Chain Composition Dependence of Luminescence Properties for Copolymers of 2-Methoxy-5-2′-ethyl-hexyloxy-1,4-phenylenevinylene and 2,3-Diphenyl-5-octyl-1,4-phenylenevinylene

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ABSTRACT: The copolymers of 2-methoxy-5-2′-ethyl-hexyloxy-1,4-phenylenevinylene (MEH-PV) and 2,3-diphenyl-5-octyl-1,4-phenylenevinylene were prepared via the Gilch route with their chain compositions and the reactivity ratios of the monomers estimated by ^{1}H NMR spectroscopy. The results indicated that the copolymers tended to form an alternative copolymer as the feed ratio of the monomers closed to one-half. When an individual copolymer solution in tetrahydrofuran was spun-cast to form a film, the MEH-PV units were able to attract the like units from the adjacent chains. As a result, the ultraviolet–visible absorption spectrum of the alternative copolymer in film form was broader than the spectra of those with different compositions. The photoluminescence spectra of the copolymers in film form exhibited the characteristic shoulder of poly(2-methoxy-5-2′-ethyl-hexyloxy-1,4-phenylenevinylene), even though the content of MEH-PV units was not great enough for the formation of repeat units in sequence. © 2003 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 41: 2180–2186, 2003

Keywords: photoluminescence; poly(2-methoxy-5-2′-ethyl-hexyloxy-1,4-phenylenevinylene) (MEH-PPV); copolymerization; light-emitting polymers; films; UV-vis spectroscopy

INTRODUCTION

Poly(1,4-phenylenevinylene) (PPV) and its derivatives have attracted widespread interest since their electroluminescence (EL) properties were discovered.[1] One of the most extensively used for polymer light-emitting diodes is poly(2-methoxy-5-2′-ethyl-hexyloxy-1,4-phenylenevinylene) (MEH-PPV) because of its good solubility, low turn-on voltage, and high EL efficiency.[2,3] MEH-PPV is an orange-red emissive polymer. Efforts to tune the color and improve the performance of MEH-PPV have frequently been made by copolymerization with other conjugated polymers.[4–6]

However, it is noteworthy that the color of copolymers is determined by the chain composition and conjugated sequences formed during copolymerization. Most researchers have focused on the luminescent performance of copolymers and have paid little attention to the actual compositions and conjugated sequences. In this study, we copolymerized 2-methoxy-5-2′-ethyl-hexyloxy-1,4-phenylenevinylene (MEH-PV) with 2,3-diphenyl-5-octyl-1,4-phenylenevinylene (DPO-PV) via the Gilch route.[7] Poly(2,3-diphenyl-5-octyl-1,4-phenylenevinylene) (DPO-PPV) is a blue-green emissive polymer.[8] The chain composition of the MEH-PV/DPO-PV copolymers was estimated by ^{1}H NMR spectroscopy, and the results were used to calculate the reactivity ratios of the monomers

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derived from the copolymerization theory.[9] As a result, the copolymerization of MEH-PPV and DPO-PPV monomers formed an alternative copolymer that was never previously reported in the literature. After the chemical structures of the copolymers were carefully studied, they were correlated to the measured luminescence properties.

EXPERIMENTAL

Materials

MEH-PPV, DPO-PPV, and their MEH-PV/DPO-PV copolymers were prepared by the Gilch route in tetrahydrofuran (THF) with excess potassium-*tert*-butoxide (Lancaster). A typical copolymerization reaction is shown in Figure 1(a). THF was distilled over sodium before use. In the beginning, 1,4-bis(chloromethyl)-2-methoxy-5-(2-ethylhexyloxy)benzene (**I**), a MEH-PPV monomer, was synthesized according to ref. 10, whereas 1,4-bis(chloro-methyl)-2,3-diphenyl-5-octylbenzene (**II**), a DPO-PPV monomer, was synthesized according to ref. 11 with some modifications; the reaction scheme is shown in Figure 1(b). In general, the latter was started with the Diels–Alder reaction of 2,5-dicarbethoxy-3,4-diphenylcyclopentadienone (**III**)[12] with 1-dectyne (Acros) in benzene to give diethyl-2,3-diphenyl-5-octyl terephthalate (**IV**). It was then reduced by lithium aluminum hydride ($LiAlH_4$) in THF to give diethyl-2,3-diphenyl-5-octyl-1,4-bis-(hydroxymethyl)benzene (**V**). The chlorination of compound **V** with thionyl chloride was conducted in dichloromethane to give compound **II**. The homopolymerization and copolymerization of compounds **I** and **II** with various chosen molar ratios were performed with 4 equiv of potassium-*tert*-butoxide in THF at room temperature. After 24 h of reaction, the mixture was poured into methanol to precipitate the polymers. After filtration, the obtained polymers were redissolved in THF and filtered again for the removal of the insoluble portion. The polymers were precipitated again by the addition of methanol. The final filtered products were dried *in vacuo* at room temperature.

