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Conjugation Length Control in Soluble Poly[2-methoxy-5-((2′-ethylhexyl)oxy)-1,4-phenylenevinylene] (MEHPPV): Synthesis, Optical Properties, and Energy Transfer

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Abstract: Poly[2-methoxy-5-((2′-ethylhexyl)oxy)-1,4-phenylenevinylene] (MEHPPV) of varying conjugation length was prepared by the selective thermal elimination of one of the substituents in a suitable precursor polymer. The precursor, a dialkoxy poly(1,4-xylylene) derivative with varying amounts of acetoxy and methoxy groups, was prepared by a competitive nucleophilic substitution of the Wessling polyelectrolyte, using methanol and sodium acetate in acetic acid as nucleophiles. Selective thermal elimination (in solution) of the acetate groups alone yielded MEHPPV of varying conjugation lengths. The selective nature of the acetate elimination was confirmed by ^{1}H NMR spectroscopy. As expected, both the absorption and emission maxima of the eliminated samples shifted to the red with increasing conjugation length. While there was very little difference between the absorption spectra of thin film and solutions of MEHPPV-*x*, there was a significant bathochromic shift in the emission spectra of the thin films when compared to their dilute solution spectra. Additionally, separate emission from the various oligomers, which are occasionally visible in solution, is absent in thin films. Energy transfer from short to longer conjugated segments, within a single polymer chain in solution, was inferred by comparison of the fluorescence spectra of the partially conjugated polymers with those expected from a system where simultaneous independent emission occurs from a similar collection of noninteracting oligophenylenevinylene (OPV) molecules. The latter was calculated assuming a statistically random substitution/elimination process of the precursor in conjunction with the fluorescence spectral data of OPV's reported by previous workers. The extent of energy transfer increases as the average conjugation length increases. Furthermore, unlike in the model oligomers, in the case of polymers the fluorescence quantum yield in solution rapidly decreases with increase in the average conjugation length.

Introduction

The discovery by the Cambridge group in 1990[1] that conjugated polymers can be used as active light emitting layers in light emitting devices triggered extensive research on this class of polymers.[2−4] Most promising and extensively studied among them is poly(*p*-phenylenevinylene) (PPV) and its derivatives. Various factors such as long lifetime of the devices, low cost, flexibility, and easy processibility have resulted in the utility of PPV in full color image sensors.[5] These conjugated polymers have been successfully used as active components in lasers,[6−8] photovoltaic devices,[9] light-emitting electrochemical cells,[10,11] field-effect transistors,[12] photodetectors,[13] and photodiodes.[14,15] The discovery that both their photoluminescence (PL) and electroluminescence (EL) spectra are essentially identical suggests that the state from which emission occurs is the same in both cases.[16,17] Hence, a great deal of attention has been devoted to the understanding of the fundamental photophysical process underlying the emission. Currently, one of the active areas of research dealing with this class of fluorescent polymers has to do with the control of color and efficiency of light emission. Segmented conjugated polymers, where conjugated segments of varying lengths are separated electronically

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by insulating spacers, is one approach to control both the color and possibly also the efficiency of emission. The latter has been postulated based on the discoveries that the efficiency of luminescence was significantly enhanced when isolation of short conjugation length was achieved, possibly because of exciton confinement.[18] The efficiency was also shown to increase when the oligomers and polymers were blended in an inert matrix like poly(styrene) or poly(methyl methacrylate);[19] the reason for this is the prevention of aggregation, which results in an enhancement of the PL quantum efficiency.

Several earlier attempts to control conjugation lengths using time[20] and temperature of elimination[21] and selective elimination in copolymer systems[22,23] resulted only in limited success. Other approaches to prepare PPV derivatives with controlled conjugation length include the following: controlled oxidation (dehydrogenation) of a precursor polymer, a cyano-substituted derivative of poly(*p*-xylylene), to the conjugated polymer, MEH−CN−PPV in solution using DDQ,[24] and the use of condensation approaches[25−27] to incorporate conjugation-breaking segments randomly along the polymer backbone. Last year, we reported for the first time a statistical control of conjugation length over a very wide range by a selective elimination of a suitable precursor containing two types of eliminatable groups.[28] A similar approach was also demonstrated by de Kok et al.[29] using a sulfone−sulfoxide precursor. Both these methods were based on the selective elimination of one of the substituents from the precursor polymer leaving the other unaffected. Our method for control of conjugation length in poly(2,5-dimethoxy-1,4-phenylenevinylene) (DMPPV) was based on the selective thermal elimination of acetate groups, without affecting the methoxy groups. Even though fine-control of conjugation length was achieved, as was confirmed from FT-IR, UV−visible, and PL spectroscopic studies of the conjugated polymer films, the resulting films were insoluble. This precluded a complete solution characterization of the final conjugated polymer. In this contribution, we describe the preparation of soluble MEHPPV with a statistical control of the conjugation length. The structural elucidation of these conjugated polymers has been carried out by ^{1}H NMR spectroscopy, and their solution and thin-film photophysical properties are examined by UV−visible and PL spectroscopic studies.

