Fluorescence Spectroscopic Studies of Solvent- and Temperature-Induced Conformational Transition in Segmented Poly[2-methoxy-5-(2′-ethylhexyl)oxy-1,4-phenylenevinylene] (MEHPPV)

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Received: March 5, 2004; In Final Form: June 6, 2004

Segmented poly[2-methoxy-5-(2′-ethylhexyl)oxy-1,4-phenylenevinylene] (MEHPPV-*x*, where *x* is the mole percent of conjugated segments) represent unique polymeric systems in which a large number of chromophores of different molecular conjugation lengths (different excitation/emission energies) are strung together in a single polymer chain, which thereby forces them to occupy a relatively small volume that is determined by the hydrodynamic size of the macromolecule. Changing the hydrodynamic volume by varying either solvent composition or temperature, therefore, provides a straightforward approach to modulate the interaction between the chromophores. Fluorescence spectroscopic studies of very dilute solutions (in dichloromethane/1,2-dichloroethane) of segmented MEHPPVs with increasing amounts of a nonsolvent (methanol/cyclohexane/ethanol) reveal an interesting inverted S-shaped variation in the emission yield with increasing nonsolvent composition, which is accompanied by a red shift of the emission maxima. Both these changes are indications of a conformational collapse of individual polymer chains, resulting in enhanced energy transfer from highly emissive short conjugation length segments to weakly emissive longer ones and/or to the formation of weakly emissive interchromophore excitons. The solvent composition at the onset of the steep decline in the S-shaped curve, termed the chain-collapse point, was found to vary with the extent of conjugation in a manner which suggests that the polymers bearing longer chromophores undergo collapse earlier than those bearing shorter ones. In samples with very low levels of conjugation, such as in MEHPPV-10, a rather unexpected observation of an initial increase in the emission yield prior to the sudden decline was seen. This is consistent with the unusual conjugation length dependence of the fluorescence quantum yield of oligoPPVs (OPV) reported by earlier workers. Fluorescence spectral variation as a function of temperature also reveals several interesting features of these systems, the most interesting of which is the observation that either an increase or a decrease of emission yields with increase in temperature could be observed, depending on the initial conformation of the polymer chain. When the chain is in a highly collapsed (or a highly solvated) state, an increase in temperature causes the expected decrease in emission yield, while in an intermediate partially collapsed conformation, a significant increase in the emission yield with temperature is observed. The latter observation is ascribed to polymer coil expansion that results in depletion of aggregated species and/or a reduction in energy transfer to weakly emitting chromophoric segments.

Introduction

Conjugated polymers have witnessed a renewed interest over the past decade because of their potential for application in a variety of optoelectronic and electrooptic devices.[1] With the discovery of soluble derivatives of the conjugated polymers, such as poly[2-methoxy-5-(2′-ethylhexyl)oxy-1,4-phenylene-vinylene] (MEHPPV), came the obvious realization that they possessed several advantages over the insoluble analogues prepared by precursor processing. The properties of the devices, fabricated by spin-coating a conjugated polymer solution, were seen to be strongly dependent on the finer details of the coating process, such as the concentration, spinning speed, nature of the solvent, etc. One of the earliest such observations was reported by Heeger's group,[2] wherein PL spectral line-narrowing was noticed only in conjugated polymer films cast from aromatic solvents. Further detailed studies by Schwartz and co-workers[3] also clearly document the influence of the nature of the solvent on the photophysical properties of the MEHPPV solutions and also on the properties of the thin-film devices fabricated therefrom.

The use of solvent mixtures permits a gradual change of the solvent quality with regard to the polymer solubility, which in turn can affect a controlled variation of the polymer-coil dimension. Conjugated polymers, especially those that are highly fluorescent, like MEHPPV, are particularly interesting in this context, as the variation of the solvent quality can lead to very drastic changes in their fluorescence spectra. In an early study, Samuel et al.[4] showed by use of time-resolved fluorescence measurements that the contribution from interchain excitons/aggregates could be readily modulated in CN−PPV derivatives by varying the solvent composition. Collison et al.[5] and Zhang et al.[6] described the fluorescence behavior of MEHPPV in mixed solvents as a function of solvent composition. Their studies suggested that with increasing amounts of nonsolvent the formation of aggregates increases, as evidenced by the observed

10.1021/jp048994t CCC: $27.50
Published on Web 08/26/2004

red-shifted emission spectra with a considerable reduction in emission intensity. Presence of aggregates even in the ground state was confirmed by distinct changes seen in the absorption spectra, especially at higher concentrations. Similar studies by Bunz and co-workers,[7] and more recently by Chu and Pang,[8] using poly(phenylene ethynylene) (PPE) derivatives also suggest the formation of such ground-state aggregates in the presence of increasing amounts of nonsolvent. Variable-temperature fluorescence studies in PPE derivatives also suggested that the formation of these aggregates is thermally reversible.[7−9] Thus, the role of polymer chain conformation in governing the photophysical properties of conjugated polymers has been extensively studied during the past few years, particularly because of their possible direct bearing on thin-film device performance.[10]

In this context, segmented conjugated polymers, like MEH-PPV-*x*, in which the extended π-conjugation is randomly truncated by varying lengths of nonconjugated segments, form an interesting class of macromolecules as they represent not only chains of varying stiffness but also ones where the backbone can be construed as being made up of chromophores of varying excitation energies. We recently showed that, in segmented MEHPPV-*x* with varying extents (*x*) of conjugation, the quantum yield of fluorescence continuously decreases with increasing conjugation,[11] quite unlike the variation seen in the case of well-defined oligomers.[14c] It was concluded that even in very dilute solution (ca. 10^{-6} M) energy transfer between chromophores of different conjugation lengths occurs within a single polymer chain. Single-molecule spectroscopic studies further reveal that the conformation of the chains are strongly dependent on the extent of conjugation, going from a defect cylinder in highly conjugated systems to a random coil in chain with low levels of conjugation.[12] Thus, segmented MEHPPVs may be viewed as polymer chains having a tunable number of fluorophores of varying excitation energies. With this in mind, we examine in this paper the fluorescence properties of these systems as a function of solvent- and temperature-induced modulation in their size.

