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Conformational transition of poly[2-methoxy-5-(2′-ethylhexoxy)-*p*-phenylene vinylene] in solutions: solvent-induced emitter change

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Abstract

The spectroscopy and fluorescence lifetime of poly[2-methoxy-5-(2′-ethylhexoxy)-*p*-phenylene vinylene] (MEH-PPV) in mixtures of a poor solvent (cyclohexane or methanol) and a good solvent (chloroform) have been studied. With an increasing proportion of the poor solvent, the absorption, excitation and emission spectra change significantly when the poor solvent proportion is above a critical value. A new component is formed with spectra (absorption, excitation and fluorescence) at longer wavelength (lower energy). Fluorescence decay in different solvents has been measured and the new component has a longer lifetime compared with that in chloroform. All the results illustrate that a new emission center (emitter) is formed when the mixed solvent of MEH-PPV contains a higher proportion of the poor solvent. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Conformational transition; MEH-PPV; Emission

1. Introduction

Polymers with a π-conjugation system in their main chain such as poly(*p*-phenylene vinylene) (PPV) and its derivatives have relatively high efficiency of electroluminescence [1–6]. The emissive region of the polymer is very important for its applications and the emission spectrum can be varied by modifying the structure of the polymer [7,8], introducing different substituents at the phenyl ring or the ethylene [9,10]. The spectrum also depends on the environment conditions of the emissive component [11–13].

Poly[2-methoxy-5-(2′-ethylhexoxy)-*p*-phenylene vinylene] (MEH-PPV), one of the most important derivatives of PPV, gives quite different emission in its neat film compared with that in liquid and solid solutions [14,15]. For the neat film, the maximum of the fluorescence appears at relatively longer wavelength and its decay process is much more complicated than in solutions. The emission properties have been extensively discussed qualitatively in terms of polarons and bipolarons in the film [16–18]. Interactions between the molecular chains and the formation of excimer are generally considered as the cause for the spectrum difference between the neat film and the solutions [19–23].

A polymer chain tends to coil and be rigid in a relatively poor solvent [24]. The conformation of the main chain changes greatly in poor solvents compared with that in a good solvent. For a polymeric molecule with conjugation structure in its main chain, this kind of conformational change can result in a significant change in its electronic structure and spectrum. In this paper, we present experimental evidence that the conformational change of MEH-PPV, forming a new conjugated structure, also plays an important role in a significant emission change in different mixtures of a good and poor solvent.

2. Experimental

MEH-PPV (average molecular weight of ∼700,000) was obtained from Prof. F. Wudl and Dr. R. Helgeson and was used without further purification. Analytical grade solvents (chloroform, cyclohexane, methanol) were purified by standard procedures and were used freshly.

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Sample solutions were prepared by dissolving MEH-PPV in an appropriate volume of chloroform, then diluted to a total volume of 5 ml with methanol or cyclohexane to obtain a solution of 5.0×10^{-5}–4.0×10^{-5} mol/l (for monomer unit). All the processes were carried out under red light. Solutions were kept in a sealed volumetric flask in the dark when not in use.

All the sample solutions were measured in a 1 cm × 1 cm square quartz cell at room temperature. The samples were bubbled with nitrogen for 15 min before the measurements. UV–visible absorption spectra were recorded on a Hitachi 557 spectrophotometer. Fluorescence spectra were measured on Hitachi F-4500 spectrophotometer with excitation at 500 nm.

Time-resolved fluorescence measurements were performed using a synchronously pumped and cavity-dumped dye laser system (Spectra Physics: SP3500 model) with a mode-locked YAG laser (Spectra Physics: SP3800 model) as the pumping source. An intracavity acousto-optically dumped Rhodamine 6G dye laser at 570 nm, pulse selecting at 800 kHz was used. A microchannel plate detector (Hamamatsu, model R1645-01u) was applied to detect single photon. The 10 mV anode signal from the detector was amplified with a Hewlett Packard HP8447f pre-amplifier. The instrument response function had a FWHM of 100 ps. Total 1024 channels of the single photon counting with 25 ps per channel were recorded. The maximum count of the measured curve was 10,000. This single-counting ORTEC system emitted light pulses of typical 30 ps duration at variable repetition rates.