Characterization

^1H NMR spectroscopy of MEH-PPV, DPO-PPV, and their MEH-PV/DOP-PV copolymers in $CDCl_3$ was performed with an Avan 500-MHz Fourier transform NMR spectrometer. Tetramethylsilane was used as an internal standard. Gel permeation chromatography (GPC) measurements with THF as a mobile phase (1 mL/min) were carried out at 40 °C with a Testhigh series III pump and a Testhigh UV detector. The molecular masses of the samples were estimated by reference to polystyrene standards with a narrow molecular mass distribution. Thermogravimetric analysis (TGA) of the polymer samples was conducted in a TA model TGA-51 thermogravimetric analyzer at a heating rate of 10 °C/min under nitrogen. Ultraviolet–visible (UV–vis) absorption spectra for both the solutions and films of samples were recorded on a Jasco 555 model spectrometer. Their photoluminescence (PL) spectra were recorded on a SPEX 1403 fluorescence spectrophotometer with a xenon lamp as an excitation source. The solutions were prepared by the dissolution of the samples in THF at a concentration of approximately 10^{-4} g/mL. The films were prepared by the spin coating of the solutions onto a glass plate with a thickness in the range of 1000–1500 Å.

RESULTS AND DISCUSSION

Composition of the Copolymers

The method of determining the chain compositions of MEH-PV/DPO-PV copolymers with NMR spectra can be illustrated as follows. Figure 2 shows the ^1H NMR spectrum of the MEH-PV/DPO-PV copolymer prepared with $f_1 = 0.5$, where f_1 is the molar fraction of the MEH-PPV monomer, that is, compound **I**, in the feed. The resonance peak at $\delta = 0.88$ ppm contributed by the protons of the —CH_3 group attached to a carbon at the end of the side chains has an integrated area of 0.5067, as shown in the figure. Because the MEH-PV unit has six such protons and DPO-PV has three, by assuming that a copolymer chain contains a MEH-PV units and b DPO-PV units, we obtain

$$6a + 3b = 0.5067 \tag{1}$$

Moreover, the resonance peak at $\delta = 3.7$ ppm, contributed by the protons of —CH_2—O— and CH_3—O— groups, has an integrated area of 0.2677. Each unit of MEH-PV has five such protons, but DPO-PV has none. Consequently, we obtain