Experimental Section

Segmented MEHPPV-*x* samples with different extents of conjugation, *x*, were prepared by the selective thermal elimination of specifically designed precursor polymers that contain predetermined mole fractions (*x*) of randomly distributed eliminatable units, interspersed with noneliminatable ones along the polymer backbone.[11a,d] The fluorescence spectra were recorded on a Perkin-Elmer LS-50B fluorescence spectrometer, with 370 nm as the excitation wavelength. Variable-temperature fluorescence spectra were recorded by use of a jacketed cell holder (with built-in stirrer), along with a constant-temperature bath-type circulator. For the fluorescence titration experiments, a stock solution of the polymer (ca. 6×10^{-5} M) was prepared in dichloromethane/dichloroethane; 0.1 mL of this stock solution was diluted to 2 mL with 1.9 mL of the required solvent mixture to ensure that the final concentration is always maintained constant at 3×10^{-6} M. The UV−vis absorption spectra of the polymers were recorded on a Hitachi U-2400 spectrometer. The reference cell always contained the same solvent composition in which the polymer was dissolved. Methanol, cyclohexane, dichloromethane (DCM), 1,2-dichloroethane (DCE), and ethanol were dried by refluxing over appropriate drying agents and distilled.[13]

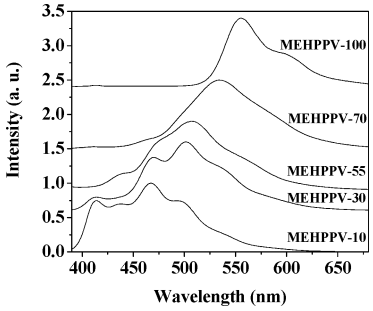
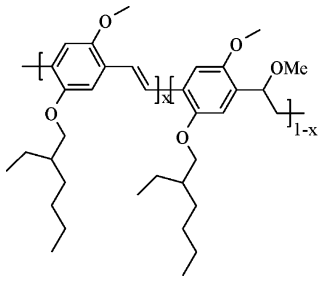


Figure 1. Fluorescence spectra of MEHPPV-*x* in DCM as a function of extent of conjugation *x*.

CHART 1: Structure of MEHPPV-*x*



Nomenclature

MEHPPV-*x* denotes MEHPPV having *x* mol % vinyl linkages and (100 − *x*) mol % units with a methoxy substituent on the benzylic carbon. OPV-*n* denotes 2,5-dipropyloxy-1,4-phenylenevinylene oligomers of Meier et al.[14] having *n* vinyl units. MEH-stilbene, MEH-distilbene, and MEH-tristilbene denote oligomeric segments of 2-methoxy-5-(2′-ethylhexyl)oxy-1,4-phenylenevinylene having 1, 2, and 3 vinyl units, respectively.

Results and Discussion

The general structure of the segmented MEHPPV-*x* with varying levels of conjugation is shown in Chart 1. These polymers are readily soluble in solvents such as DCM, toluene, tetrahydrofuran (THF), etc., while they are insoluble in solvents such as methanol, ethanol, hexane, etc. The solution fluorescence spectra of MEHPPV-*x* in DCM (Figure 1) with increasing levels of conjugation (*x*) reveal the expected variation in the relative populations of conjugated segments of different conjugation lengths.

As reported in our earlier paper,[11a] these spectra are modulated to varying levels by the occurrence of intrachain interchromophore energy transfer, which typically causes the loss of fine structure accompanied by a red shift in the emission maximum. The extent of such energy transfer would depend on the average interchromophore distance, which in turn depends on both the size and number (both of which are controlled by *x*) of chromophores in the polymer chain. One way to modulate the average interchromophore distance in a given segmented MEHPPV polymer molecule is to vary the dimension of the polymer coil by varying either the solvent quality or the temperature. Thus, the effects of varying the solvent composition were studied for three different solvent−nonsolvent combinations, namely, dichloromethane (DCM)−MeOH, DCM−cyclohexane, and 1,2-dichloroethane (DCE)−ethanol. The former two pairs were selected so as to cause opposite effects on the net solvent polarity, while the last pair was selected to enable variable-temperature experiments.

Dichloromethane−Methanol Mixtures. The fluorescence spectra of pure MEHPPV (MEHPPV-100) in DCM (at 3×10^{-6}

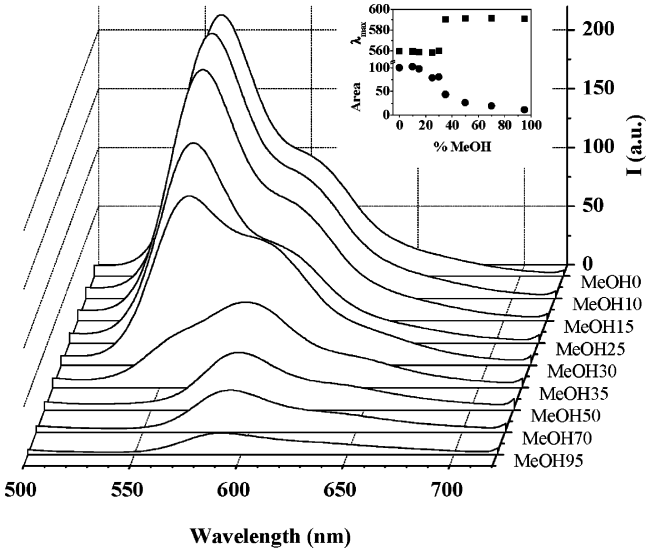


Figure 2. Fluorescence spectra of MEHPPV-100 in DCM as a function of methanol composition. Inset depicts the variation in the normalized emission area and the emission maxima as a function of solvent composition.

