Fluorescence Quantum Yield of Poly(*p*-phenylenevinylene) Prepared via the Paracyclophene Route: Effect of Chain Length and Interchain Contacts

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Abstract: The monomer 9-[(*tert*-butyldimethylsilyl)oxy][2.2]paracyclophan-1-ene (**1**) is polymerized by Mo(NAr)-(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$ (Ar = 2,6-diisopropylphenyl) in a living manner. Block copolymers containing poly(**1**) and polynorbornene (poly(NBE)) can be prepared and have narrow polydispersities. Treatment of poly(**1**) with NBu$_4$F produces poly(9-hydroxy[2.2]paracyclophan-1-ene) which dehydrates to poly(*p*-phenylenevinylene) (PPV) under mild conditions. Block copolymers containing segments of size-specific and defect-free PPV with poly(NBE) of various dimensions can be prepared readily and are soluble in a variety of common organic solvents. These polymers serve as excellent candidates to measure the effect of chain length and frequency of interchain contacts on PPV's fluorescence quantum yield (Φ_f). Solution and solid-state quantum yield determinations, coupled to fluorescence lifetime measurements, reveal an acute drop in Φ_f as the degree of polymerization of the emissive species increases and as the average distance between PPV chains decreases. PPV$_x$-*block*-poly(NBE)$_y$ prepared in solution consistently shows larger Φ_f than material prepared by solid-state dehydration. The poly(NBE) companion block also serves to protect PPV from atmospheric degradation.

Introduction

Emissive conjugated polymers are subject to considerable worldwide attention. Their study stems, in part, from their application as emissive material in electrooptic devices, and in particular light-emitting diodes (LED's). Polymers are attractive components for this function because of their superior processability, relative to inorganic components, and their intrinsic amorphous nature, *i.e.*, they are incapable of crystallizing, a problem associated with sublimed molecular films. Initial reports of conjugated polymer electroluminescence involved poly(*p*-phenylenevinylene) (PPV) displaying a quantum efficiency (number of photons per injected electron) of only 0.05%.[1] Despite the poor performance, this discovery opened the opportunity to fabricate single-layer low-voltage emission display panels, promoting considerable research in academic and industrial settings. Further optimization in polymer synthesis and structure together with progress in device engineering,[2] particularly charge transport considerations and injection electrodes,[3] has resulted in efficiencies of up to 4%[4] as well as a wide range of emitted frequencies.[5] Nonradiative exciton decay processes limit the usefulness of PPV. The origin of these relaxation mechanisms may be intrinsic to the nature of the

polymer chains, such as deactivation of the excited state by internal conversion, or extrinsic, for example, in the form of low-energy traps.[6−9] It has been difficult to ascertain exactly to what extent each of these unrelated effects is operative by measuring bulk PPV since traditional syntheses offer negligible control over chain length and molecular weight distribution. Coupled with these problems are the extensive variety of derivatives and dependence of material performance on preparation protocol and device structures.[10] Thus, a cohesive understanding of excitation decay is missing.[11,12]

Our recently reported paracyclophene route to PPV offers distinct advantages for the preparation of compounds purposely designed to address the uncertainties raised above.[13] The PPV-precursor polymer is prepared via living ring-opening metathesis

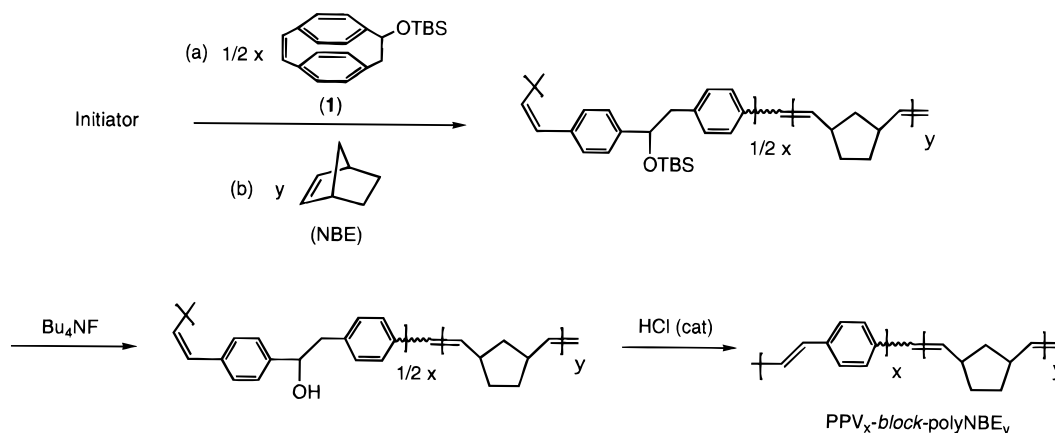[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1996.