$$5a = 0.2677 \tag{2}$$

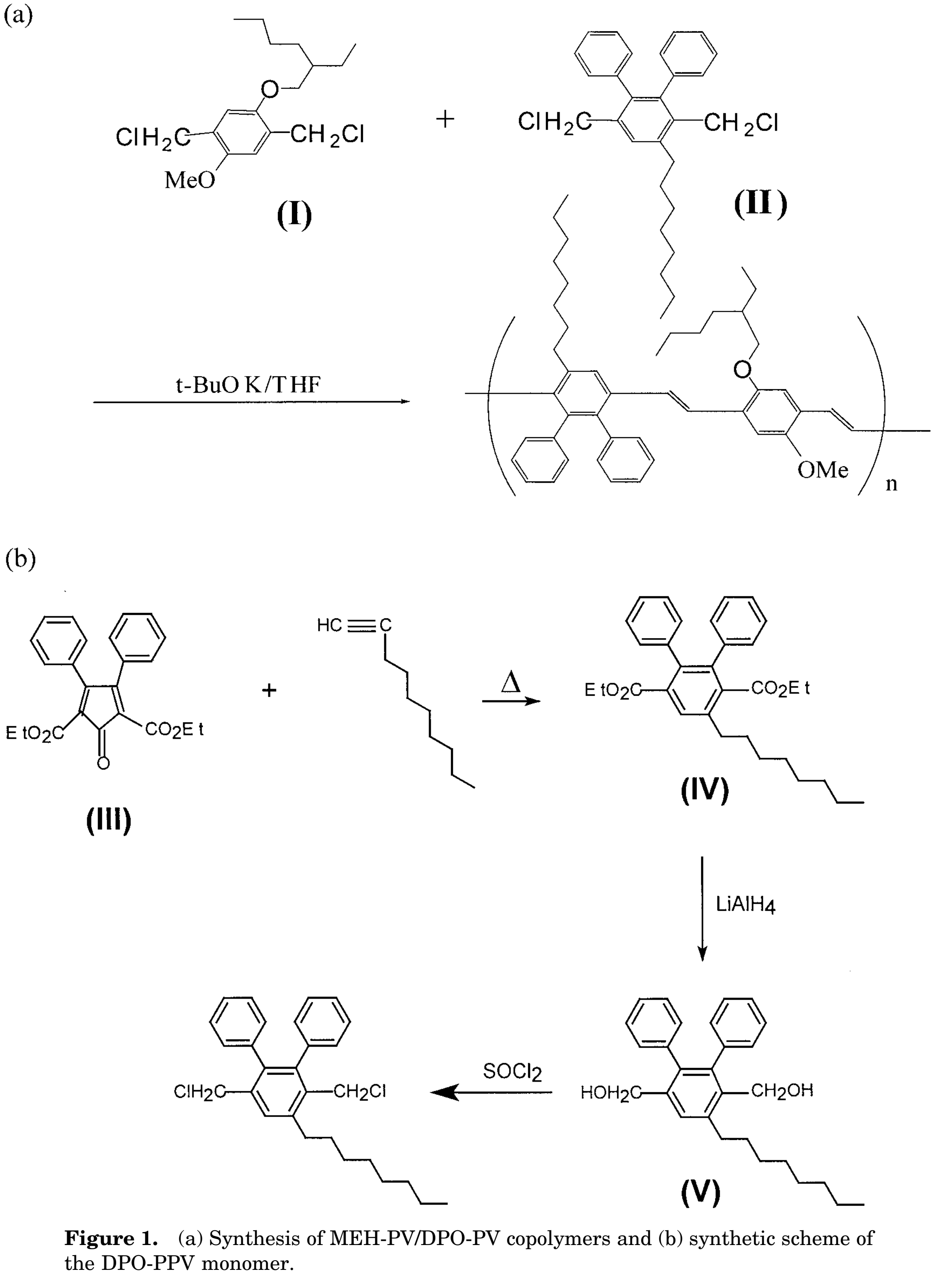

Figure 1. (a) Synthesis of MEH-PV/DPO-PV copolymers and (b) synthetic scheme of the DPO-PPV monomer.

Therefore, from eqs 1 and 2, a = 0.05354 and b = 0.06182 were obtained, and the molar fraction of MEH-PV units in the copolymer, F_1, was estimated to be 0.47. By the same token, the F_1 values of other MEH-PV/DPO-PV copolymers with various f_1 values were estimated from the NMR spectra, and the results are listed in Table 1. The plot of F_1 versus f_1 shown in Figure 3 shows that