Experimental Section

Methods. ^{1}H NMR spectra were recorded using a Bruker 200 MHz spectrometer, with $CDCl_3$ as the solvent and TMS as internal reference. FT-IR spectra of the films coated on KBr pellets were recorded on a Bruker Equinox 55 FT-IR spectrometer. UV−visible spectra of the polymers were recorded on a Hitachi U-3400 spectrophotometer and their emission spectra were recorded using a Hitachi F-2000 fluorescence spectrophotometer and a Perkin-Elmer LS-50B luminescence spectrometer. Solution UV−visible and fluorescence spectra of the polymers were recorded in very dilute solutions of $CHCl_3$ and CH_2Cl_2, respectively. The solutions were purged with dry N_2 for 10 min before measurements. Thin-film samples for UV−visible and PL studies were made by spin-coating $CHCl_3$ solutions of the polymer onto quartz plates. All the emission spectra were recorded using 370 nm as the excitation wavelength. The quantum yield of fluorescence Φ_f of the polymers was estimated by comparing the integrated areas of their fluorescence spectra with that of the standard, quinine sulfate (10^{-6} M in 0.1 N H_2SO_4), which has a Φ_f value of 0.55. GPC measurements were performed on a Polymer Laboratories P1gel system equipped with a Shimadzu LC-10AT pump and a linear UVIS-205 absorbance detector; $CHCl_3$ was used as the solvent and molecular weights were determined using a calibration plot constructed with polystyrene standards.

Synthesis of Poly((2-methoxy)-5-((2′-ethylhexyl)oxy)-1,4-(α-methoxy)xylylene-*co*-(2-methoxy)-5-((2′-ethylhexyl)oxy)-1,4-(α-acetoxy)-xylylene). In a typical experiment, 2.8 mL of ice-cold, N_2-purged dry-methanolic NaOH solution (1.25 M) was added in a slow stream to an ice-cold, N_2-purged dry-methanolic solution of the bis(sulfonium chloride) monomer **A** (2 g, 3.93 mM in 15 mL of methanol). The polyelectrolyte **B** was obtained by stirring the reaction mixture at 0 °C for 2 h. For acetate incorporation of less than 50 mol %, the required amount of 1 M solution of sodium acetate in acetic acid (containing 5% v/v acetic anhydride) was added directly to the polyelectrolyte solution after completion of polymerization. For higher acetate incorporation, the methanol was first completely removed under reduced pressure and the residue was dissolved in a solution of sodium acetate in acetic acid containing the required amount of methanol (for more details see ref 28). The mixture was stirred at room temperature for 2 h; the polymer that precipitated out was isolated, washed with methanol, filtered, and redissolved in THF. The THF solution was then filtered, concentrated, and the polymer precipitated from methanol. This process of dissolution−reprecipitation was repeated four times to ensure that the polymer was devoid of any low molecular weight acidic impurities. The polymer was then dried at 65 °C under reduced pressure for 1 h and at room temperature for an additional 4 h. The yield of the polymer ranged from 20 to 35%. The composition of the precursors was determined from their ^{1}H NMR spectra. The maximum mole fraction of acetate in the precursor, when no methanol was added during the nucleophilic substitution step, was found to be 67%. When the polymerization was done on a 1 g scale, the extent of premature substitution by methanol was reduced[28] and a precursor containing 85% acetate groups was obtained in a yield of 250 mg (45%).

Thermal Elimination. Typically, 24 mg of the precursor polymer was dissolved in 12 mL of dry xylene and 10 drops (170 mg) of triethylamine was added. The solution was filtered into a constricted glass tube and degassed by 4 freeze−pump−thaw cycles. The tube was then vacuum-sealed and heated at 220 °C for 6 h in a hot-air furnace. A special cell holder was designed so that the fluorescence spectra of the solution in these sealed tubes could be directly monitored after various time intervals during the thermal elimination. After the completion of thermal elimination (at which time little change in the fluorescence spectra was seen), the solution was cooled and filtered and xylene was removed under reduced pressure at 75 °C. The precipitated polymer was washed by stirring with 20 mL of warm methanol for a few minutes. Then, 20 mL of fresh methanol was added, and the polymer was filtered, air-dried, and subsequently dried in vacuum (0.05 mm of Hg) for 5 h. Yield: 21 mg. For solid-state elimination, thin films of the precursor polymers were cast on KBr pellets and heated under a dry-N_2 purge at 250 °C for 1 h, as before.[28]

Nomenclature. PPX-*x* and MEHPPV-*x* denote the precursor polymers and eliminated polymers, respectively, where *x* represents the mole percent of acetate groups in the former, while in the latter case, it is the mole percent of elimination. OPV-*n* denotes 2,5-dipropyloxy-1,4-phenylenevinylene oligomers with “*n*” vinyl groups.