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Scheme 1

Figure 1. GPC traces (in CHCl$_3$) of (a) poly($\mathbf{1}$)$_5$-*block*-poly(NBE)$_{200}$; poly(9-hydroxy[2.2]paracyclophan-1-ene)$_5$-*block*-poly(NBE)$_{200}$; and (c) PPV$_{10}$-*block*-poly(NBE)$_{200}$.

polymerization (ROMP) of paracyclophene-based monomers.[14] Excellent control is offered over the average degree of polymerization and the range of molecular weights in the precursor material. Conditions for PPV formation in solution are remarkably mild (50−80 °C in the presence of acid catalyst), and as a result, problems associated with thermal degradation are alleviated.[15]

It is possible using the paracyclophene route to include size-specific and defect-free PPV segments in block copolymer structures. The companion block can have a variety of complementary functions. For example, polynorbornene enhances solubility and does not interfere with the photophysical processes of interest, allowing the study of typically intractable PPV using standard solution characterization techniques. By changing the concentration of these PPV solutions, it is possible to modulate the frequency of interchain contacts and therefore probe its role in determining bulk properties.
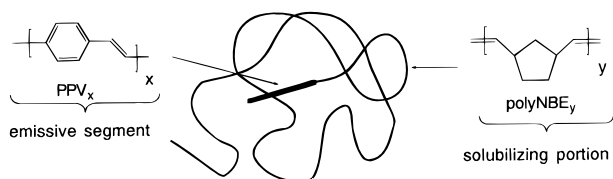
In this paper we report the complete details for the paracyclophene synthesis of PPV. We take advantage of this methodology and the resulting high quality of material to investigate how chain length and interchain separation influence the photoluminescence (PL) quantum yield (Φ_f) of PPV. Findings from these studies are technologically relevant in view of the relationship between PL and electroluminescence (EL). Emission in both processes results from radiative recombination of singlet excitons generated by photoexcitation in the case of PL and by carrier injection in EL.[16]

Results and Discussion

Polymer Preparation. Copolymers of PPV and poly(NBE) (NBE = norbornene) were prepared according to the sequence of steps shown in Scheme 1 for PPV$_x$-*block*-poly(NBE)$_y$. In this nomenclature the subscripts refer to the average degree of

polymerization ($\overline{\text{DP}}$) of each block and are estimated from the ratio of monomer added to the reactive propagating species. We illustrate the overall procedure for PPV$_{10}$-*block*-poly-(NBE)$_{200}$. The Schrock initiator, Mo(NAr)(CHCMe$_2$Ph)(OCMe-(CF$_3$)$_2$)$_2$ (Ar = 2,6-diisopropylphenyl),[17] is first reacted with 5 equiv of 9-[(*tert*-butyldimethylsilyl)oxy][2.2]paracyclophan-1-ene ($\mathbf{1}$) over a period of 2−3 h (10 equiv of $\mathbf{1}$ requires approximately 3−4 h, while 20 equiv about 4−5 h). To minimize decomposition of the propagating alkylidene and obtain maximum control over molecular weight distribution, polymerization of $\mathbf{1}$ relies on vacuum line techniques using freshly distilled, rigorously dry toluene. The required amount of NBE (200 equiv in this case) is then added quickly under vigorous stirring and reacted for 15 min. Finally, the metal species is cleaved from the organic polymer using benzaldehyde as the termination agent. Two subsequent steps generate PPV from poly($\mathbf{1}$)$_5$-*block*-poly(NBE)$_{200}$. The silicon protecting group is removed by treatment with (*n*-Bu)$_4$NF producing poly(9-hydroxy[2.2]paracyclophan-1-ene)$_5$-*block*-poly(NBE)$_{200}$ which is isolated and purified by precipitation. Dehydration from this polyalcohol occurs readily, since both reactive sites are benzylic, and is promoted by a catalytic amount of acid. Note that the resulting PPV has an average degree of polymerization twice that of the original poly($\mathbf{1}$). Copolymers containing poly(NBE) are soluble in a variety of common organic solvents (hexane, aromatics, etc.) and are best purified by double precipitation of concentrated CH$_2$Cl$_2$ solutions into methanol. ^{1}H and ^{13}C NMR spectra are a superposition of the spectra from the two homopolymers in the appropriate ratio. These data confirm the "blockiness" of the polymers, *i.e.*, no portions containing randomly distributed monomer units exist.

(14) PPV can also be obtained via ROMP of a functionalized bicyclo-[2.2.2]octene, see: Conticello, V. P.; Gin, D. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 9708.

(15) Carbonyl functionalities which arise during the conversion step in PPV formation have been shown to be effective exciton traps and reduce considerably the emission quantum yield. See work in ref 6.