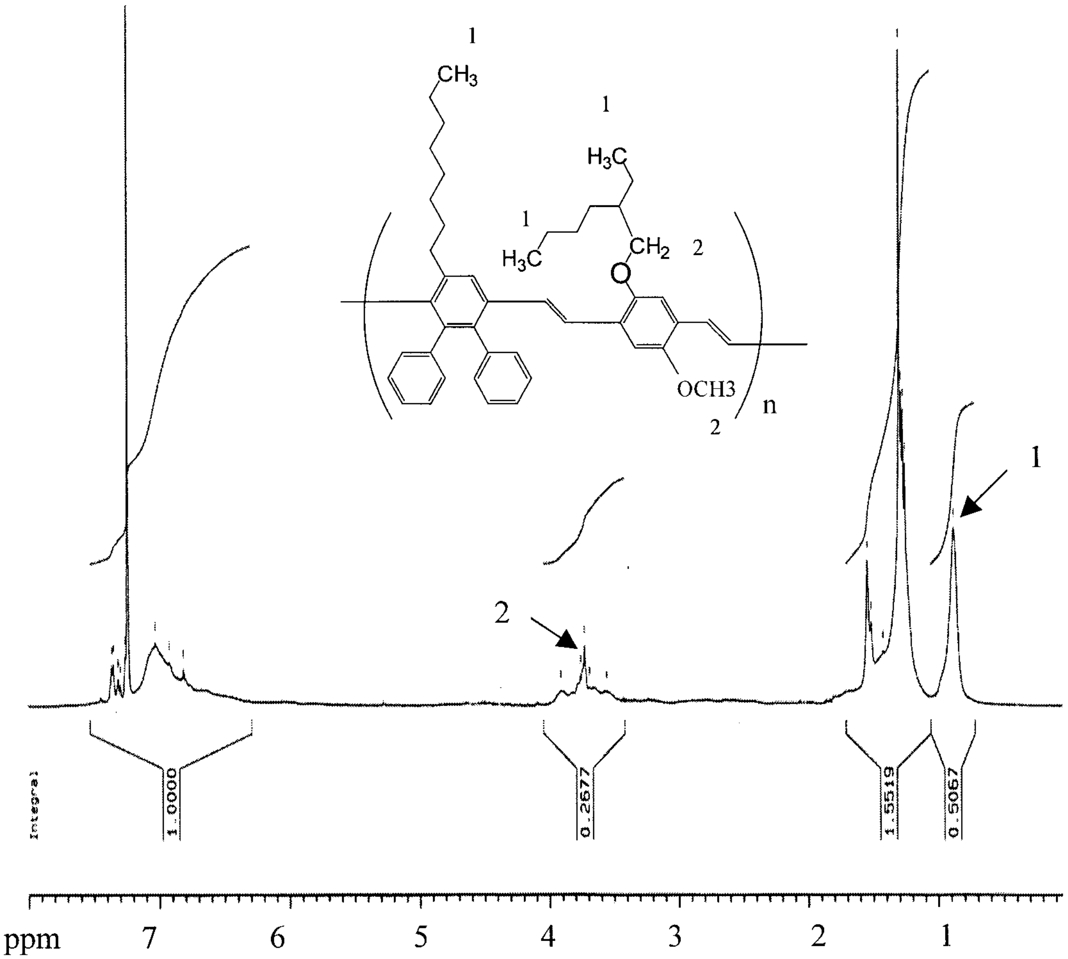

Figure 2. ^{1}H NMR spectrum of the MEH-PV/DPO-PV copolymer prepared with f_1 = 0.5.

F_1 is larger than f_1 when f_1 is smaller than 0.25 but is smaller than f_1 when f_1 is larger than 0.75. To explain this phenomenon, we employed the following copolymerization equation[9] to estimate the reactivity ratios of MEH-PPV and DPO-PPV monomers:

Table 1. Data for MEH-PPV, DPO-PPV, and MEH-PV/DPO-PV Copolymers

f_1	F_1	M_n (g/mol)	M_w (g/mol)	M_w/M_n
0	0	21,000	83,000	3.90
0.14	0.22	148,000	311,000	2.11
0.25	0.43	125,000	544,000	4.35
0.5	0.47	128,000	701,000	5.49
0.75	0.62	82,000	348,000	4.22
0.86	0.66	174,000	822,000	4.73
1	1	64,000	266,000	4.13