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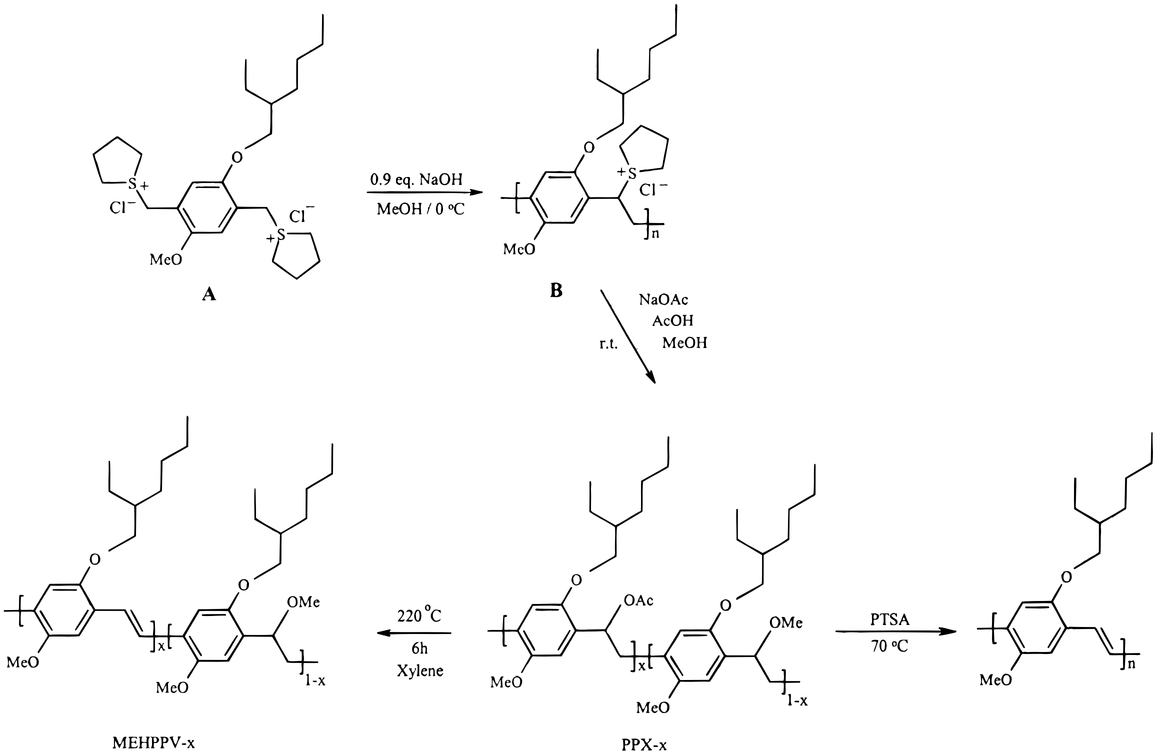
Scheme 1. Synthesis of MEHPPV-*x* and Subsequent Conversion to MEHPPV-100



Results

Synthesis of the Precursor Polymer. The bis(sulfonium chloride) monomer **A** was prepared according to the 4-step procedure of Burn et al.[30] (Scheme 1). The sulfonium chloride polyelectrolyte precursor of MEHPPV was prepared according to a slightly modified procedure of Wessling et al.[31,32] As reported by us previously,[28,33] the polyelectrolyte was treated with varying mole ratios of sodium acetate−methanol in acetic acid solution at room temperature to give the required neutral precursor polymer. A few typical ^{1}H NMR spectra of the precursor polymers are shown in Figure 1. The composition of the precursor copolymers was determined by comparing the intensities of the peaks due to the benzylic methine protons adjacent to the methoxy groups (−C**H**−OMe) at 4.9 ppm with those adjacent to the acetoxy groups (−C**H**−OAc) at 6.4 ppm. The mole fraction of acetate in the precursor polymers was readily varied from 0 to 85%. The molecular weights of all the precursors were found to be very high; M_w lies in the range − 220 to 260 kDa, as determined by GPC using polystyrene standards.

Thermal Elimination. In the expectation that all the thermally eliminated MEHPPV-*x* samples will be soluble, we first carried out the thermal elimination of the precursor films at 250 °C, as was done previously.[28,33] Although the IR spectral investigations pointed to the occurrence of a selective elimination of the acetate groups, with the expected red-shift in both their UV−visible and PL spectra as in the case of DMPPV, the resulting polymers were found to be only partially soluble. This pointed to the possibility of some kind of cross-linking during the solid-state elimination process. A similar observation was reported by Burn et al.,[34] who utilized this insolubility to their advantage in preparing multilayer devices. In an effort to overcome this insolubility problem we carried out the thermal elimination in solution.

Xylene was selected as the solvent to carry out the thermal elimination for the following reasons: (a) both the precursors and the eliminated polymers, MEHPPV-*x*, are readily soluble in xylene, (b) it is inert at the high temperatures of elimination, and (c) it has a fairly high boiling point (138 °C) and hence is more amenable to the sealed glass tube elimination conditions. Typically, the elimination was carried out at 220 °C using 0.2 wt % solutions of the precursor in xylene, which was degassed by several freeze−pump−thaw cycles prior to vacuum sealing. Initial studies of solution elimination yielded partially eliminated samples with poor control over the extent of elimination; often precursors with low acetate content gave unexpectedly high extents of elimination. This suggested that there was uncontrolled elimination of both acetate and methoxy groups in these cases. Control experiments confirmed that the elimination is not catalyzed by acetic acid, which is one of the products of elimination. Based on previous observations[28,33] that the elimination of methoxy group is readily catalyzed even in the presence of trace amounts of a stronger acid, we argued that trace amounts of acidic impurities could be present in the precursor. Since rigorous purification of the precursor polymers by repeated reprecipitations did not improve the selectivity of elimination, we felt that the acid, if present, was being generated during the elimination. Therefore, the elimination was carried out in the presence of 2% v/v of triethylamine in xylene and it was found to be very selective; the acetate groups could be completely eliminated leaving behind the methoxy groups in tact.