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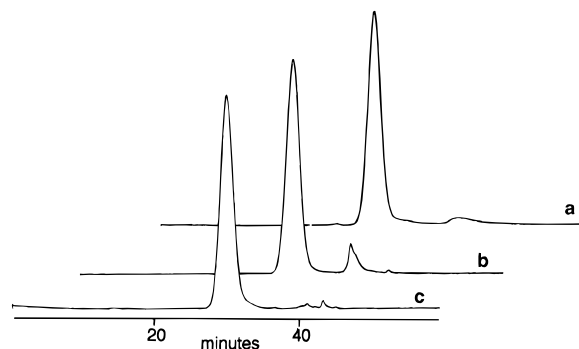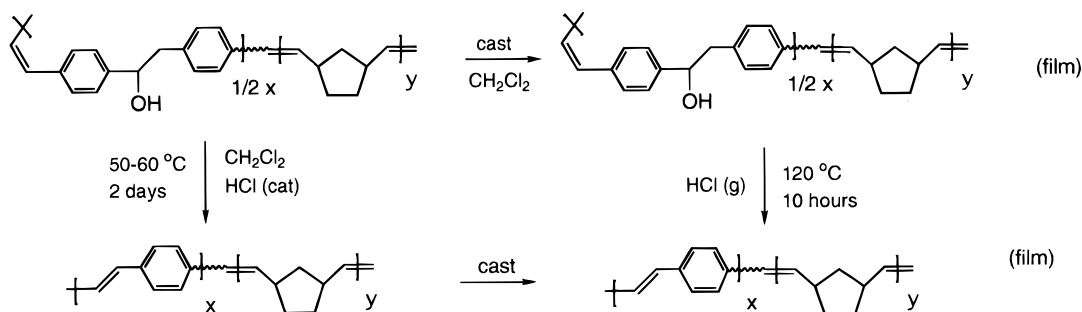
(17) (a) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C., Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875. (b) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158.

Scheme 2

Gel permeation chromatography[18] (GPC) traces of these blocks at different stages of conversion are shown in Figure 1. The molecular weight distribution, or polydispersity index (PDI), of poly(**1**)$_5$-*block*-poly(NBE)$_{200}$ is approximately 1.1. Therefore, we are confident that all of poly(**1**) incorporates poly(NBE) and there is no runaway propagation after NBE addition. Neither broadening of the peak nor higher molecular weight species are observed at either the polyalcohol or PPV stages. Smaller peaks appearing at longer retention times are assigned to residual small molecules trapped within the polymer as it precipitates. Additionally, UV/vis spectra of the eluent, measured using a photodiode array detector located immediately after the GPC columns, are consistent with the presence of the correct chromophore throughout the polymer peak area. The absorbance spectra of traces a and b of Figure 1 show a λ_{max} at approximately 300 nm, characteristic of the stilbene constituents, while trace c has a considerably red shifted absorption ($\lambda_{max} = 400$ nm). Therefore, PPV formation, in CHCl$_3$ or CH$_2$Cl$_2$ and with this PPV/NBE ratio, results in negligible cross-linking.

Films of PPV-copolymer for spectroscopic analysis were obtained via two different methods (Scheme 2). The standard technique, free or spin casting of precursor polymer film and thermolysis in the presence of HCl (g), requires temperatures of up to 120 °C for a period of 10 h. These solid-state conditions typically yield yellow films with $\lambda_{max} \sim 410$ nm which are easily peeled off from the support except in those samples where the $\overline{\text{DP}}$ of poly(NBE) is greater than 200 which are tacky, very much like poly(NBE) homopolymer. Alternatively, the dehydration step can be accomplished in solution. Precursor polymer in anhydrous CH$_2$Cl$_2$ is placed inside a glass bomb and degassed via several freeze−pump−thaw cycles. Anhydrous HCl gas is then transferred over the solution and the vessel is sealed by way of a Teflon needle valve. All procedures are done using high-vacuum line techniques to minimize oxygen contamination. Gentle heating (50−80 °C) and stirring of the sealed vessel over a period of 24−48 h results in solutions having an absorbance $\lambda_{max} = 410$ nm. Removal of HCl produces solutions from which PPV-containing films are easily cast. The two PPV preparation methods yield spectroscopically (UV/vis, fluorescence, and FT-IR) identical films.

Fluorescence Quantum Yield Determinations. Fluorescence spectra of the PPV$_x$-*block*-poly(NBE)$_{200}$ series (where x = 10, 20, and 40) in the solid state (shown in Figure 2) are virtually identical and independent of whether the conversion step was performed in solution or in the solid state. There is abundant precedent in the literature for the quick saturation of emission λ_{max} as $\overline{\text{DP}}$ increases. It seems that, regardless of $\overline{\text{DP}}$, the average conjugation length of the emitting species is approximately six or seven. Bond rotations likely interrupt a longer arrangement of coplanar aryl rings. However, Φ_f
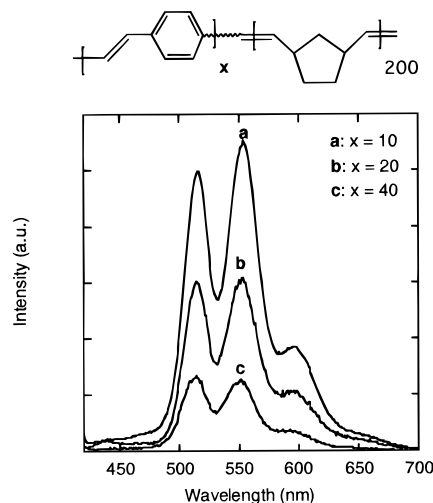
(18) All GPC measurements are made relative to polystyrene standards.