M), as a function of varying volume fractions of methanol are shown in Figure 2. Two distinct features are apparent from the figure: (i) a significant red shift in the emission maximum at high methanol content and (ii) a drastic decrease in the overall emission yield with increasing methanol content. Upon careful examination, it is apparent that the main peak at ca. 560 nm depletes rapidly in intensity, while the shoulder to the red becomes the dominant peak, at ca. 590 nm, beyond a certain concentration (>30%) of methanol. The absorption spectra also exhibit a similar but significantly smaller red shift, which may be ascribed to simple solvatochromism as well as possibly some aggregate formation.[5a] The significantly larger effect seen in the fluorescence spectra is partly due to the inherently higher sensitivity of the excited states toward solvent polarity but more importantly due to enhanced occurrence of excited-state interchromophore interactions, as we shall see later. These results with pure MEHPPV are generally in accordance with those reported by earlier workers, although no quantitative discussions of these variations were presented.[5,6]

To follow this variation more quantitatively, the variation in the total area under the emission envelope (emission yield) as well as the emission maximum (λ_{max}) is plotted as a function of methanol composition in Figure 2 (inset). In both cases there appears to be a sudden change occurring over a small composition variation, suggestive of a cooperative effect reminiscent of the conformational transitions observed in biopolymers. This kind of sudden change cannot be ascribed to simple solvatochromic effects but is clearly suggestive of a drastic change in the conformation of the polymer chains, which in turn affects parameters such as aggregation, energy transfer, interchain exciton formation, etc. The onset of the steep decline, in the typical inverted S-shaped plots that describe the emission area variation versus solvent composition, was taken as the chain collapse point. A similar S-shaped curve is also seen for the variation in the emission maxima with solvent composition, and the onset point of this curve matched fairly well with that from the emission area curve. Since these measurements are carried out at very dilute solution ($\sim 10^{-6}$ M), these variations may be ascribed primarily to an isolated single-chain conformational transition, although interchain effects may also contribute to some extent, especially at higher nonsolvent compositions. Some

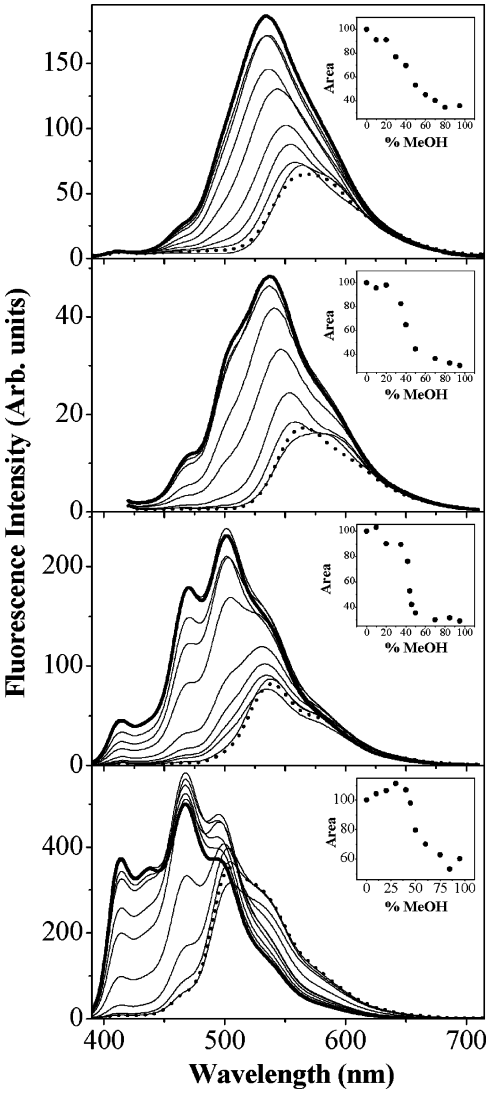


Figure 3. Fluorescence spectra of MEHPPV-70 (a), MEHPPV-55 (b), MEHPPV-30 (c), and MEHPPV-10 (d) in DCM as a function of methanol composition. Insets depict the variation in the normalized emission area as a function of solvent composition. For clarity the initial and final spectra during the titration are shown as bold solid and dashed lines, respectively.

other experiments that provide evidence in support of the former contention are described in a later section.

We carried out similar studies for four different segmented MEHPPV-*x* samples, where $x = 10$, 30, 55, and 70, and the changes in their fluorescence spectra are depicted in Figure 3. For clarity, the starting spectra in pure DCM and the final spectra, in 95% methanol, are depicted as bold solid and dashed lines, respectively. It is generally noticed that in all cases there is a drastic reduction in emission yield accompanied by a red-shifted emission, with increasing methanol content. In case of MEHPPV-10, the fluorescence spectrum in pure DCM exhibits distinct peaks due to both MEH-stilbene (415 nm) and MEH-distilbene units (460 nm), with a tailing indicative of the presence of other higher homologues. If one looks at the calculated population histogram[15] (Figure 4), it is apparent that a large majority of the chromophores in fact belong to these two types of oligomers with a very small contribution from MEH-tristilbene unit ($n = 3$). An intriguing feature in this case is that there is a very clear increase of emission yield in the early stages of the titration (till about 30% methanol) prior to the sudden decrease (see inset).

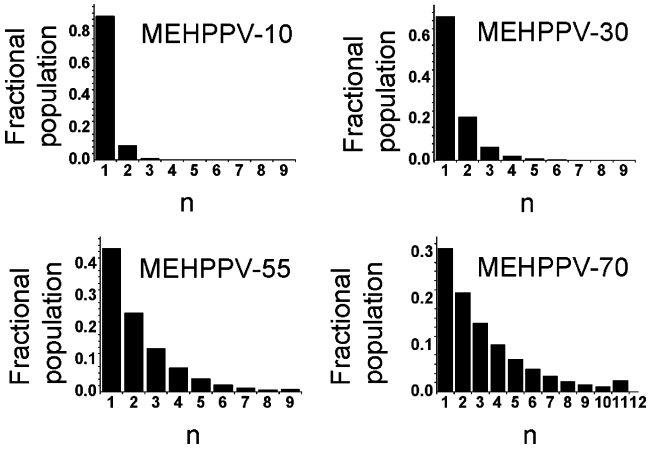


Figure 4. Calculated histogram showing the fractional population of the various conjugation length segments in MEHPPV-*x* as a function of extent of elimination (*x*).