3. Results

Fig. 1 shows the absorption spectra of MEH-PPV in chloroform–cyclohexane. With an increasing proportion of cyclohexane, the absorption maximum first shifts to a shorter wavelength due to the decrease of the solvent polarity. When the proportion is higher than 30% an absorption shoulder grows up at ~550 nm and the main peak shifts to longer wavelength.

MEH-PPV exhibits a strong structured emission in the solutions. In chloroform, the maximum of the emission is at 560 nm and there are two shoulders at ~600 and ~670 nm. In the binary solvent of chloroform and cyclohexane, shown in Fig. 2, the maximum of the emission shifts to shorter wavelength and the intensity drops a little when the volume proportion of chloroform is higher than 30% (hereafter, the proportion in this paper is in volume). With further increasing cyclohexane in the solvent, the emission changes dramatically. The maximum (around 560 nm) drops suddenly and a new maximum appears at about 590 nm. The position of this new maximum changes mildly at lower proportions of chloroform, while the intensity at 555 nm keeps dropping. The inset in Fig. 2 shows normalized emissions of MEH-PPV in pure chloroform and in the mixture with

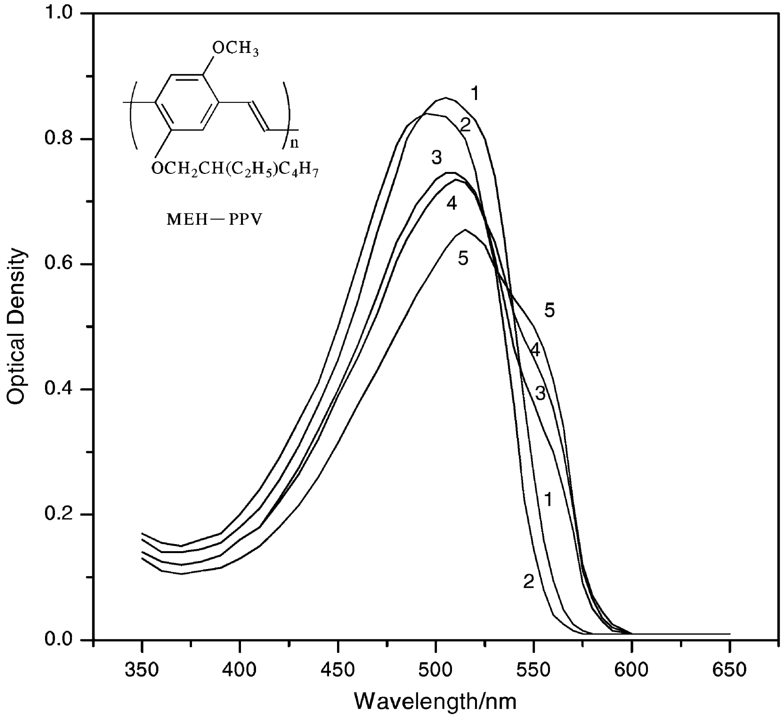

Fig. 1. Absorption spectra of MEH-PPV in chloroform–cyclohexane. The proportion in volume of chloroform in the solvent: (1) 100%; (2) 50%; (3) 20%; (4) 15%; (5) 10%.