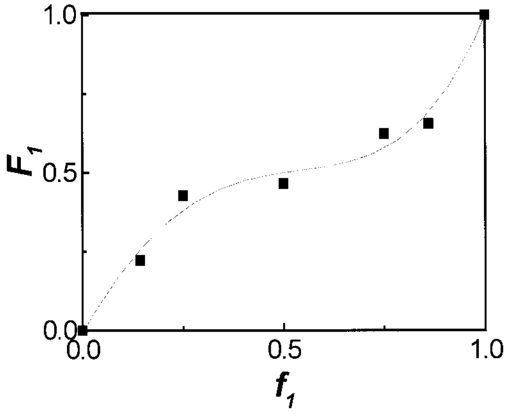

Figure 3. Plot of the composition ratio of MEH-PV units (F_1) in the MEH-PV/DPO-PV copolymers versus the feed ratio of the MEH-PPV monomers (f_1).

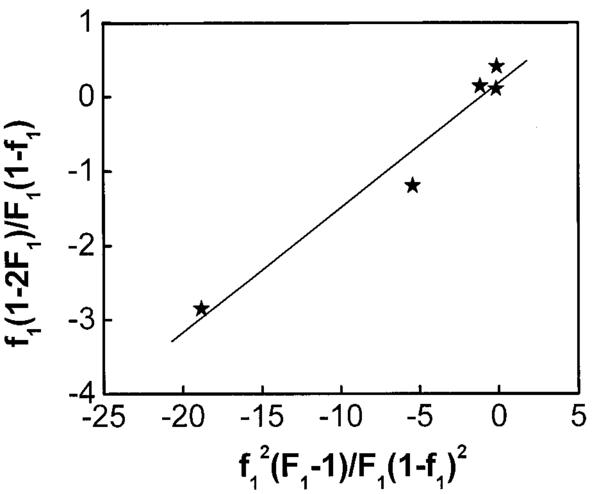

Figure 4. Linear regression of $f_1(1 - 2F_1)/F_1(1 - f_1)$ data versus $f_1^2(F_1 - 1)/F_1(1 - f_1)^2$ for the determination of the reactivity ratios r_1 and r_2 of the MEH-PV/DPO-PV copolymers.

$$f_1(1 - 2F_1)/F_1(1 - f_1) = r_1[f_1^2(F_1 - 1)/F_1(1 - f_1)^2] + r_2 \quad (3)$$

where f_2 is the feed ratio of DPO-PPV monomers and F_2 is the composition ratio of DPO-PV units in the copolymers. r_1 and r_2 are the reactivity ratios of MEH-PPV and DPO-PPV monomers, respectively:

$$r_1 = \frac{k_{11}}{k_{12}} \quad \text{and} \quad r_2 = \frac{k_{22}}{k_{21}} \quad (4)$$

where k_{11}, k_{12}, k_{21}, and k_{22} are the individual reaction constants of compound **I** with **I** and **II** and compound **II** with **I** and **II**. By using the data of Table 1 and performing a linear regression of the plot of $f_1(1 - 2F_1)/F_1(1 - f_1)$ versus $f_1^2(F_1 - 1)/F_1(1 - f_1)^2$ (see Fig. 4), we obtained $r_1 = 0.16$ and $r_2 = 0.19$. Because both r_1 and r_2 were much smaller than 1, the MEH-PV/DPO-PV copolymer had a tendency to form an alternative copolymer if f_1 was equal to 0.5.

The number-average molecular masses (M_n's) and weight-average molecular masses (M_w's) of MEH-PPV, DPO-PPV, and their copolymers measured from GPC are listed in Table 1. M_n of MEH-PPV was 64,000 g/mol, and that of DPO-PPV was 21,000 g/mol. The MEH-PV/DPO-PV copolymers had higher molecular masses than both MEH-PPV and DPO-PPV homopolymers. This might be due to the fact that both monomers preferred to react with other monomers instead of themselves.

The TGA thermograms of MEH-PPV, DPO-PPV, and their copolymers shown in Figure 5 indicate that although MEH-PPV was the most vulnerable to heat, it was still thermally stable up to 350 °C under a nitrogen atmosphere. The decomposition temperature was increased with the content of DPO-PV in the copolymers and reached the highest value for the DPO-PPV homopolymer.