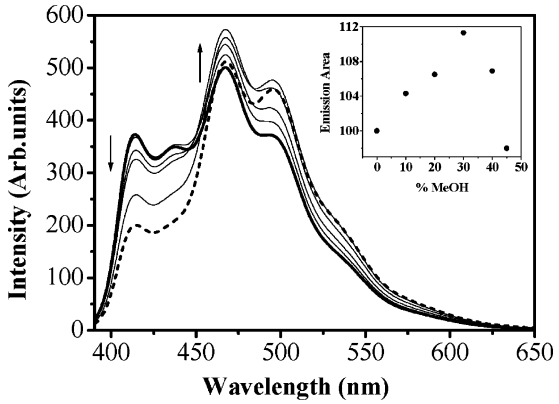


Figure 5. Expanded region of the fluorescence spectra of MEHPPV-10 in DCM as a function of methanol composition. For clarity the initial and final spectra are shown as bold solid and dashed lines, respectively. Inset shows the increase in the normalized emission area during the initial stages of the titration.

Upon careful examination of the expanded region of the spectral evolution (Figure 5), a very interesting and rather unprecedented feature becomes apparent. Initially as the intensity of the 415 nm emission band decreases, the intensities of the peaks at 460 and 496 nm increase. To explain this behavior, we need to consider the variation of fluorescence quantum yields (Φ_f) of well-defined oligomers. The Φ_f of oligomeric dipropyloxy-PPVs (OPV-*n*) were reported to exhibit a rather unusual variation as a function of oligomer length[14c] the smallest oligomer, stilbene (OPV-1), has a fluorescence quantum yield of ca. 0.45, which goes up to about 0.8 for distilbene (OPV-2) and further to ca. 0.81 for OPV-3, before falling drastically for the higher oligomers. It remains essentially constant around 0.4 for oligomers with $n \geq 6$. Given this unusual variation of quantum yields of OPVs, the origin for the initial enhancement of emission yield in MEHPPV-10 is readily explained.[16] Energy transfer from a MEH-stilbene chromophore to MEH-distilbene/tristilbene segments results in the generation of an excited state with intrinsically higher quantum yield for emission. Hence, while there is a decrease in the intensity of the peak due to the MEH-stilbene unit (415 nm), there is an enhancement of the peak due to MEH-distilbene (467 nm), and probably MEH-tristilbene (495 nm). However, at much higher concentrations of methanol, the emission yield decreases due to energy transfer to higher oligomers ($n > 4$) and/or due to the formation of interchromophore excitons.

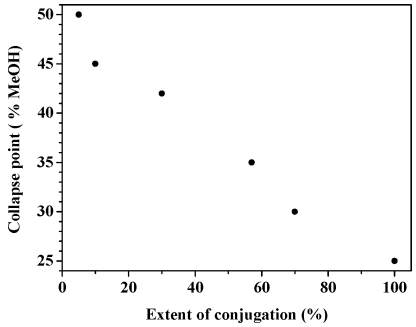


Figure 6. Variation of the chain-collapse point as a function of extent of conjugation.

To further understand this apparent conformational collapse, the chain-collapse point of various segmented MEHPPV-*x* samples is plotted as a function of extent of conjugation (*x*) in Figure 6. It is clear from this plot that as one increases the extent of conjugation, the amount of nonsolvent required to effect chain collapse decreases. Earlier workers, who have studied fully conjugated MEHPPV, have ascribed the sudden drop in fluorescence yield to the dimensional change of the polymer chain leading to enhanced formation of intrachain interchromophore excitons (aggregates), which have considerably lower emission quantum yields.[5a] In segmented MEHPPV-*x* samples, however, apart from the enhanced probability of aggregate formation, it is clear that energy transfer to higher oligomers with lower emission efficiency is also important.

The occurrence of the intrachain interchromophore energy transfer, from shorter to longer conjugation length chromophores, leading to a red-shifted emission was shown to occur even in pure DCM solutions of MEHPPV-*x*, and the extent of such energy transfer was shown to increase with increase in the extent of elimination.[11a] Since the starting molecular weights of all the polymers are roughly the same, especially since all of the precursor polymers with varying values of *x* are made from a single polymeric intermediate, namely, the Wessling precursor,[11] the initial hydrodynamic volume of the various MEH-PPV-*x* samples may be taken to be roughly the same.[17] Thus, as the extent of elimination increases, one may expect that the average interchromophore distance within the hydrodynamic volume of the polymer chain decreases. If we were to assume that, as far as the fluorescence measurements are concerned, the collapse is visualized as soon as the average interchromophore distance reaches a certain threshold value *r*, then this threshold is reached at an earlier stage (larger hydrodynamic volume) for highly conjugated samples (larger values of *x*) than for less conjugated ones. This can be schematically represented, in what can be termed as a Forster/aggregation ruler, as depicted in Figure 7. Thus, our argument gives greater weight to the variation in the average interchromophore distance, assuming that intrinsic variations in the hydrodynamic volumes of segmented MEHPPV-*x* as a function of *x* is less important. Despite the very low concentration, interchain aggregate formation, which can also explain this behavior, cannot be completely ruled out, especially at higher nonsolvent composition. Independent verification of this is possible only if simultaneous measurement of sizes of the polymer molecules is also made.

DCM−Cyclohexane Solvent Mixtures. Methanol being a poor solvent for both the precursor as well as the fully eliminated MEHPPV samples, it causes an indiscriminate desolvation of both the conjugated and nonconjugated segments. Cyclohexane, on the other hand, dissolves the uneliminated precursor polymer but does not dissolve fully eliminated MEHPPV. Furthermore,

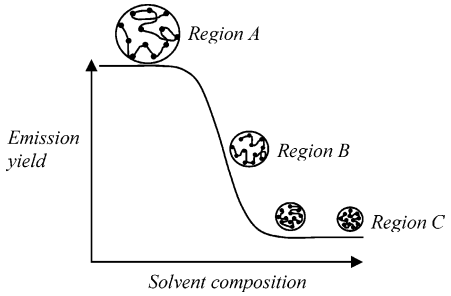


Figure 7. Schematic representation of the coil collapse transition. The black beads, which represent the chromophores, remain constant in number but the average interchromophore distance decreases as the coil collapses.