Figure 2. Fluorescence spectra (films, $\lambda_{\text{excitation}} = 420$ nm) of PPV$_x$−*block*-poly(NBE)$_{200}$: (a) $x = 10$; (b) $x = 20$; (c) $x = 40$.
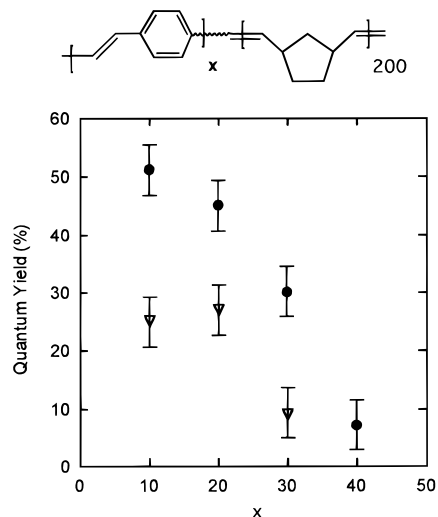

Figure 3. Quantum yield (films on quartz plate, $\lambda_{\text{excitation}} = 420$ nm) versus x in PPV$_x$−*block*−poly(NBE)$_{200}$ (each entry corresponds to the average of three independent determinations). Solid circles correspond to samples converted in solution, while triangles are for solid-state conversion samples.

depends strongly on $\overline{\text{DP}}$ as shown in Figure 3. Complete details for Φ_f determination (both film and solution) are found in the Experimental Section. Note that precise determination of Φ_f for PPV films is nontrivial. Well-matched fluorescent dye standards with known efficiencies and similar structure are unavailable, and Φ_f is sensitive to the material's refractive index and arrangement of dipoles within the film.[19] While some error may exist in the absolute magnitudes of Φ_f, relative to each other, these values are meaningful since all measurements
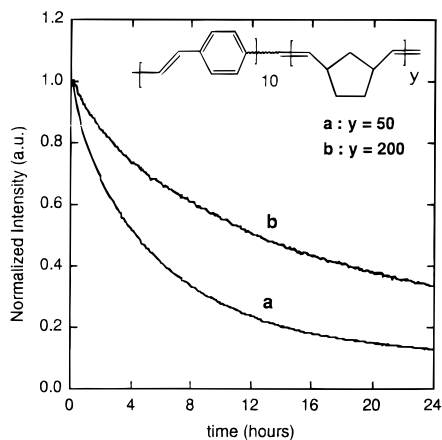
Figure 4. Emission intensity of PPV$_{10}$-*block*-poly(NBE)$_y$ film as a function of time ($\lambda_{\text{excitation}} = 410$ nm): (a) $y = 50$; (b) $y = 200$.

Figure 5. Dependence of fluorescence quantum yield on concentration for (a) PPV$_{10}$-*block*-poly(NBE)$_{200}$, (b) PPV$_{20}$-*block*-poly(NBE)$_{200}$, and (c) PPV$_{40}$-*block*-poly(NBE)$_{200}$. Measurements are in CHCl$_3$, $\lambda_{\text{excitation}} = 420$ nm.

Figure 6. Relative quantum yield versus y in films of PPV$_{20}$-*block*-poly(NBE)$_y$ (films cast on quartz plate).

involve the same emitting species in similar configurations and are thus self referencing. It is clear, therefore, that increasing the average degree of polymerization from 10 to 40 results in a 10-fold decrease in Φ_f and that films converted in the solid state do not perform as well, consistently showing lower Φ_f values.

Recent reports on the reduction of Φ_f by thermal oxidation[6] prompted us to further investigate the air stability of the emissive species and the influence of the poly(NBE) component on the decay rate. As Figure 4 shows, the emission intensity in films of PPV$_{10}$-*block*-poly(NBE)$_y$, prepared from the solution method and stored under nitrogen prior to measurements, decreases significantly over a period of 24 h at room temperature when exposed to air. Figure 4 also reveals that the decay rate of emission from PPV$_{10}$-*block*-poly(NBE)$_{50}$ is almost twice than that of PPV$_{10}$-*block*-poly(NBE)$_{200}$. These observations indicate that the poly(NBE) component protects the PPV segments from atmospheric decomposition.

Determination of Φ_f values in solution is more reliable since the sample is homogeneous, thereby eliminating problems associated with film thickness and heterogeneity. It is possible, by varying the concentration of emissive PPV species, to obtain information highlighting the effect of interchain contacts. Φ_f values for PPV$_x$-*block*-poly(NBE)$_{200}$ ($x = 10$, 20 and 40) at different concentrations, shown in Figure 5, confirm the solid-state results. Shorter chain samples have an intrinsic higher Φ_f. It is interesting to note that for $x = 10$ and 20, Φ_f decreases with increasing concentration, a phenomenon that is less pronounced with the larger $x = 40$ copolymer, at least within the concentration range studied (lowest and highest concentrations are determined by instrument limitations). It is possible that for the longer polymers independent conjugated segments come into contact as a result of chain conformations. Alternatively, strong attraction between the the PPV blocks may result in a micellar-like aggregation throughout the range of accessible concentrations. In either case the proximity between conjugated units will not depend strongly on concentration. The almost linear behavior in the longer samples argues against a substantial reabsorption problem in concentrated solutions.