PL Properties

Figure 6 shows the UV–vis absorption spectra of MEH-PPV, DPO-PPV, and their copolymers in THF solutions and spun-cast films. When F_1 was less than 0.62, the spectra of the solutions was substantially redshifted with the MEH-PV content. After F_1 was greater than 0.62, the extent of redshifting was reduced but still distinguishable. This indicates that the UV–vis absorption of the copolymer with $F_1 = 0.5$, which was close to that of the alternative copolymer, was more affected by the further incorporation of DPO-PV units (i.e., $F_1 < 0.5$) than by the incorporation of MEH-PV units (i.e., $F_1 > 0.5$). When the solutions were spun-cast to form a film, the UV–vis absorption was further redshifted because of the packing of polymer chains. The UV–vis spectra of the copolymer with $F_1 = 0.47$ ($f_1 = 0.5$) in film form was broadly distributed, and the wavelength of the front edge was even higher than that of the copolymer with $F_1 = 0.62$. This suggested that MEH-

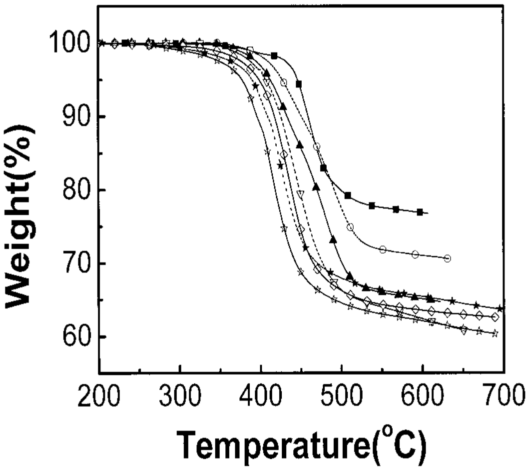

Figure 5. TGA thermograms of MEH-PPV, DPO-PPV, and various MEH-PV/DPO-PV copolymers with (■) $F_1 = 0$, (○) $F_1 = 0.22$, (▲) $F_1 = 0.43$, (▽) $F_1 = 0.47$, (◇) $F_1 = 0.62$, (★) $F_1 = 0.66$, and (☆) $F_1 = 1$.

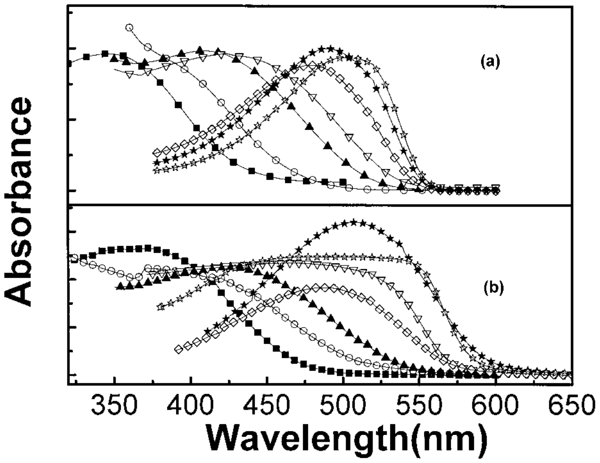

Figure 6. UV–vis absorption spectra of MEH-PPV, DPO-PPV, and various MEH-PV/DPO-PV copolymers in (a) THF solutions and (b) spun-cast films, with the following composition ratios: (■) $F_1 = 0$, (○) $F_1 = 0.22$, (▲) $F_1 = 0.43$, (▽) $F_1 = 0.47$, (◇) $F_1 = 0.62$, (★) $F_1 = 0.66$, and (☆) $F_1 = 1$.

PV/DPO-PV copolymers with an alterative sequence had more of a chance of like units being attracted to one another so that π electrons could delocalize in interchain segments. This was highly possible because MEH-PV units contained two ether linkages, providing strong a dipole moment for mutual attraction. Because the UV–vis absorption of the copolymer with $F_1 = 0.47$ in film form covered a wider range of wavelengths than other copolymers, the copolymer should have greater potential for photovoltaic cell applications.[13,14] A further study on this issue is ongoing.