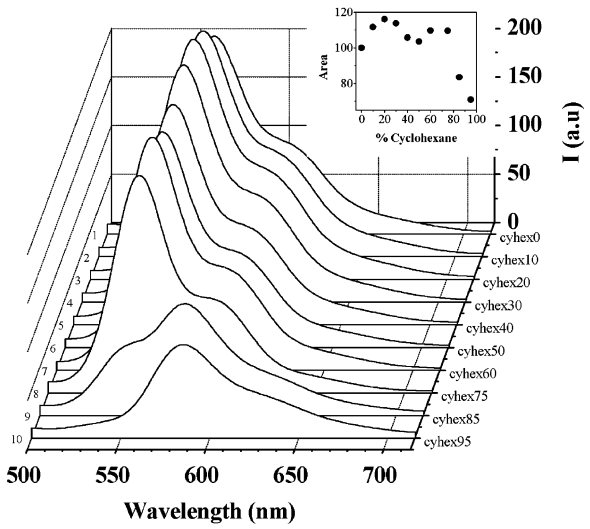


Figure 8. Fluorescence spectra of MEHPPV-100 in DCM as a function of cyclohexane composition. Inset depicts the variation in the normalized emission area as a function of solvent composition.

partially conjugated samples, up to MEHPPV-55, are completely soluble in cyclohexane, while beyond this value of *x* they become insoluble. Hence, cyclohexane may be considered as a good solvent for the uneliminated segment while a nonsolvent for longer conjugated segments. Thus, it would be interesting to study whether, by use of DCM−cyclohexane solvent mixtures, one could affect a preferential desolvation of the longer conjugated segments, causing a selective clustering of the longer units alone. In addition, by titration with cyclohexane, which is a relatively nonpolar solvent, the simple effect of solvatochromism can be readily separated from that of chain collapse.

Figure 8 shows the change in fluorescence spectra of MEHPPV-100 as a function of cyclohexane composition. One distinct difference when compared to methanol is readily apparent: there is an initial blue shift of the emission maximum that is accompanied by a small increase in the emission yield. This behavior may be ascribed to solvatochromism in the presence of a solvent with significantly lower dielectric constant. The variation of the emission area of MEHPPV-*x* as a function of the amount of cyclohexane exhibits a slightly different behavior as compared to methanol; the onset of the steep decrease occurred only at very high volume fractions of cyclohexane and furthermore the extent of decrease was also lower. This lower extent of depletion in the emission yield in the case of cyclohexane when compared to methanol suggests that the relative extent of collapse of the chains in cyclohexane is much smaller, thereby leading to a lower extent of formation of weakly emissive states.

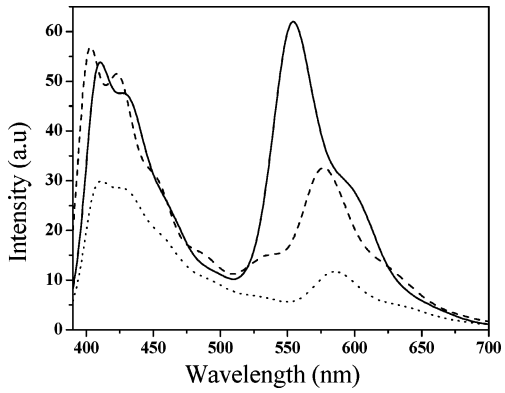


Figure 9. Fluorescence spectra of a mixture of MEHPPV-85 and MEHPPV-8 in pure DCM (solid line), in a mixture of DCM−cyclohexane (5:95 v/v) (dashed line), and in a mixture of DCM−methanol (30:70 v/v) (dotted line).

Similar experiments were carried out with MEHPPV-85, MEHPPV-55, and MEHPPV-30. In the case of polymers having lower levels of conjugation (<55%), only the expected solvatochromic blue shift is observed with very little loss of emission yield. As mentioned earlier, MEHPPV-55 and those having lower levels of conjugation are completely soluble in cyclohexane. Hence, in general the effect of increasing the concentration of cyclohexane was largely limited to solvatochromism, with the effect of solvent-induced chain collapse becoming prominent only in the case of highly conjugated samples, and that too only at very high cyclohexane volume fractions. None of the experiments, however, provided any evidence for the occurrence of the anticipated selective desolvation, probably because of the wide conjugation length distribution that masks any such occurrence.

Evidence for Isolated Single-Chain Collapse. As all our studies are carried out at micromolar concentrations (far below the chain overlap concentration *c**), the energy transfer and interchromophore exciton formation are assumed to occur within a single macromolecule. In an effort to demonstrate this experimentally, two different segmented MEHPPV-*x* samples, MEHPPV-8 and MEHPPV-85, were dissolved together in dichloromethane. Their concentrations were adjusted so that the maximum emission intensity from each of them is roughly similar. This required use of a mixture in the molar ratio MEHPPV-8:MEHPPV-85 of 1:2. MEHPPV-8 and MEHPPV-85 were selected to ensure minimum overlap in their emission spectra—MEHPPV-8 has a structured emission in the region 390−520 nm, while MEHPPV-85 has emission between 520 and 700 nm (Figure 9). The emission spectrum of the mixture in DCM clearly demonstrates independent emission from both samples with little inter-polymer chain interaction.[18] The spectrum of an identical mixture at the same concentration in a cyclohexane−DCM (95:5 v/v) mixture exhibit some very interesting features: the emission spectra due to MEHPPV-8 polymer undergoes a blue shift with little change in its fine structure and intensity, while the emission due to MEHPPV-85 undergoes a large red shift with a considerable decrease in the emission yield. The former is due to the expected solvatochromic shift (very little change in the conformation of MEHPPV-8 is expected), while in the case of MEHPPV-85, cyclohexane serves as a nonsolvent and causes a chain collapse leading to decreased intensity of emission accompanied by a red shift (due to aggregate emission). Similarly, when the spectrum of an identical polymer mixture was recorded in a DCM−methanol mixture (70:30 v/v), wherein both the polymer chains are