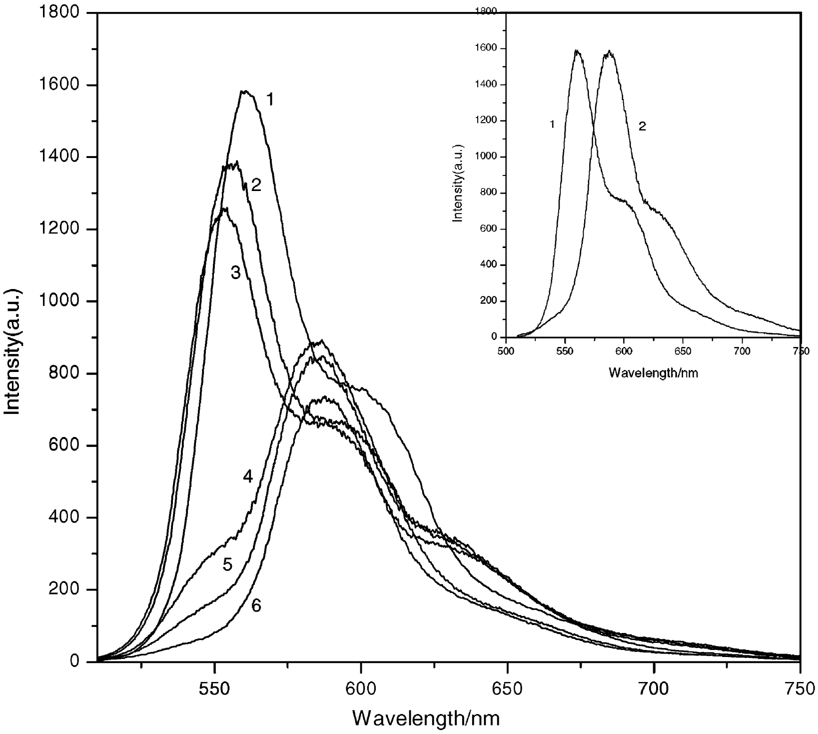

Fig. 2. Emission spectra of MEH-PPV in chloroform–cyclohexane. The proportion in volume of chloroform in the solvent: (1) 100%; (2) 50%; (3) 30%; (4) 20%; (5) 15%; (6) 10%; excitation wavelength: 500 nm. Inset: normalized emissions of MEH-PPV in pure chloroform (1) and in the mixture with 10% chloroform (2), respectively.

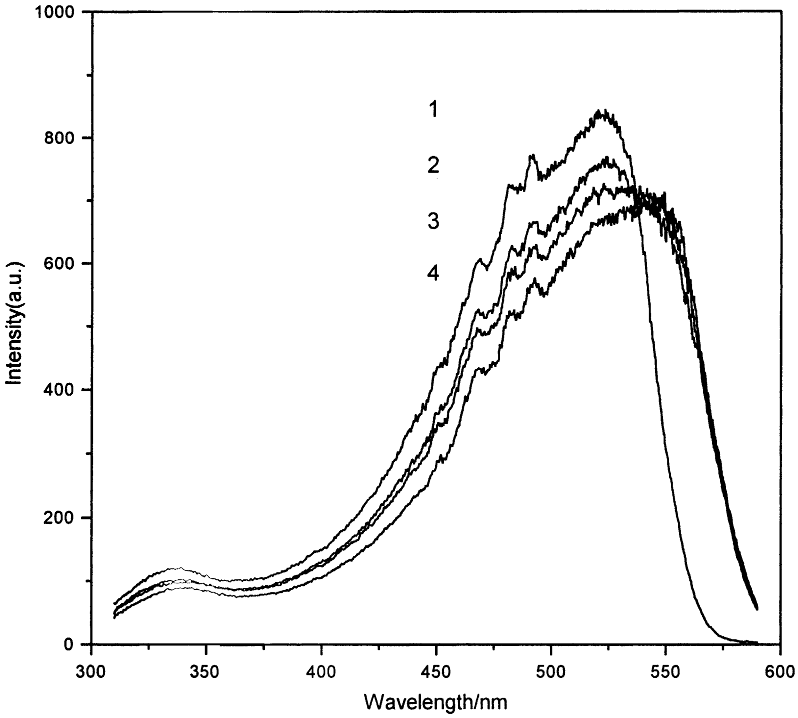

Fig. 3. Excitation spectra of MEH-PPV in chloroform–cyclohexane. The proportion in volume of chloroform in the solvent: (1) 100%; (2) 20%; (3) 15%; (4) 10%; emission wavelength: 600 nm.