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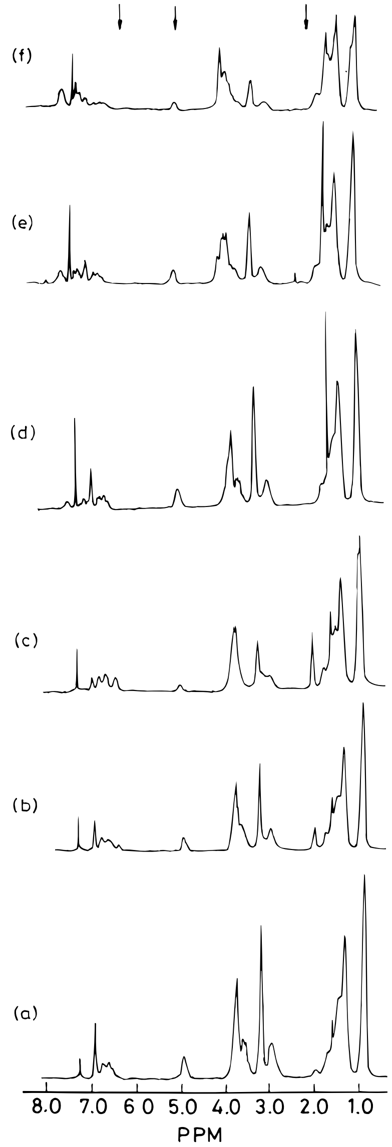

Figure 1. ^{1}H NMR (200 MHz, $CDCl_3$) spectra of copolymers: (a) PPX-10; (b) PPX-30; (c) PPX-69; (d) MEHPPV-10; (e) MEHPPV-30; and (f) MEHPPV-69. The arrows indicate the peaks due to the protons, $-C\mathbf{H}(OAc)$ (at 6.9 ppm), $-C\mathbf{H}(OMe)$ (at 4.9 ppm), and $-OCOC\mathbf{H}_3$ (at 2.0 ppm).

Our earlier studies on unsubstituted PPV precursors[33] suggested that there is often a small but finite extent of nucleophilic displacement of the sulfonium group in the polyelectrolyte by the chloride counterion, which results in the incorporation of chlorine in the benzylic methine position. This, we believe, also occurs in the dialkoxy precursors, although probably to a much smaller extent; the signal corresponding to the methine protons adjacent to the chlorine could not, therefore, be detected in their ^{1}H NMR spectra. The facile elimination of this chloride generates HCl, which in turn catalyzes the elimination of the methoxy groups leading to the observed erratic results. Triethylamine serves to capture the liberated HCl, leading to the selective elimination of the acetate groups alone. All the eliminated samples prepared in this manner were readily soluble in solvents such as chloroform, methylene chloride, THF, xylene, and chlorobenzene. The hypothesis of chloride incorporation was supported by the elemental analysis results, which showed the typical chlorine content in the precursor polymer to be about 0.35%, indicating that about 2.5% of the benzylic methine positions are substituted with chlorine. This may also account for the insolubility of thermally eliminated MEHPPV films, because the C−Cl bonds can also homolytically cleave to form radicals, which in the solid state may lead to cross-linking rendering the polymer insoluble.

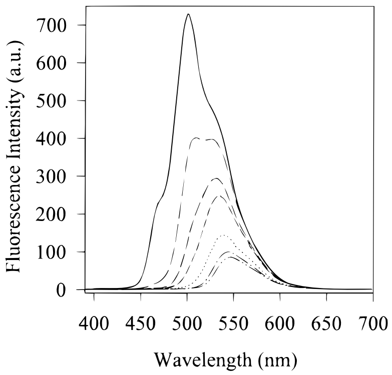

Figure 2. Evolution of fluorescence spectra of the precursor PPX-30 solution (0.2 wt % in xylene, $\lambda_{excitation} = 370$ nm) with time of heating at 220 °C: 30 min (−), 60 min(− −), 90 min (− − −), 120 min(- - -), 210 min (···), 270 min (- • -), and 360 min (- • • -).

In an attempt to follow the process of elimination, the fluorescence spectra of the solutions were recorded after every 30 min of heating at 220 °C. It was observed that there was a continuous bathochromic shift in the emission maxima ($\lambda_{max,emi}$) with time, which was also accompanied by a decrease in the overall intensity of emission. Typical variation of the fluorescence spectra of the precursor as elimination proceeds is shown in Figure 2.[35] The evolution of conjugation length, as elimination proceeded, is clearly visible and so also is the saturation tendency as the elimination approaches completion. Complete elimination of the acetate groups typically took about 6 h at 220 °C, after which little change in the fluorescence spectra was seen; in all cases, the near saturation of the fluorescence spectra was taken to imply complete elimination of the acetate groups. The partially eliminated samples, thus prepared, are left with only methoxy groups, which are very sluggish to elimination in the absence of an acid catalyst, and hence these samples are stable to further thermal elimination. The IR spectra of films of such partially eliminated polymers were also shown to undergo very little change upon prolonged heating even at temperatures as high as 200 °C, for several hours.[33] Completely eliminated MEHPPV-100 was readily prepared by heating the precursor polymer with a catalytic amount of *p*-toluenesulfonic acid (PTSA). In this case, a significantly lower temperature of 70 °C was sufficient to effect the complete elimination.