expected to undergo chain collapse, it is seen that there is a decrease in emission intensity arising from both the polymers, although to different extents, as expected. Thus even when both the polymers experience poor-solvent conditions, it appears that there are no interchain interactions. If indeed interchain interactions were present, it would cause both the polymer chains to possibly coaggregate and should lead to a drastic reduction in the emission intensity due to MEHPPV-8 (in the blue region), which is not seen. Thus, these experiments suggest that there is little interaction between chromophores belonging to different polymer chains during the collapse in dilute solutions, although at very high nonsolvent compositions, some level of interchain interactions could be present.

Variable-Temperature Studies. It is well-known that polymer chains typically undergo coil expansion with increasing temperature, which in turn may be expected to modulate the intrachain interchromophore interactions, in terms of energy transfer as well as interchromophore exciton formation. Variable-temperature studies can be carried out in three distinct regions of the collapse transition curve: region A, wherein the chain is highly solvated; region B, wherein it is in an intermediate state of collapse; and region C, wherein it is in a completely collapsed state (see Figure 7). To carry out variable-temperature studies under these three different conformational states, we selected 1,2-dichloroethane (DCE)−ethanol as the solvent combination because it offers a larger temperature window for study. Solvent titration studies demonstrated that the variation of emission yield as a function of solvent composition with this solvent pair is very similar to that seen in the case of DCM−methanol.[19]

Figure 10 shows the variation of fluorescence spectra of MEHPPV-100 as a function of temperature. In pure DCE, which is a good solvent for MEHPPV (region A), increasing temperature causes a steady decrease in emission intensity with a blue shift of the emission maxima. A similar variation is also seen when the polymer chain is in a very poor solvent (completely collapsed state, region C; 5:95 DCE−ethanol v/v), while in an intermediate state of collapse (region B) the effect of temperature is quite the opposite.

As is evident from Figure 10 (middle), for MEHPPV-100 in 40:60 DCE−ethanol, an increase in temperature causes an increase in the emission yield (see inset). This diametrically opposite temperature dependence of the same polymer, depending on its initial starting conformational state, may be rationalized as follows. Increasing temperature can exert two effects on the fluorescence spectrum: one is the intrinsic effect of temperature on the fluorescence quantum yield of the individual chromophoric segments, and the other is an indirect effect that results from the temperature-induced modulation of the polymer chain conformation. The former generally causes a reduction in emission intensity, while the latter could either cause an increase or a decrease depending on the specific system. In the case of MEHPPV-100, in both regions A and C, the dominant effect is the former, while in region B, the effect of temperature-induced coil expansion is dominant. Expansion of the polymer coil evidently reduces the population of weakly emitting aggregated excitonic states and an increase in the emission from the nonaggregated species, thereby causing a significant increase in the emission yield, accompanied by the expected blue shift in the emission maximum. In regions A and C, a blue shift in the emission maximum with increasing temperature is also noticed, which is ascribed to the simple temperature dependence of the solvent dielectric.

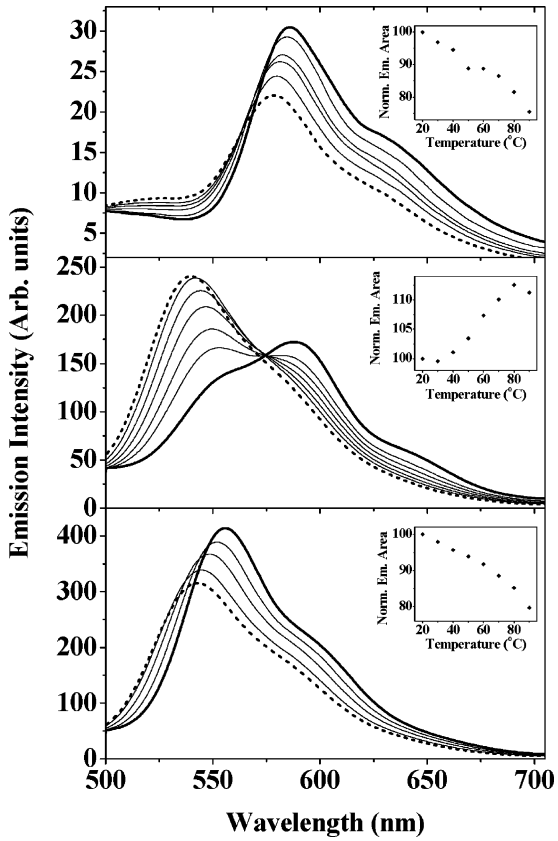


Figure 10. Fluorescence spectra of MEHPPV-100 as a function of temperature in pure DCE (bottom), in 40:60 v/v DCE−ethanol (middle), and in 5:95 v/v DCE−ethanol (top). Inset depicts the variation in the normalized emission area as a function of temperature. For clarity the spectra at the lowest (25 °C) and highest temperatures (90 °C) are shown as bold solid and dashed lines, respectively.

Figures 11, 12, and 13 depict the spectral changes observed when samples MEHPPV-70, MEHPPV-30, and MEHPPV-10, respectively, are subjected to a similar set of experiments. In general, all the polymers behave similarly in region A, showing a simple decrease in the emission yields with increasing temperature. In region C also, a similar monotonic decrease is seen in all cases expect in MEHPPV-70 (see Figure 11), wherein an apparent isoemissive point, indicative of a decrease in emission due to aggregated states and a concomitant increase due to that of the free species, is observed.[20] The increase in the emission yield is, however, not as high as one might expect because of the concurrent decrease in the intrinsic quantum yield of emission due to increase in temperature. In region B, however, all the polymers exhibit an increase in the emission yield, as seen in the case of MEHPPV-100. The extent of increase in the emission yield in this region is seen to be higher in cases of the lower conjugated samples.