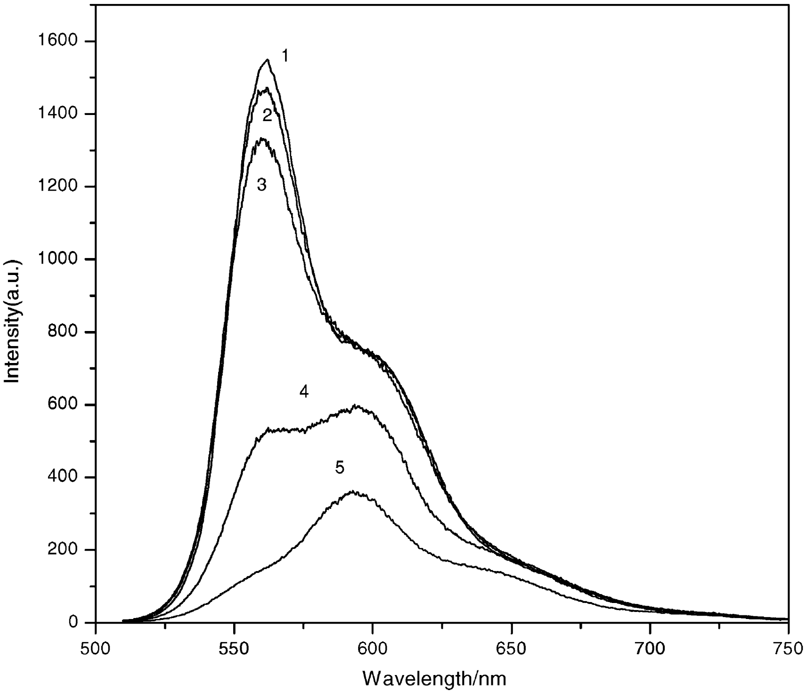

Fig. 4. Emission spectra of MEH-PPV in chloroform–methanol. The proportion in volume of chloroform in the solvent: (1) 100%; (2) 80%; (3) 70%; (4) 65%; (5) 60%; excitation wavelength: 500 nm.

10% chloroform, respectively. It can be seen that in these two solvents, MEH-PPV has almost the same spectrum except for the red shift in the latter by about 900 cm^{-1}.

The excitation spectra of MEH-PPV in the binary solvents are presented in Fig. 3 (the fluctuation from 450 to 500 nm comes from the instrument respondence). It is evident that a new excitation maximum appears at ~550 nm when the proportion of chloroform is lower than 30%.

Similar results could be observed in other binary solvents composed of chloroform and a polar solvent, methanol, as shown in Fig. 4. With an increasing proportion of methanol, the emission first changes slightly and then the maximum of the emission drops sharply as the fraction of chloroform changes from 70 to 65%. Corresponding to this drop, a shoulder appears at about 550 nm in the absorption and excitation spectra, as shown in Fig. 5.

The decays of the emission in different solutions monitored at different wavelengths were measured. Fig. 6 shows the time-resolved fluorescence emission of MEH-PPV in chloroform and two kinds of binary solvents, respectively, monitored at 600 nm with 575 nm excitation. The fluorescence lifetimes are listed in Table 1. Similar results were obtained when monitored at 650 nm. The results indicate that the lifetimes of MEH-PPV in the binary solvents are longer than in chloroform.

4. Discussion

PPV and its derivatives consist of long chain molecules with π-conjugated emissive units in its main chain. One emitting unit only contains several monomer units in solutions [12,13]. Fig. 7 shows titration curves of MEH-PPV in the binary solvents for the emission intensity at the maximum in chloroform. There is a dramatic change of about 65% of chloroform in methanol and of about 30% of chloroform in cyclohexane, respectively. In solutions, this kind of emission change usually indicates that there is a significant

Table 1
Fluorescence lifetime of MEH-PPV in chloroform and methanol and chloroform and cyclohexane (excited, 575 nm; measured, 600 nm)[a]

Solvent	Exponential fitting			
	a_1	t_1 (ns)	a_2	t_2 (ns)
Chloroform (100%)			1	0.35
Chloroform (15%) in (cyclohexane + chloroform)	0.034	1.22	0.966	0.57
Chloroform (10%) in (cyclohexane + chloroform)	0.072	1.29	0.928	0.57
Chloroform (60%) in (methanol + chloroform)	0.040	0.79	0.960	0.41

[a] a_1, a_2: relative amount of the decay curve associated with the corresponding t; t: lifetime.