Analogous dilution studies are possible in the solid by holding the $\overline{DP}$ of the PPV segment constant while increasing the size of the poly(NBE) block. All films have an identical history and are cast from a PPV solution in CH$_2$Cl$_2$. Figure 6 shows that the quantum yield of PPV$_{20}$-*block*-poly(NBE)$_y$ increases
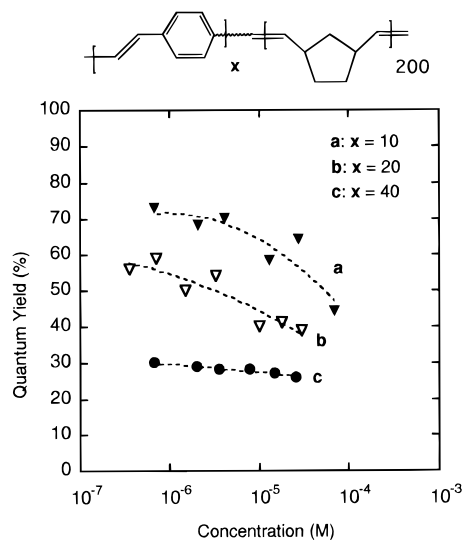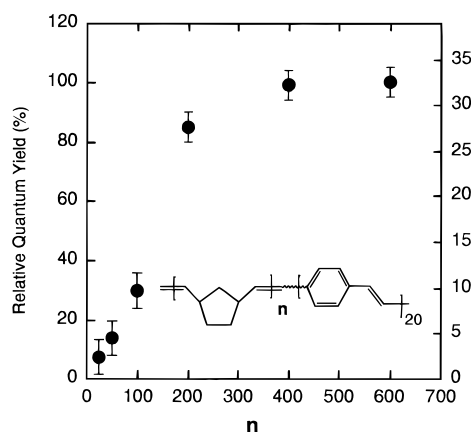
significantly as y increases from 25 to 400 and then saturates between 400 and 600. Concentrating the PPV chains decreases the average interchain distance which in turn diminishes Φ_f. Trends observed in Figure 6 are corroborated by fluorescence lifetime measurements using the technique of time-correlated single photon counting.[20] It is evident, from inspection of Figure 7, that increasing the proximity of PPV chains reduces the lifetime of emitting species.[21] Related work has also shown an improvement in Φ_f when packing of chains is discouraged by cis linkages.[22] It is important to note here that phase separation into PPV-rich areas cannot be ruled out in copolymers with low poly(NBE) content. These materials will display photoemissive properties similar to those of PPV homopolymer. Phase separation in copolymers containing conjugated portions has precedent in the literature.[23]

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(21) Shorter lifetimes are characteristic of samples with low Φ_f, see: (a) Friend, R. A. *Synth. Met.* **1993**, *54*, 281. (b) Bässler, H. *Appl. Phys. Lett.* **1993**, *62*, 2827. (c) Sun, B. J.; Bazan, G. C.; Conwell, E. Submitted.

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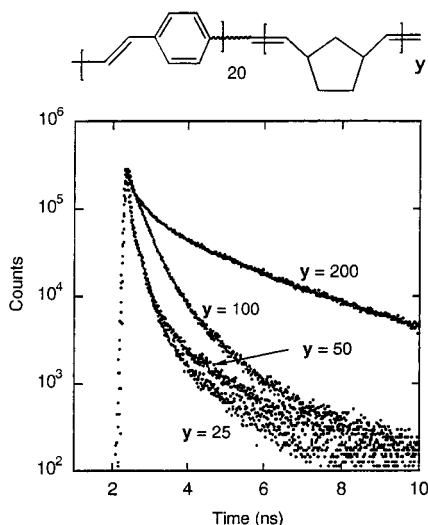
Figure 7. Fluorescence lifetime measurements ($\lambda_{\text{excitation}} = 420$ nm, decay monitored at 610 nm) for films of PPV$_{20}$-*block*-poly(NBE)$_y$ (y = 25, 50, 100, and 200).