The ^{1}H NMR spectra of a few representative eliminated MEHPPV-*x* samples, along with their precursors, PPX-*x*, are shown in Figure 1. It is apparent that the peaks due to the acetate group (at 6.9 ppm due to $-C\mathbf{H}OAc$ and at 1.95 ppm due to $OCOC\mathbf{H_3}$) have completely disappeared in all of them whereas that due to $-C\mathbf{H}-OMe$ at 4.9 ppm remains essentially invariant. The extent of inadvertent elimination of the methoxy groups under these conditions rarely exceeds 5%; this was confirmed by comparison of the relative intensities of the terminal $C\mathbf{H}_3-$ protons of the alkoxy group (at 1.0 ppm) and that of $-C\boldsymbol{H}OMe$, before and after thermal elimination. Normalized FT-IR spectra of the solution-eliminated films also confirmed the selective nature of the elimination (see Figure 3). The peak due to C=O stretching at 1743 cm^{-1} disappeared completely, while that at 1095 cm^{-1} due to the methoxy group remained unaltered.

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(35) The fluorescence spectra, in this case, were recorded at a very high concentration, typically 10^3 times higher than those shown in Figure 5, and hence they often appear red-shifted and featureless due to aggregation.

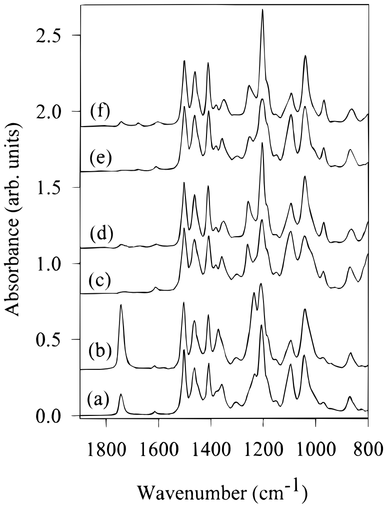

Figure 3. FT-IR spectra (films on KBr pellets) of copolymers: (a) PPX-20; (b) PPX-69; (c) MEHPPV-20; (d) MEHPPV-69; and (e and f) samples of MEHPPV-20 and MEHPPV-69, respectively, eliminated in the solid state. The spectra are normalized with respect to the invariant peaks at 1502 and 1464 cm^{-1} and have been Y-offset for clarity.

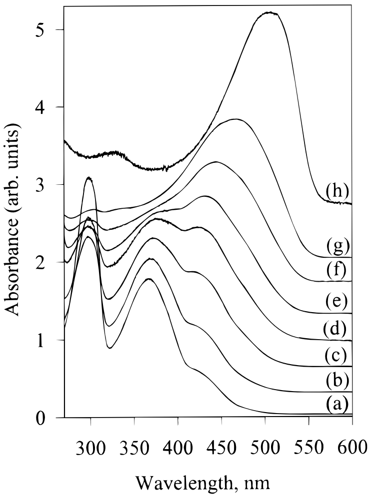

Figure 4. UV−visible absorption spectra (ca. 10^{-5} M $CHCl_3$ solutions) of copolymers MEHPPV-x: (a) $x = 10$; (b) $x = 20$; (c) $x = 30$; (d) $x = 45$; (e) $x = 55$; (f) $x = 69$; (g) $x = 85$; and (h) $x = 100$. The spectra are normalized in intensity and have been Y-offset for clarity.

Another advantage of the solution elimination method is that inadvertent oxidation that is often observed in solid-state elimination (appearance of a small peak at 1679 cm^{-1}) is suppressed during solution elimination. The absence of any carbonyl impurities in these conjugated samples is important, as their luminescence quantum efficiencies have been shown to be drastically reduced by the presence of such carbonyl impurities.[36,37]

UV−Visible and Photoluminescence Studies. The absorption spectra of MEHPPV-x in $CHCl_3$ are shown in Figure 4. It is apparent that there is a continuous bathochromic shift in the absorption maxima with increase in the extent of conjugation. At lower extents of elimination the variation in the intensity pattern of the fine structure reflects a gradual increase in the population of longer conjugated segments; the intensities of the longer wavelength bands increase at the cost of the shorter wavelength ones. At higher extents of elimination, however, the absorption band becomes broad and envelops the various oligomer bands within it. The absorption spectra of thin-film samples were essentially identical, except in a few cases where a very small bathochromic shift of the tail was observed. To gain an estimate of the conjugation length distribution in our samples, our data were compared with those of the oligomers of poly(2,5-dipropyloxy-1,4-phenylenevinylene) (PDPPV), OPV-*n*.[38,39] The expected saturation behavior with increase in conjugation length was observed by Meier et al.;[39] the variation in the λ_{max} values was small after OPV-8, and the longest oligomer synthesized by them, OPV-11, had a λ_{max} value of 481 nm, which matched well with that of the polymer, PDPPV. On the other hand, the λ_{max} value of pure MEHPPV-100 (at 508 nm) is significantly higher, suggesting a much higher effective conjugation length. The electronic effect of the alkoxy substituents in both cases being very similar, the higher *effective* conjugation length in MEHPPV-100 probably reflects the greater intrinsic chain rigidity due to the presence of bulkier substituents.[40]

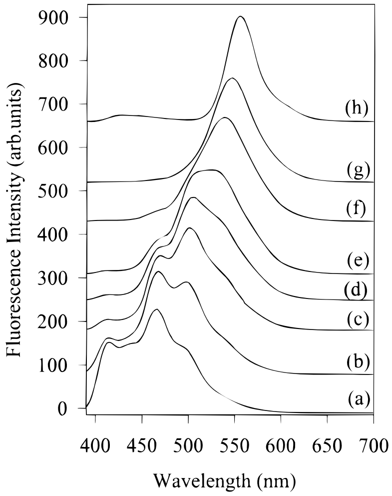

Figure 5. Fluorescence spectra (ca. 10^{-6} M CH_2Cl_2 solutions, $\lambda_{excitation} = 370$ nm) of copolymers MEHPPV-x: (a) $x = 10$; (b) $x = 20$; (c) $x = 30$; (d) $x = 45$; (e) $x = 55$; (f) $x = 69$; (g) $x = 85$; and (h) $x = 100$. The spectra are normalized in intensity and have been Y-offset for clarity.