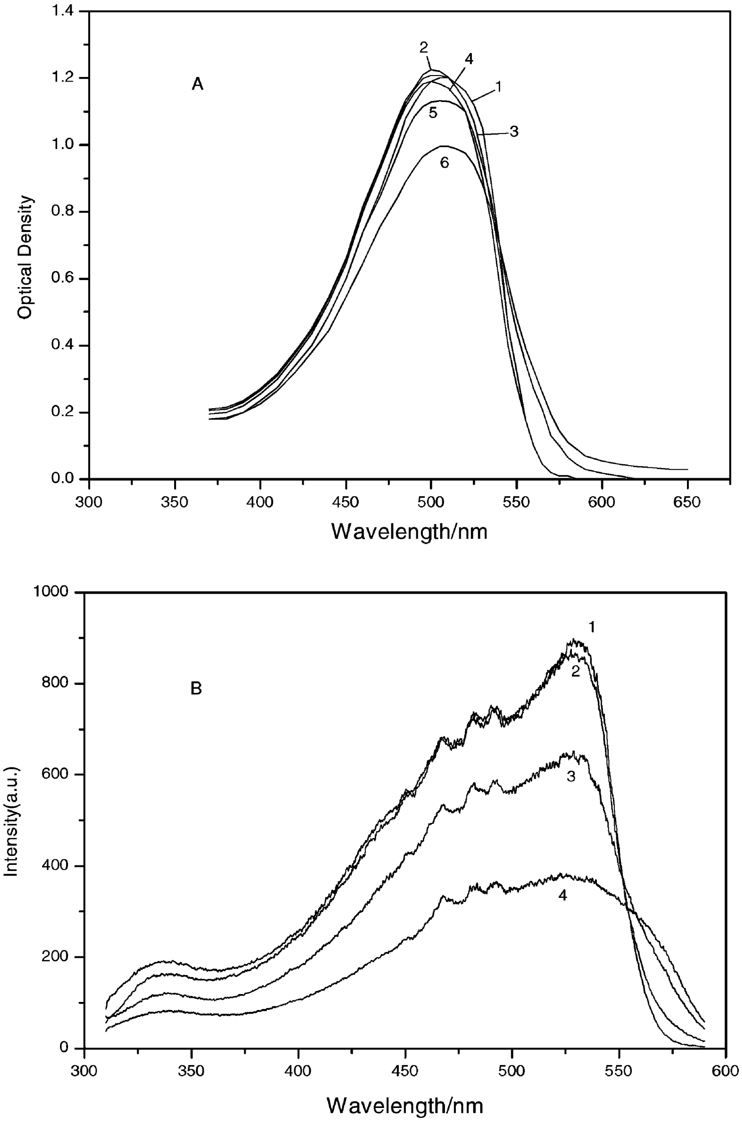

Fig. 5. (A) Absorption spectra of MEH-PPV in chloroform–methanol. The proportion in volume of chloroform in the solvent: (1) 100%; (2) 95%; (3) 80%; (4) 70%; (5) 65%; (6) 60%. (B) Excitation spectra of MEH-PPV in chloroform–methanol. The proportion in volume of chloroform in the solvent: (1) 95%; (2) 70%; (3) 65%; (4) 60%; emission wavelength: 600 nm.

event of the emitters. For the MEH-PPV polymeric chain, it could be one of the two possibilities, aggregation and chain self-coiling.

Long chain molecules may form aggregates under different conditions, e.g. in poor solvents and at lower temperature [11,12,25]. When aggregates are formed, the spectral properties, absorption and emission intensity and shape, may greatly change due to interactions between molecular chains. In some cases, a new emission from excimers could be observed. Similar phenomena could be observed in the self-coiling of the molecular chain. Temperature affects both self-coiling of one molecular chain and aggregation of molecules. But concentration of the solution may only affect the formation of the aggregates. So increasing temperature would break both the aggregates of the molecules and the self-coiling structure of one chain. Dilution of the sample solution, however, can only destroy the structure of the aggregates. Therefore, testing the spectra in the solutions with different concentrations is a usual method to distinguish between the aggregation of molecules and self-coiling of one molecular chain.