Conclusion

It is interesting that films containing PPV prepared from dehydration in solution have higher Φ_f's than films converted in the solid state. The most obvious difference between the two procedures is the milder dehydration temperature required in solution. We can identify two factors for this difference. First, HCl can diffuse readily into CH$_2$Cl$_2$ to access all polymer sites and therefore catalyzes this transformation more effectively. Secondly, in the solid chain dynamics are dampened. We note that significant geometrical rearrangements are required for the polymer chains to achieve a delocalized conjugated segment. In the precursor polymer, the bond between two sp^3 carbons gives the chain significant configurational freedom, especially with respect to the relative orientation of the aromatic units. Adjusting the chain geometry, so that rings become coplanar and conjugated, requires bond rotations and significant structure reorganization. In solution these motions simply displace nonviscous solvent molecules. Once cast as a film, chains are intertwined, effectively locked, making structural rearrangements energetically costly. Higher temperatures are required for longer periods of time. Harsh conversion conditions are typical of most other methodologies and apparently introduce defects that negatively affect bulk performance.[6]
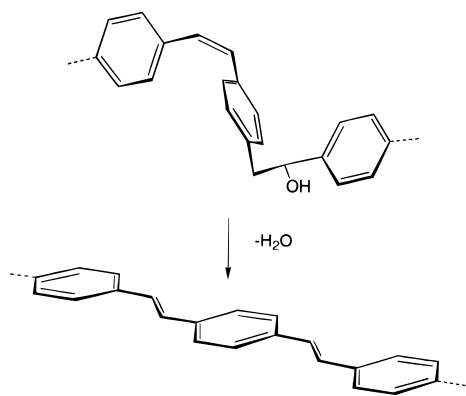
Stability studies show that the Φ_f of PPV decays quite quickly upon exposure to air, even under the partial protection of inert media like poly(NBE). The manipulation of samples in the

process of physical characterization is therefore an important consideration in order to obtain meaningful data.

A clear message relayed by these studies is the quenching effect of longer chains. While there are several precedents for this observation, the acute dependence of Φ_f on $\overline{DP}$ in spectroscopically identical samples is somewhat surprising. Significantly, optimized PPV segments have very large Φ_f values and are competitive with efficient organic fluorophores. It is not obvious from these studies if longer chains degrade easily to some unspecified exciton trap or whether they intrinsically have a lower Φ_f (*i.e.*, by means of internal conversion).[24] Regardless of the precise mechanism, because of facile energy migration in conjugated polymers, longer chains affect disproportionally collective bulk properties,[25] making the distribution of chain lengths within the conjugated polymer sample an important factor to optimize. A living polymerization offers the best control for molecular weight homogeneity relative to other mechanisms, producing polymers with polydispersities in the 1.1−1.2 range.[26] A graphical illustration of this point is shown in Figure 8, where the weight fraction (w_x) distribution of polymers having similar $\overline{DP}$ but prepared via different mechanisms is plotted against chain length (x).[27] The Poisson distribution, characteristic of living polymerizations, contains the majority of chains close to the average value. Polymers derived from Wittig-type polycondensations[28] or the Wessling sulfonium polyelectrolyte route[29] will have a significantly larger proportion of longer chains, regardless of $\overline{DP}$.

Polymers which have as structural components discrete chromophores, either in the backbone or pendant, represent an extreme in conjugated segment length control and have successfully been utilized in device configuration.[30] Separating and isolating PPV chromophores using a large amorphous companion copolymer, as shown in Figures 5 and 6, improves Φ_f by

(24) The rate of internal conversion increases with decreasing energy difference (ΔE) between the zero point vibrational levels of the states undergoing internal conversion. For a detailed discussion of the "Energy Gap Law", see Chapter 6 in the following: Turro, N. J. *Modern Molecular Photochemistry*; University Science Books: Mill Valley, CA, 1991.

(25) Webber, S. E. *Chem. Rev.* **1990**, *90*, 1469 and references therein.

(26) PDI values of 10 are usual for polymers prepared via the sulfonium route. See: Burn, P. L.; Kraft, H.; Boigent, D. R.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H.; Gigmer, R. W.; Holesm, A. R.; Jackson, R. W. *J. Am. Chem. Soc.* **1993**, *115*, 10117.

(27) Flory determined weight fraction distribution (w_x) of the *x*-mer obtained from a living polymerization is given by

$$w_x = [\nu/(\nu + 1)]e^{-\nu}x\nu^{x-2}/(x - 1)!$$

where ν is the amount of monomer consumed or, alternatively, at the end of the polymerization, the initial monomer to initiator ratio. The expression is a Poisson distribution and assumes that the weight contribution remaining from the initiating species in the polymer is approximately equal to that of one monomer unit (this error is insignificant for large values of ν). The weight fraction for condensation polymers is provided by the expression

$$w_x = (1 - p)^2xp^{x-1}$$

where p is a variable that reflects the extent of reaction, namely the fraction of reacted functional groups. The degree of polymerization ($\overline{DP}$) for a condensation polymer is given by

$$\overline{DP} = 1/(1 - p)$$

From: (a) Flory, P. J. *J. Am. Chem. Soc.* **1940**, *62*, 1561. (b) Flory, P. J. *J. Am. Chem. Soc.* **1936**, *58*, 1877. Deviations from Poisson behavior are negligible when k_p/k_i (k_p = rate of propagation; k_i = rate of initiator) is in the order of 10. See: Gold, L. *J. Chem. Phys.* **1958**, *28*, 91. Other types of distributions can be found in the following: Peebles, L. H., Jr. *Molecular Weight Distributions in Polymers*; Interscience: New York, 1971.