The fluorescence spectra of the dilute solutions of MEHPPV-x in CH_2Cl_2 also showed the expected bathochromic shift with increase in conjugation length (Figure 5). Additionally, it is clear that, as the conjugation length increases, the emission from different individual conjugated segments disappears and a continuously narrowing emission peak is observed (for MEHPPV-69 and above). The quantum yield of fluorescence (Φ_f) (relative to standard quinine sulfate) also decreased monotonically with increase in the conjugation length (Figure 6). This is in contrast to that observed in the case of pure oligomers OPV-*n*, where the Φ_f value was observed to attain a maximum for OPV-3 and then decreases before it levels off at around 0.4 after OPV-6.[41] This difference probably arises due to the presence of a statistical distribution of conjugation lengths in the case of polymers, and is compounded by the occurrence of

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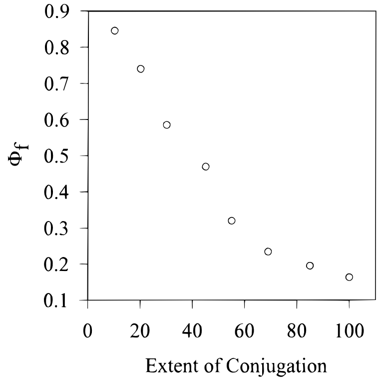


Figure 6. Variation of fluorescence quantum yield, Φ_f (ca. 10^{-6} M CH_2Cl_2 solutions, $\lambda_{excitation} = 370$ nm), of copolymers MEHPPV-*x* with *x*.

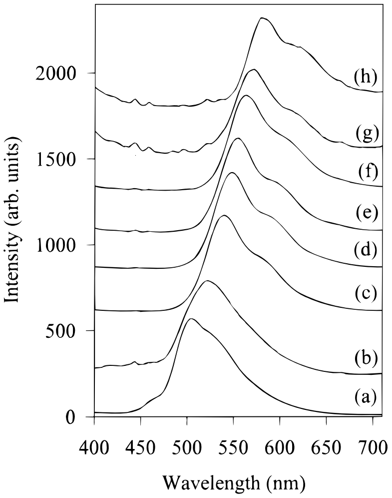


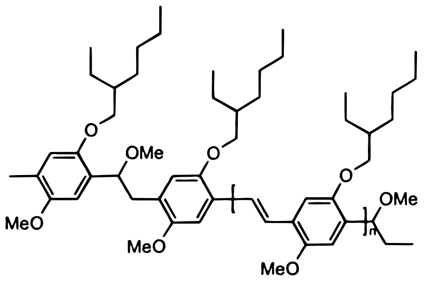
Figure 7. Photoluminescence spectra (films on quartz plate, $\lambda_{excitation} = 370$ nm) of copolymers MEHPPV-*x*: (a) $x = 10$; (b) $x = 20$; (c) $x = 30$; (d) $x = 45$; (e) $x = 55$; (f) $x = 69$; (g) $x = 85$; and (h) $x = 100$. The spectra are normalized in intensity and have been Y-offset for clarity.

intrachain energy transfer. The solid-state photoluminescence (PL) spectra of MEHPPV-*x* (Figure 7) also showed a continuous bathochromic shift in the $\lambda_{max,emi}$ values with increase in the extent of elimination. Expectedly, these values in films of MEHPPV-*x* were 20−40 nm higher than those in solution, probably because of the formation of aggregates in films, leading to emission from interchain excitons.[19,42−45] More interestingly, the spectra of thin films are devoid of any fine structure due to individual oligomer emission even in the case of MEHPPV-20, again because of energy transfer that occurs more rapidly in films when compared to dilute solutions.[46] The results of the UV−visible and the emission spectroscopic studies of MEHPPV-*x* in the solution and film are summarized in Table 1.

Discussion

In our approach to control conjugation length we rely on the statistically random placement of acetate and methoxy groups in the precursor during the competitive nucleophilic substitution of the Wessling polyelectrolyte, and further on the selective elimination of the acetate groups. This would lead to the generation of truncated MEHPPV oligomers of varying conjugation lengths even within a given polymer chain, the average value of which increases with increasing extents of elimination. In an effort to ascertain this distribution of conjugation lengths, we attempted to fit both the absorption and fluorescence spectra of MEHPPV-*x* using the spectral data of OPV-*n*[39] as the starting point. The fitting process, however, failed to give unequivocal answers. As an alternative, we chose to reconstruct the absorption spectra of the polymers using those of the various OPV-*n* oligomers, assuming a statistically random elimination process.