In Fig. 8, we present the concentration effect of MEH-PPV in chloroform–cyclohexane. It can be seen that there is no other difference for the emission shape and only the intensity decreases with the decreasing of concentration. This proves that the sudden changes of the spectra in the binary solvents are due to self-coiling of MEH-PPV molecular chains. The results of the fluorescence decay processes (discussed later) also indicate that the formation of aggregates in the mixed solvents may be ignored because the interaction between the

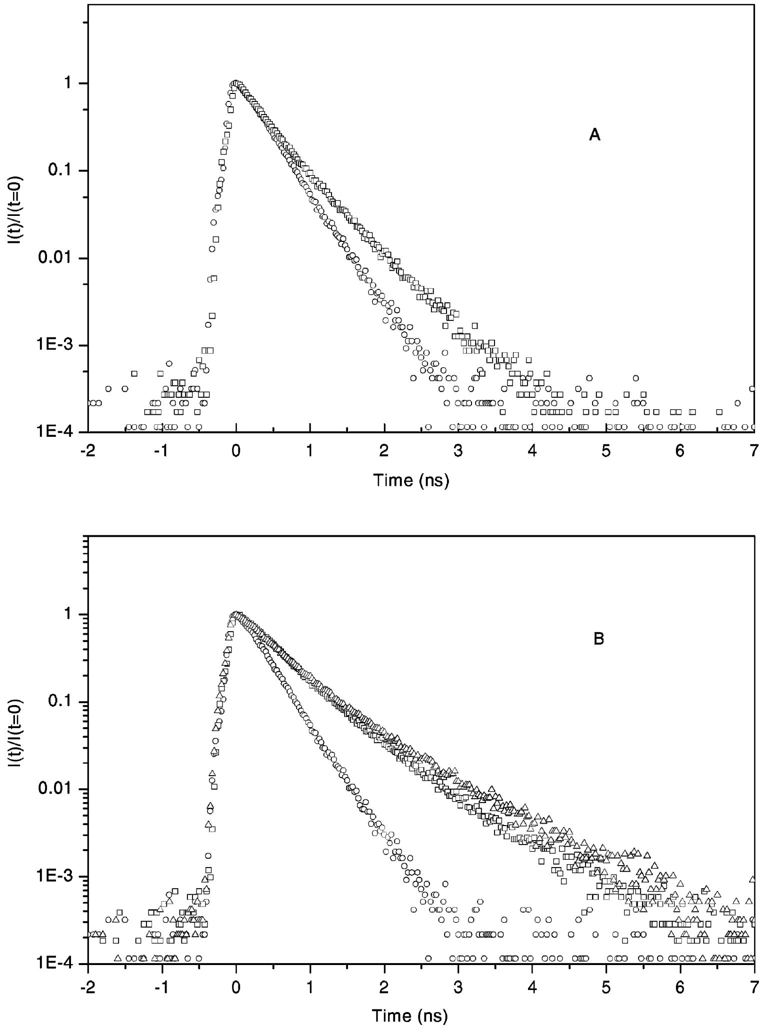

Fig. 6. Fluorescence decay of MEH-PPV in solvents; excitation wavelength, 575 nm; emission wavelength, 600 nm: (A) chloroform (○) and chloroform (60%) in (methanol + chloroform) (□); (B) chloroform (○); chloroform (15%) in (cyclohexane + chloroform) (□); chloroform (10%) in (cyclohexane + chloroform) (△).

conjugated units is not the main effect in the fluorescence change.

The next question is where the new emission comes from. Since there are several conjugated emissive units in the main chain, the new emission spectra in the solution with higher proportion of poor solvent (cyclohexane or methanol) could be the results of three causes:

1. the same emitter as that in chloroform but great shift due to stronger π–π interactions between the conjugated units;
2. the excimer or excimer-like structure formed by the emitters that have the same conjugation as in chloroform due to the closing contact due to the coiling;
3. novel emitter with larger conjugated structure, according to the absorption and emission spectra.