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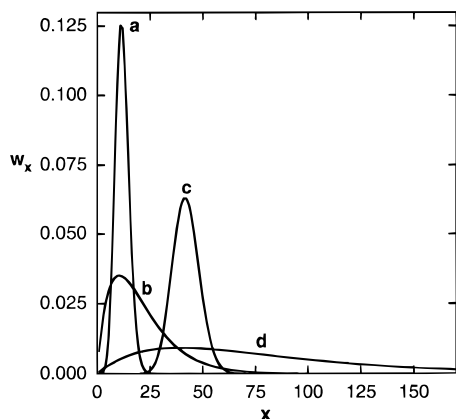
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Figure 8. Effect of $\overline{DP}$ and mechanism of polymerization on molecular weight distribution for (a) $\overline{DP}$ = 10, living polymerization; (b) $\overline{DP}$ = 10, condensation polymerization; (c) $\overline{DP}$ = 40, living polymerization; and (d) $\overline{DP}$ = 40, condensation polymerization (w_x = weight fraction of x-mer).

reducing energy migration and/or deactivation by interactions between chains. This strategy allows us to understand better the properties of isolated chains, *i.e.*, the dependence of Φ_f on $\overline{DP}$. It is not likely to be useful in bringing enhancement for EL quantum yields since other factors, such as charge injection and transport, will likely now become limiting processes.

Experimental Section

General Considerations. All manipulations involving organometallic reagents were carried out using either high-vacuum or glovebox techniques as described previously.[31] ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX-400 NMR spectrometer at 400.1 and 100.6 MHz, respectively. Infrared spectra were recorded on a Perkin-Elmer 1600 FT-IR instrument, UV/vis absorption spectra on a Perkin-Elmer Lambda 19 instrument, and PL spectra on a Spex Fluorolog 2 spectrometer. Time-correlated single photon counting experiments were carried out on an instrument consisting of a mode-locked Nd:YLF laser operating at 76 MHz as the primary laser source. The second harmonic of the Nd:YLF laser was used to synchronously pump a dye laser circulating Rhodamine 6G in ethylene glycol as the gain medium. The pulse width of the dye laser was typically 8 ps, as determined by autocorrelation, and the laser was cavity dumped at a rate of 1.9 MHz. The dye laser was tuned to the desired wavelength for sample excitation. The single-photon pulses from the MCP detector were amplified and used as the stop signal for a time-to-amplitude converter while the signal from a photodiode, detecting a small fraction of the dye laser output, was used as the start signal for the TAC. The start and stop signals for the TAC were conditioned before entering the TAC by passing through two separate channels of a constant fraction discriminator. The output of the TAC was connected to a multichannel analyzer interface board installed inside a 486DX2 personal computer. The MCA was controlled by software from Edinburgh Instruments. Solid-state spectra of polymers were measured on films cast on quartz plates. The molecular weights were obtained by gel permeation chromatography (GPC) relative to TSK polystyrene standards (Tosoh Corp.) which ranged from 1051 to 1.9×10^5 MW in HPLC grade chloroform solution using a Waters HPLC instrument equipped with a Shodex column (K-800P, 805, 804, 802.5, KF-801) arranged in series and a Waters 996 photodiode array UV detector. Chloroform was filtered through a Millex-SR 0.5 μm filter before chromatography. Toluene for polymerization was vacuum distilled from benzophenone ketyl immediately before use. Norbornene was distilled from Na/K alloy. The syntheses

of Mo(NAr)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$ (Ar = 2,6-diisopropylphenyl)[32] and **1**[13] are available in the literature.

Poly(1) Homopolymer. In a nitrogen-filled glovebox a round-bottomed flask equipped with a vacuum line adapter was charged with **1** (336 mg, 1.0 mmol) and Mo(NAr)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$ (8 mg, 0.01 mmol). The apparatus was placed under vacuum, and dry toluene (25 mL) was condensed into the flask at -78 °C. The resulting light yellow solution was allowed to warm up to room temperature and stirred for an additional 24 h. The reaction was quenched by addition of 20 μL of dry benzaldehyde under a counterflow of argon, stirred an additional hour, and concentrated to one-fourth of the original volume. The product was isolated by precipitation into 200 mL of MeOH and centrifugation. The resulting solids are redissolved in CH$_2$Cl$_2$, reprecipitated into 200 mL of MeOH, collected by centrifugation, and placed under vacuum for 24 h to yield 285 mg (85%) of poly(**1**), M_n = 26 273 and PDI = 1.1 vs polystyrene standards (M_n = 59 351 and PDI = 1.3 for poly(**1**)$_{200}$). IR (KBr, thin film) ν_{max} (cm^{-1}): 3017, 2953, 2927, 2855, 1512,1471,1360, 1256, 1082, 934, 887, 834, 776. ^{1}H NMR (C$_6$D$_6$): δ 7.31−7.03 (8H, aromatic C-H's), 6.53 (2H *cis*-olefin), 4.75(1H, OCH), 2.87 (2H, benzylic CH_2), 0.93 (9H, C(CH_3)$_2$), 0.15 (6H, Si(CH_3)$_2$). [13]C (100 MHz, CDCl$_3$): δ 144.1, 137.9, 136.0, 135.1, 130.0, 128.5, 126.0, 125.8, 76.5, 47.5, 25.9, 17.9, −4.9, −5.1.

