detected at 22.5° from the incident radiation beam. Thin films of good optical quality were prepared by spin coating of polymer solutions in formic acid onto fused silica, followed by heating under vacuum to remove the solvent.

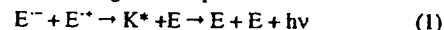
The structure of bilayer LED devices is shown in Figure 3. To prepare the LED, a layer of approximately 500 Å poly(vinyl carbazole) (PVK) was deposited on the ITO (indium tin oxide) coated glass substrate (the anode) by spin coating from chloroform solution. The PVK layer functions as the hole transporting and electron blocking layer to confine electrons within the emissive layer. A 500-700 Å emissive layer of copolymer 2 was then spin coated from formic acid solution. Since PVK does not dissolve in formic acid, no interfacial mixing occurred. An aluminum electrode (the cathode) of 500 - 1000 Å thick and ca. 7 mm² in area was thermally evaporated onto the devices at high vacuum (4×10^{-6}

torr). EL spectra were recorded with a Spex Fluorolog-2 Spectrofluorometer equipped with Spex DM3000f spectroscopy computer. Current-Voltage and luminance-voltage curves were recorded simultaneously by connecting an HP4155A semiconductor parameter analyzer together with a Grasby S370 optometer equipped with a luminance sensor head. The EL quantum efficiencies were calculated using the method proposed by Greenham *et al.* (13). No correction was made for losses due to absorption, reflection, or waveguiding effects of the glass. The values given therefore represent lower limits of the efficiency in terms of photons emitted per charge transported. All measurements were performed under ambient conditions.

RESULTS AND DISCUSSIONS

The results of our extensive studies of the model compounds (HBO, HBT) and several polymers, whose structures are in Figure 1, suggest that incorporation of HBO or HBT into the backbone of a stiff-chain conjugated polymer does not ensure the occurrence of ESIPT in the polymer. The polymers pHPBO and HPBT were found to form excimers and both do not exhibit ESIPT (6,8). The important distinction between excimer emission and ESIPT emission was made by observing the effects of concentration on the PL emission spectrum: ESIPT emission is independent of concentration whereas excimers do depend on the concentration. Figure 4 illustrates the PL emission spectra of pHPBO and its dilute (0.1 to 1%) blends with poly(vinyl acetate) (PVAc), showing ESIPT emission that is independent of blend composition. In all the cases where ESIPT emission is observed, the π -conjugation along the polymer backbone is interrupted either by a meta linkage or by an sp³ 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 2. All of the polymers which exhibit ESIPT emit at ~515 nm, 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. In the case of polymers with extended conjugation, the barrier is sufficiently high to block the ESIPT channel completely.

A further confirmation that extended conjugation in pHPBO and HPBT inhibits ESIPT was obtained by studies of copolymers 2 in which ESIPT was observed for compositions with 40% HPBT or less. The photoluminescence (PL) and electroluminescence spectra of copolymer 2b are shown in Figure 5 and the electrical characteristics are shown in Figure 6. The PL and EL emission band centered at ca. 540 nm clearly arises from emission of the excited keto tautomer (K*) and the minor band at 450 nm is attributed to the normal enol tautomer (E*) emission (7). The mechanism of formation of K* by photoexcitation is well documented (2-5) to occur by a rapid proton transfer from E*. However, formation of K* by the new EGIPT reaction is yet to be elucidated. The simplest representation of the overall EGIPT reaction is given in eq. 1.



Electrical injection of holes and electrons into 2 results in the immediate generation of enol radical anions, E^{-•} and enol radical cations, E^{•+}. After this occurs, however, it is not clear whether K* forms simply through tautomerization of E*, or by combination of radical ions of the keto form which may arise from tautomerization of enol radical ions, of which many pathways can be supposed. Any model invoked to explain the observed EGIPT luminescence needs to account for the observation of emission from primarily K* and a minor emission from the E* state. Since stimulated emission and electroluminescence have been observed in the same materials (7), the intrinsic population inversion implied by EGIPT suggests that electrically pumped organic diode lasers may be feasible.

ACKNOWLEDGMENT

This research was supported by the Office of Naval Research and the National Science Foundation (CTS 9311741, CHE-9120001).