In general, the probability of finding any oligomer with "*n*" number of vinyl groups is given by $P(n) = (1 - x')^2 x'^n$, where x' (same as $x/100$) is the mole fraction of the eliminated segments.[25] A similar statistical approach has been utilized by others in the case of both segmented PPV copolymers[47] as well other luminescent conjugated rigid rod-random coil block copolymer systems.[48−50] The individual probabilities of finding the various oligomer segments in each of the MEHPPV-*x* samples were thus calculated and the absorption spectra of the OPV-*n* oligomers were factored (to reflect this expected oligomer concentrations) and summed up to generate the reconstructed absorption spectra.[51] Only oligomers whose expected concentrations exceeded 0.4% were used for this analysis. A few such reconstructed spectra alongside the measured ones are shown in Figure 8. The reconstructed spectra matched very well with the observed ones inasmuch as the relative populations of the various oligomers are concerned (as seen from the overall similarity in their shapes[52]), although the measured spectra, in many cases, are significantly red-shifted (~12−15 nm). As stated earlier, this could be due to an intrinsic difference between the λ_{max} values for the actual MEHPPV oligomers and those for OPV-*n* oligomers, which is also reflected in the ca. 26 nm difference in $\lambda_{max,emi}$ of PDPPV when compared to MEHPPV-100. Despite these limitations, the overall one-to-one correspondence in shape between the reconstructed and the observed absorption spectra amply supports



Oligo-MEHPV-n

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(52) The mismatch in the intensities of the peak at around 290 nm is because this arises from the isolated 1,4-dialkoxybenzene units of the uneliminated segments, which are not taken into account during the reconstruction of the spectra.

Table 1. Solution UV−Visible Absorption and Emission Spectroscopic Data of MEHPPV-*x*

sample	UV−vis absorption λ_{max} values (nm)[c]		emission λ_{max} values (nm)[c]	
	solution[a]	film	solution[b]	film
MEHPPV-10	366.6 (415.0)	367.0 (415.0)	466.0 (494.0, 412.5)	504.5
MEHPPV-20	369.8 (416.0)	369.8 (416.0)	498.5 (468.0, 412.5)	522.5
MEHPPV-30	372.2 (417.0)	376.6 (427.0)	502.0 (469.5, 413.0)	539.5
MEHPPV-45	374.6 (422.0)	378.6 (428.0)	508.0 (523.0, 472.0)	547.5
MEHPPV-55	432.0 (393.0)	435.2 (394.0)	533.5 (474.0)	554.0
MEHPPV-69	443.2	450.6	542.5 (475.0)	563.0
MEHPPV-85	466.8	466.6	550.5 (584.5)	571.5
MEHPPV-100	508.0	512.6	558.5 (593.0)	579.5

[a] Recorded in $CHCl_3$. [b] Recorded in CH_2Cl_2 at a concentration of ca. 10^{-6} M. [c] The values in parentheses represent shoulders or peaks of lower intensity.

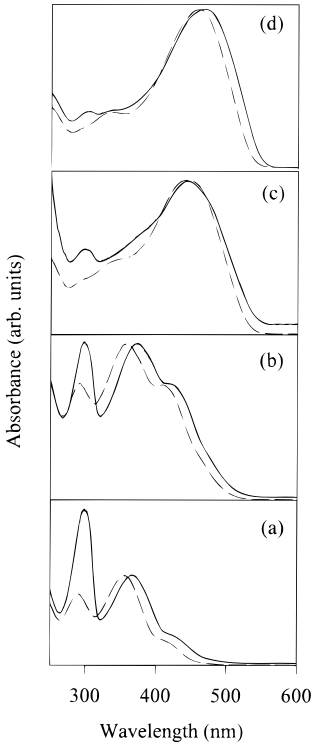

Figure 8. Overlay of recorded (continuous lines) and reconstructed (broken lines) UV−visible spectra ($CHCl_3$ solutions) of MEHPPV-*x*: (a) $x = 10$; (b) $x = 30$; (c) $x = 69$; and (d) $x = 85$.

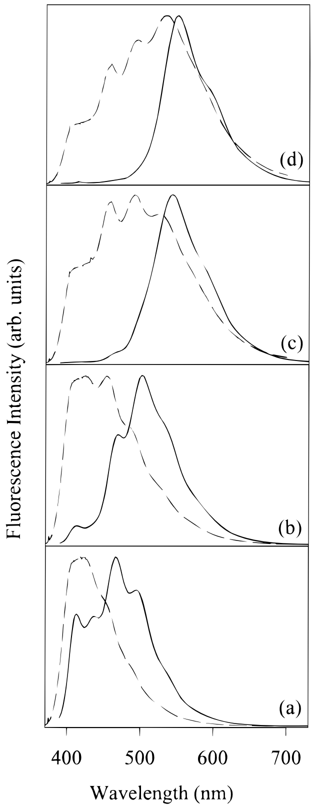

Figure 9. Overlay of recorded (continuous lines) and reconstructed (broken lines) fluorescence spectra (CH_2Cl_2 solutions) of MEHPPV-*x*: (a) $x = 10$; (b) $x = 30$; (c) $x = 69$; and (d) $x = 85$.

the hypothesis of a statistically random evolution of conjugation lengths in the MEHPPV-*x* samples.