The transient emission results illustrate that the former two cases may be neglected in the new emissive system. In the first case, the decay of the emission should be faster than in chloroform because of the energy gap law and stronger interactions between the conjugated units. In the second case, if the emission came from the excimer or excimer-like structure, it should have a structureless spectrum and the emissions at different peak positions should exhibit different decay processes. However, from the time-resolved fluorescence decay results, it can be seen that the lifetime of the new emission is longer than in chloroform and the decay processes at different wavelengths are almost the same. This means that the whole emission spectrum comes mainly from the same excited state. A reasonable explanation for the new emission is that a new emitter with a larger conjugated structure is formed in the solution with a higher proportion of cyclohexane or methanol in chloroform, leading to a longer lifetime and bathochromic shift of the fluorescence spectrum in the mixed solvent. The difference of decay processes between two binary solvents,

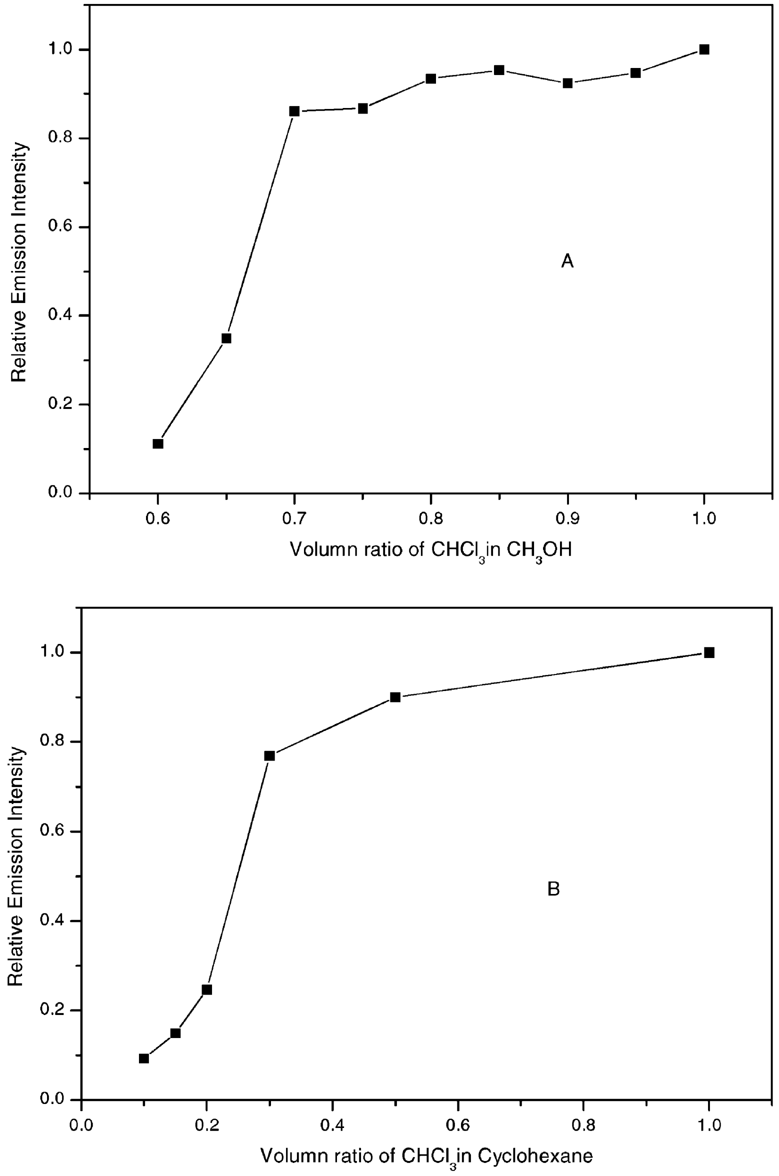

Fig. 7. (A) The intensity change of the emission in chloroform and methanol at the position of the peak in chloroform (562 nm); (B) the intensity change of the emission in chloroform and cyclohexane at the position of the peak in chloroform (554 nm).

chloroform–cyclohexane and chloroform–methanol (slower in the former solvent), is due to the different polarity of the solvents. The slower fluorescence decay processes in the binary solvents also confirm that the new emission spectrum does not come from the aggregates. In the aggregates, there are stronger interactions between the emissive conjugated units and a faster decay process should be observed.