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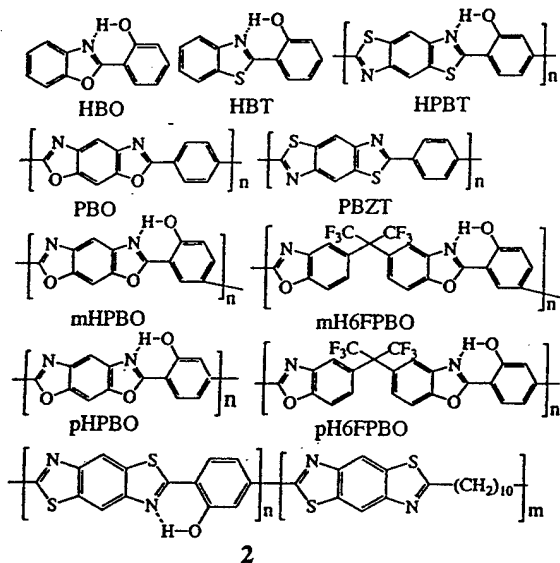


Figure 1. Molecular structures of proton transfer polymers and related molecules.

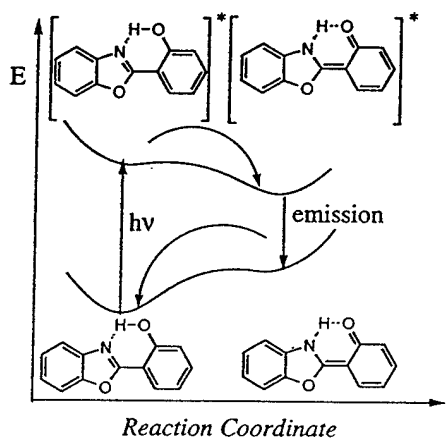


Figure 2. Schematic illustration of the ESIPT process for HBO.

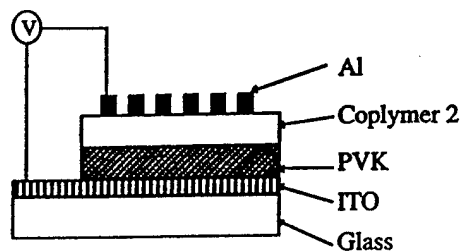


Figure 3. LED device architecture for EGIPT and proton transfer electroluminescence.

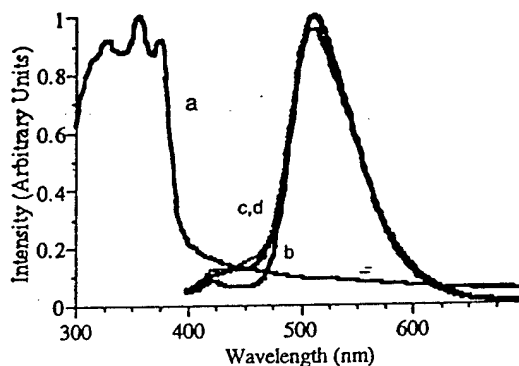


Figure 4. UV and photoluminescence spectra of pH6FPBO thin films: UV of pure polymer (a); emission of pure polymer (b); emission of 1% (c) and 0.1% (d) pH6FPBO in PVAc.

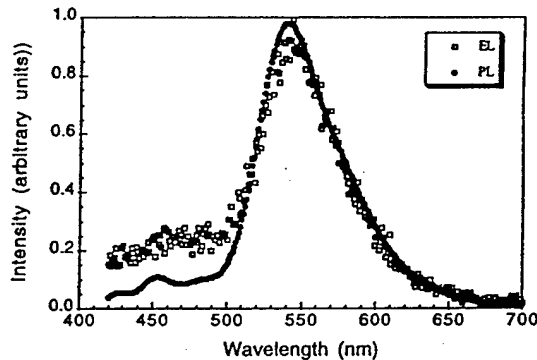


Figure 5. PL ($\lambda_{exc} = 396$ nm) and EL (12 V bias) spectra of copolymer 2b.

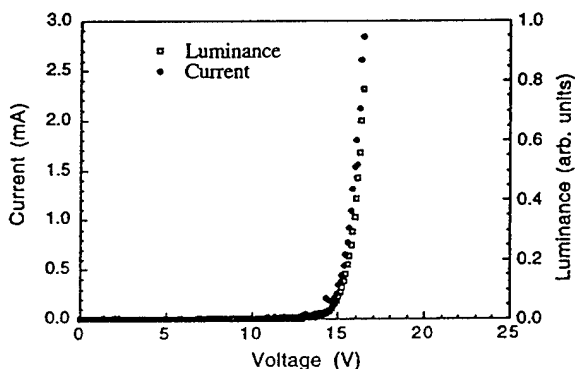


Figure 6. Current-voltage and luminance-voltage characteristic of copolymer 2b.