Typical Copolymer Preparation. A round-bottomed flask with a needle valve adapter was charged inside the glovebox with **1** (43.6 mg, 0.13 mmol) and Mo(NAr)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$ (10 mg, 0.013 mmol). The assembly was attached to a high-vacuum line, and dry toluene (15 mL) was condensed over the reactants at -78 °C. The resulting clear yellow solution was allowed to warm to room temperature and stirred for an additional 4 h. A solution of NBE (246 mg, 2.6 mmol) in toluene (10 mL) was then added via syringe under vigorous stirring and stirred for 15−20 min. After quenching with 20 μL of benzaldehyde, the solution was concentrated to one-third of the original volume and precipitated into 150 mL of methanol. The product (poly(**1**)$_{10}$-*block*-poly(NBE)$_{200}$) appears as a white fibrous solid which is isolated by centrifugation and placed under vacuum overnight to remove residual solvent; yield 225 mg (85%), M_n = 23 600; PDI = 1.2. The spectrum of copolymers is a superimposition of the two component homoblocks in the appropriate ratio.

PPV Block Copolymer Solutions. Under an inert atmosphere, approximately 20 mg of precursor copolymer was dissolved in 50 mL of CH$_2$Cl$_2$. Under argon flow, pure HCl gas was transferred into the solution for 5 s. The solution turned yellow after being heated at 40 °C for 24−48 h. The solvent was evaporated off and the remaining residue dried under vacuum. The residue was then redissolved in CH$_2$Cl$_2$ for further analysis.

PPV Block Copolymer Films from PPV Block Copolymer Solutions. A concentrated solution of the PPV copolymer in CH$_2$Cl$_2$ was spin cast onto a glass or quartz plate. Air exposure was minimized throughout the process with a maximum exposure time of 15 min. The rate of spin casting and the concentrations of copolymer solution were carefully controlled so that the absorbance of the films at 400 nm was on the order of 0.10(5).

PPV Block Copolymer Films from Precursor Films. A concentrated solution of precursor block copolymer in CH$_2$Cl$_2$ was spin cast onto a glass plate. The thickness of the film was controlled via concentration and spin rate so that the absorbance of the film was approximately 0.10(5). The film was placed into a reaction kettle which was evacuated and initially flushed with nitrogen or argon followed by a slow stream of HCl gas. The film was then heated to 120 °C for approximately 24 h and then allowed to cool under argon. The period of heating varies according to sample; in all cases, it was optimized such that final λ_{max} = 410 nm.

Procedures for Quantum Yield Determination. Solutions. A stock solution of PPV$_x$-*block*-poly(NBE)$_y$ was prepared by combining a carefully weighed amount of precursor material with a measured volume (or weight) of CH$_2$Cl$_2$ followed by HCl treatment as described

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above. The total concentration of polymer in stock solutions was precisely known and typically on the order of $1-10$ parts per thousand by weight.

Solutions for fluorescence measurements were prepared to specific concentrations by weighing a few drops of stock solution followed by dilution using a known amount of $CHCl_3$. All manipulations were performed inside a glovebox, and the solutions were introduced into a quartz cuvette equipped with a Teflon needle valve to minimize contact with air. Fluorescence was measured at right angles using a 1 cm cuvette except for the highest concentration (optical density ~ 0.3), which was done by front face measurement using 1 mm cuvette. The quantum yield was calculated from the relation

$$\Phi_{unk} = \Phi_{std} \left[\frac{A_{std}(\lambda_{std})}{A_{unk}(\lambda_{unk})} \right] \left[\frac{I_{std}(\lambda_{std})}{I_{unk}(\lambda_{unk})} \right] \left[\frac{D_{unk}}{D_{std}} \right]$$

where the subscripts std and unk indicate the standard and unknown sample, $A(\lambda)$ corresponds to the absorbance of the solution at the exciting wavelength λ, $I(\lambda)$ is the intensity of the exciting beam (assumed to be equal for both measurements), and D is the integrated luminescence spectrum. The standard fluorophore for solution measurements was Coumarin 504 with $\Phi_f = 77\%$.

Films. Absolute Φ_f determinations in PPV are less accurate in the solid state due to the lack of well-matched standards. In our case, we used a thin film of poly(methyl methacrylate) containing 9,10-diphenylanthracene ($\sim 10^{-3}$ M) in the same optical configuration as the standard ($\Phi_{fstd} = 83\%$). D_{unk} was measured from thin films of PPV$_x$-*block*-poly(NBE)$_y$ for which A_{unk} (λ_{unk}) was approximately 0.1.