Unlike in the highly conjugated samples, in MEHPPV-30 and MEHPPV-10 the dominant effect of temperature in the partially collapsed state (region B) appears to result from less efficient energy transfer to weakly emitting units ($n \geq 4$), as opposed to aggregate formation. From the population histogram (Figure 4), it is clear that majority of the chromophores in these samples will have conjugation lengths ≤ 4. Therefore, uncoiling of the partially collapsed state would result in less efficient energy transfer and more direct emission from the highly emissive oligomeric units ($n = 2$ and 3). Qualitatively, in the case of MEHPPV-10 this can be seen from the drastic increase in the direct emission from the highly emissive MEH-distilbene and MEH-tristilbene segments, at 469 and 500 nm, respectively. In

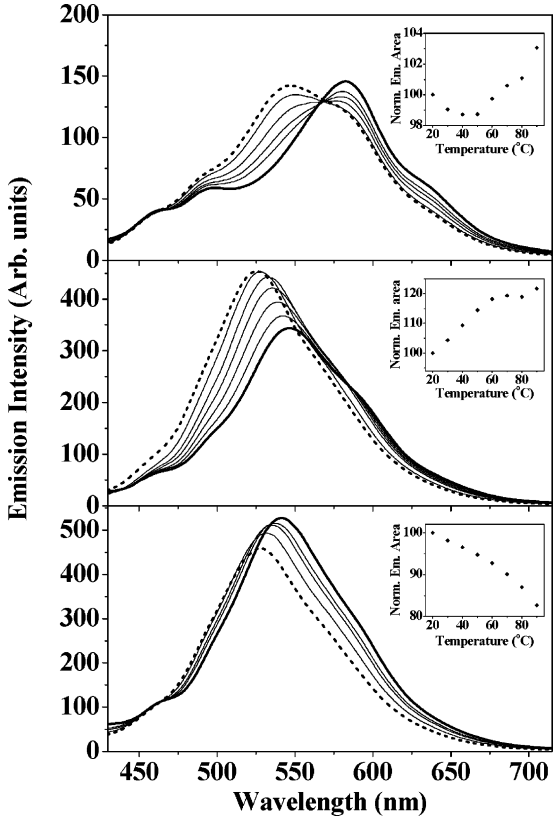


Figure 11. Fluorescence spectra of MEHPPV-70 as a function of temperature in pure DCE (bottom), in 40:60 v/v DCE−ethanol (middle), and in 5:95 v/v DCE−ethanol (top). Inset depicts the variation in the normalized emission area as a function of temperature. For clarity the spectra at the lowest (25 °C) and highest temperatures (90 °C) are shown as bold solid and dashed lines, respectively.

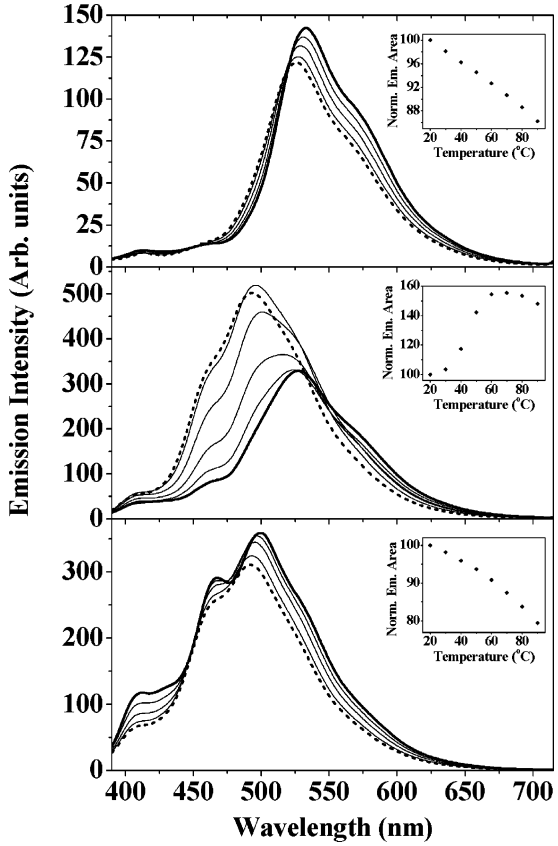


Figure 12. Fluorescence spectra of MEHPPV-30 as a function of temperature in pure DCE (bottom), in 40:60 v/v DCE−ethanol (middle), and in 5:95 v/v DCE−ethanol (top). Inset depicts the variation in the normalized emission area as a function of temperature. For clarity the spectra at the lowest (25 °C) and highest temperatures (90 °C) are shown as bold solid and dashed lines, respectively.

contrast, in highly conjugated samples the increase in emission yield in region B may be ascribed more to inhibition of aggregated excitonic species. This may be expected, as the average interchomophore separation within a single polymer chain is far greater in samples with low conjugation levels. In addition, in both these cases one notices that the normalized emission area (in region B) goes through a maximum as temperature is increased (see insets in Figures 12 and 13). It is thus apparent that the two factors are now competing with each other; the effect of uncoiling dominates first, while the intrinsic effect on the fluorescence quantum yield appears to dominate during the later stages.

Conclusion

Segmented MEHPPVs with varying levels of conjugation have been taken as models to study the conformational changes in isolated single polymer chains. Examining the dilute solution fluorescence spectral variation as a function of solvent−nonsolvent composition reveals several interesting features. As the coil dimension is reduced by the presence of increasing amounts of the nonsolvent, the onset of strong intrachain interchromophore interactions, specifically by formation of weakly emissive excitonic states as well as increased energy transfer to weakly emitting longer conjugation length units, leads to a sudden drop in emission yields, exhibiting a typical inverted S-shaped curve. It is argued that the relative contributions of the two effects toward the observed depletion in emission yield vary with extent of conjugation in the segmented MEHPPVs. The contribution due to aggregate formation (excitons) is large at higher levels of conjugation, while energy transfer to longer conjugated segments appears to be more important in the case of very low levels of conjugation. Although specifically designed experiments, using a mixture of low and highly conjugated polymer samples, point to the predominance of intrachain effects, interchain aggregate formation could become important in highly conjugated samples, particularly at higher nonsolvent compositions. Further experiments, which will enable one to directly monitor chain dimensions during the titrations, are essential to resolve this issue unequivocally.