In general, when a poor solvent is added into a dilute polymer solution in a good solvent, the chain contracts [23]. For MEH-PPV, the segments of the main chain move freely in good solvents, it is easier to form a favorable conformation in which several monomer units are conjugated. However, the main chain is relatively rigid in the poor solvents, the molecular chains form a more stable structure with larger conjugation. When the conjugated units are excited they exhibit lower energy emission at relatively longer wavelength. Similar results were obtained in a frozen solution, in which the molecular chains were more rigid than in the liquid solution. Structured emission of MEH-PPV at 77 K was observed at longer wavelength than at room temperature [11].

The reason for the emitter containing different conjugated units under different conditions is probably due to its intrinsic stability of conjugation energy at different conformations. Further theoretical research is needed, especially for the emitter with larger conjugation in the rigid molecular chain, because of its application potential.

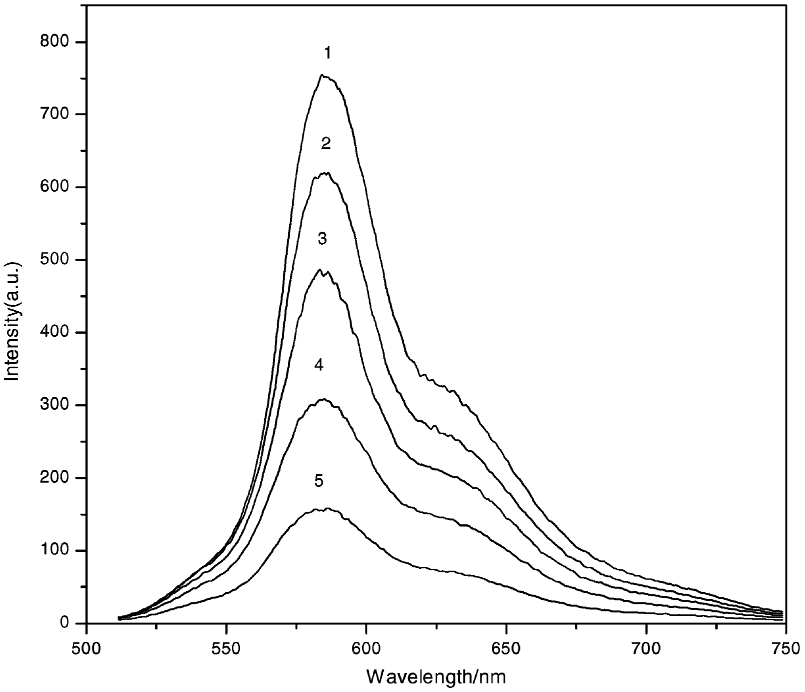

Fig. 8. Concentration effect of MEH-PPV in chloroform–cyclohexane. The proportion in volume of chloroform in the solvent, 15%. (1) 5.0×10^{-4} mol/dm^3 (for monomer unit); (2) 0.8 of 5.0×10^{-4} mol/dm^3; (3) 0.6 of 5.0×10^{-4} mol/dm^3; (4) 0.4 of 5.0×10^{-4} mol/dm^3; (5) 0.2 of 5.0×10^{-4} mol/dm^3; excitation wavelength: 500 nm.

5. Conclusion

The molecular chains of MEH-PPV become coil when a poor solvent is added into its dilute chloroform solution. This conformational transition causes a novel conjugated emitter that gives lower energy emission and slower decay processes compared with that in pure chloroform. This kind of emitter probably exists in MEH-PPV neat film, combined with other kinds of emitter, to form its complicated emission.

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