Having established the statistical nature of the evolution of conjugation lengths, we proceed to examine the issue of intrachain energy transfer. It is well-known that in thin films of PPV derivatives selective excitation of shorter conjugation length segments does not result in emission from these segments alone; significant energy transfer to neighboring longer conjugated segments occurs prior to emission.[53,54] This leads to the apparent insensitivity, in shape and position, of the fluorescence spectra to the excitation wavelength. Time-resolved fluorescence measurements have also confirmed the occurrence of such an energy transfer in solid thin films of PPV.[55] In an effort to understand energy transfer in solutions of conjugated polymers, the fluorescence spectra of MEHPPV-*x* were also reconstructed using a similar statistical weighting and summing up of the various OPV-*n* fluorescence spectra. Unlike in the case of the absorption spectra, the reconstructed fluorescence spectra differ considerably from the observed ones in all cases (see Figure 9). The spectra of MEHPPV-*x* samples often lack the well-resolved fine structure (especially in highly eliminated samples), which suggests that separate emission from the individual chromophores of varying conjugation lengths is not seen, and also the majority of the emission occurs at considerably lower energy when compared to the reconstructed spectra. Both these aspects reflect the occurrence of energy transfer. As these spectra were recorded under very dilute conditions, the energy transfer may be assumed to occur primarily via an intrachain pathway.[19,44] Further, it is pertinent to add here that unlike in the absorption spectra, the difference in the emission maxima of pure MEHPPV solution and that of PDPPV is very small; MEHPPV-100 has a $\lambda_{max,emi}$ value of 559 nm, while PDPPV has a value of 552 nm.[39] Hence, the reconstructed fluorescence spectra would be a more accurate reflection of the expected spectra in the absence of energy transfer.

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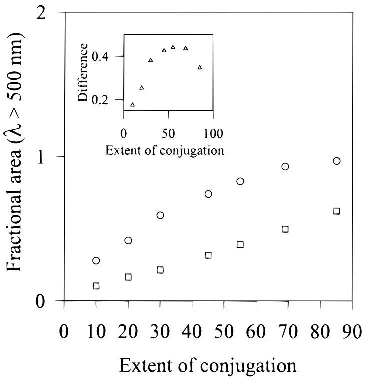

Figure 10. Plot of fractional area under the emission curve (CH_2Cl_2 solutions) for $\lambda > 500$ nm ($\mathrm{Area}_{\lambda>500}/\mathrm{Area}_{\mathrm{total}}$) as a function of extent of conjugation *"x"*. Open circles correspond to the recorded spectra, while open squares are for the reconstructed spectra. Inset: Variation of the difference of the fractional areas between the recorded and reconstructed spectra as a function of *"x"*.

In an attempt to quantify the extent of energy transfer, the fractional areas under the emission curves below and above 500 nm were calculated for both the reconstructed and the observed spectra. The fractional areas above 500 nm in both cases were plotted as a function of the extent of conjugation "*x*" and the plot is shown in Figure 10. In the case of the reconstructed spectra, no energy transfer is assumed to occur, and hence the difference in the fractional areas between the observed and reconstructed spectra is a reflection of the extent of energy transfer that has occurred in the polymers. The inset figure shows a plot of this difference versus extent of elimination. It is clear from the plot that the extent of energy transfer increases with increase in conjugation till it levels off, except in the case of MEHPPV-85.[56] Thus, we can conclude that even in very dilute solutions, conjugated polymers containing truncated chromophores of varying conjugation lengths experience intrachain energy transfer; the extent of such a transfer increases as the probability of finding neighboring longer conjugation length segments increases. Further studies using time-resolved fluorescence measurements are essential to confirm and quantify this more thoroughly.

Conclusions

The synthesis of soluble MEHPPV samples with varying extents of conjugation was achieved by selective elimination of the acetate groups from a precursor that contains a random distribution of acetate and methoxy groups. It was shown that trace amounts of inadvertent substitution by the chloride counterion lead to erratic results during thermal elimination; this was readily suppressed when the elimination was done in the presence of a weak base like triethylamine. With increase in the extent of elimination both the absorption and emission spectra exhibited the expected bathochromic shift; the color of emission was thus tunable between 466 and 559 nm in solution and 504 and 580 nm in the films. Comparison of the solution spectra with those of thin-film samples showed that while the difference is minimal in the case of the absorption spectra, a significant difference is seen in the emission spectra. The emission spectra in thin films are considerably red-shifted and are devoid of any fine structure that reflects separate emission from segments with different conjugation lengths. The formation of interchain excitons in thin films explains the red-shift, while energy transfer causes the obliteration of the fine structure. Assuming a statistically random elimination process, it was possible for the first time to gain insight into the extent of intrachain energy transfer in dilute solutions of MEHPPV-*x*; the extent of energy transfer was shown to increase with conjugation length. Finally, unlike in the case of model oligomers, the fluorescence quantum yields of MEHPPV-*x* samples decreases monotonically with increase in the extent of conjugation; the presence of a distribution of conjugation length within a single polymer chain facilitates energy transfer probably leading to this difference.

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Supporting Information Available: A description of the statistical approach utilized for the spectral reconstruction based on the oligomeric PPV derivatives (OPV-*n*), along with their normalized UV−visible and fluorescence spectra that were provided to us by Ulf Stalmach (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[56] The apparent reduction in the case of MEHPPV-85 is a reflection of the approach we have chosen to quantify the energy transfer. The fractional areas above 500 nm in the emission curve of the polymers have a limiting tendency as this value approaches unity, while those of the reconstructed spectra continuously increase, causing this apparent decrease in the difference.