Segmented MEHPPVs with very low levels of conjugation, such as MEHPPV-10, exhibited yet another unusual behavior at the early stages of the solvent−nonsolvent titration. The emission yield is seen to increase slightly prior to the sudden drastic drop. This was ascribed to the rather peculiar dependence of the intrinsic emission quantum yield of oligoPPVs as a function of conjugation length. Energy transfer to the intrinsically most emissive oligomeric segments, namely, MEH-distilbene and MEH-tristilbene units ($n = 2$ and 3, respectively), from the smaller MEH-stilbene unit causes this unusual increase in the emission yield, providing another direct confirmation for intrachain energy transfer in these systems.

Variable-temperature fluorescence studies of segmented MEHPPVs also reveal several interesting characteristics. First, the spectral evolution is strongly dependent on the initial conformational state of the polymer chain: small changes in temperature have maximum effect when the polymer chain is in an intermediate state of chain collapse. In this state, an increase of temperature causes a drastic change in the spectral features, accompanied by a significant increase in the emission yield.

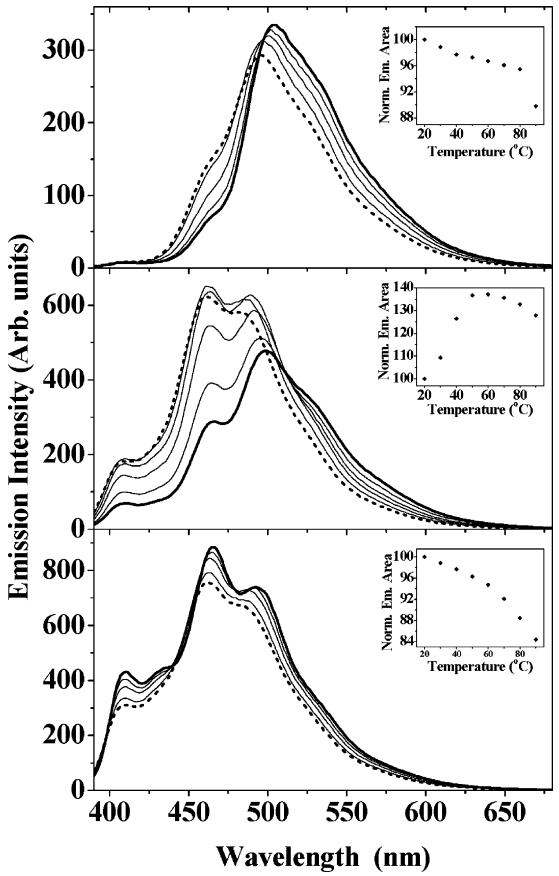


Figure 13. Fluorescence spectra of MEHPPV-10 as a function of temperature in pure DCE (bottom), in 40:60 v/v DCE−ethanol (middle), and in 5:95 v/v DCE−ethanol (top). Inset depicts the variation in the normalized emission area as a function of temperature. For clarity the spectra at the lowest (25 °C) and highest temperatures (90 °C) are shown as bold solid and dashed lines, respectively.

However, in both very good and very poor solvents (expanded and collapsed coils), increasing temperature generally caused a small decrease in the emission yield, often accompanied by a small blue shift in the emission maxima. Such a diametrically opposite response of the fluorescence spectra depending on the initial conformation of the polymer chain is due to the fact that, in an intermediate state of collapse, the average interchromophore distance is very close to a characteristic threshold distance for energy transfer/exciton formation. Therefore, small changes in the coil dimension cause a drastic depletion in both these processes, leading to an apparent chain collapse as revealed by the inverted S-shaped solvent titration curve. In the other two extreme conformational states, however, the effect of conformation-induced spectral modulation is minimal and the effect of temperature is limited to the intrinsic effect on the chromophore directly.

Acknowledgment. We thank CSIR, New Delhi, for financial support and also 3M-India for their generous funding to our lab. Our sincere thanks are due to Professor H. Meier and Dr. Ulf Stalmach for providing us with data on the oligomer absorption and fluorescence. We also thank Mr. K. Nagesh for carrying out some additional fluorescence measurements that were required during the reviewing process.

Supporting Information Available: Complete spectral variation of all the segmented MEHPPV samples in DCE−ethanol mixtures. This information is available free of charge via the Internet at http://pubs.acs.org.

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(15) The histograms were calculated by use of a simple statistical model that was described in ref 11a. The fractional populations of the oligomeric segments with $n > 10$ were taken to be spectroscopically indistinguishable and hence have been summed up together in the histogram, as seen for instance in the case of MEHPPV-70.

(16) We assume that the variation of Φ_f in the case of MEH oligomeric units in the polymer chain follows a similar behavior with conjugation length.

(17) However, due to the varying levels of chain stiffness at different extents of elimination, their hydrodynamic volumes may differ despite their chain length being similar, but we make this assumption as a first approximation. The assumption is supported by the similar values of the Mark-Howink exponent a that we measure for different MEHPPV-x samples; this varied between 0.64 and 0.67. These were measured by GPC in conjunction with a Viscotek Triple detector system.

(18) The emission spectra of both the pure samples in DCM were very similar to those seen in the mixture.

(19) The complete spectral variations of all the segmented MEHPPV samples in DCE−ethanol mixtures are provided in the Supporting Information.

(20) Similar isoemissive points could have been observed in several other variable-temperature experiments, except that in most of these the variations are accompanied by significant changes in the emission areas. In this particular case the change in the net emission area is very small and hence this isoemissive point is readily visualized.