Figure 7 illustrates the PL spectra of MEH-PPV, DPO-PPV, and their copolymers in THF solutions and spun-cast films. A single broad peak at 475 nm was found for DPO-PPV in solution, whereas MEH-PPV had a peak at 557 nm and an additional shoulder at 602 nm. The shoulder in the PL spectrum has been well recognized as a characteristic of MEH-PPV. When $f_1 \leqq 0.5$ ($F_1 \leqq 0.47$), the PL spectra of the copolymers showed a single peak, indicating that only DPO-PV units had a chance to be reacted in sequence during copolymerization. Until $f_1 \geqq 0.75$ ($F_1 \geqq 0.62$), MEH-PV units had a chance to be reacted in sequence. This conformed to the NMR results, that the reactivity of the DPO-PPV monomer was slightly higher than that of the MEH-PPV monomer, that is, $r_2/r_1 = k_{22}/k_{11} = 1.19$.

When the individual solutions were spun-cast to form films, the PL spectra of the copolymers in film form were redshifted about 20–30 nm in comparison with those in solution, as shown in Figure 7. Moreover, the PL spectra of copolymers in film form began to have the characteristic shoulder of MEH-PPV when F_1 reached 0.43 ($f_1 = 0.25$). It should be noted here that the MEH-PV units in the copolymers with $F_1 = 0.43$ and 0.47 had little chance to exist in sequence. Therefore, the experimental results suggested that the MEH-PV units in the copolymers preferred to pack adjacent to the like units from different chains so that the excited π electrons could delocalize in interchain segments, and this conformed to the results of UV–vis absorption spectroscopy. It is noteworthy that the PL spectrum of the copolymers was more sensitive to the packing of polymer chains than the absorption spectrum because the characteristic shoulder of MEH-PPV appeared at a little lower content of MEH-PV units. This indicated that the excitons that formed after absorption were prone to move to the packing sites of MEH-PPV units because the energy state was lower. Many researchers[15–17] have also reported that the excitons formed in MEH-PPV films could exist in some kind of interchain species. It is generally agreed that the chain aggregation of MEH-PPV in a film can be attributed to the formation of interchain excitons.

CONCLUSIONS

The composition ratios of MEH-PV/DPO-PV copolymers estimated by ^{1}H NMR spectroscopy

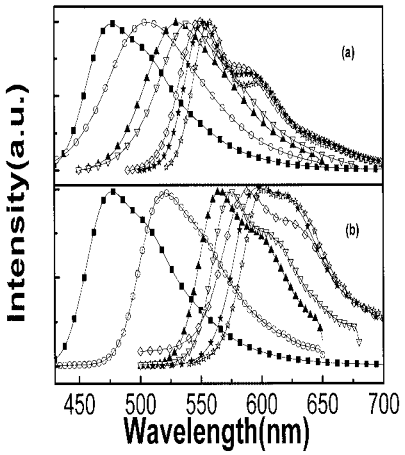

Figure 7. PL spectra of MEH-PPV, DPO-PPV, and various MEH-PV/DPO-PV copolymers in (a) THF solutions and (b) spun-cast films, with the following composition ratios: (■) $F_1 = 0$, (○) $F_1 = 0.22$, (▲) $F_1 = 0.43$, (▽) $F_1 = 0.47$, (◇) $F_1 = 0.62$, (★) $F_1 = 0.66$, and (☆) $F_1 = 1$.

were used to calculate the reactivity ratios of the monomers. As a result, an alternative copolymer was expected to form when f_1 was equal to 0.5. Both UV–vis absorption and PL spectra of the copolymers in solution were redshifted with the content of MEH-PV units. However, when they were spun-cast into films, MEH-PV units tended to attract the like units from adjacent chains, and this resulted in a broader UV–vis absorption spectrum for the alternative copolymer and an early appearance of the characteristic shoulder of MEH-PPV in PL spectra even though MEH-PV units in the copolymers had little chance of existing in sequence. Studies on the packing effect of MEH-PV units in MEH-PV/DPO-PV copolymers on the EL and photovoltaic properties are ongoing.

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