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Optical properties of poly(2-methoxy-5-(2′-ethyl-hexyloxy)-phenylene vinylene) deposited on porous alumina substrates

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Abstract

Thin films of poly(2-methoxy-5-(2′-ethyl-hexyloxy)-phenylene vinylene) (MEH-PPV) were deposited from solutions prepared with different solvents, on alumina–1%Mg substrates with different pore sizes from 18 to 118 nm to study the effects of the size on the optical properties of the polymer. The photoluminescence (PL) spectra of films cast from solutions using chloroform, toluene or xylene are almost similar, suggesting that the solvents have little effect on the solid films. In the composite systems, a blue shift of the polymer PL spectra was observed when the pore size decreases. Raman spectra recorded on these samples did not show significant changes compared to that of the polymer, suggesting that the structure of the polymer was preserved. The modifications observed in the PL spectra are attributed to the nanosize effect of the polymer deposited in the pores resulted from the chain conformation, which depends on the nature of the solvents used.
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1. Introduction

Among the derivatives of poly(*p*-phenylene vinylene) (PPV), poly(2-methoxy-5-(2′-ethyl-hexyloxy)-phenylene vinylene) (MEH-PPV) is the most widely used and investigated because it can be synthesized by a relative simple technique and has good optical and electrical properties. Light emitting devices with MEH-PPV as an active layer have been intensively studied [1–3]. These diodes emit a red light ($\lambda_{max} \sim 590$ nm) [1] with a good efficiency. It has been observed that the optical properties of the polymer are dependent on the nature of the solvent used to cast the film [4–6] by modifying the aggregation state and the conformation of the polymer chain. Besides, when threaded into silica channels, a great part of the polymer chains are aligned while those unincorporated would be aggregated [7]. The energy transfer between chain–chain segments are found to be many orders of magnitude higher than that related to intrachain process, leading to a change in

the photoluminescence (PL) spectra of the polymer. Similar optical processes in oriented polymers have been observed in PPV and its derivatives [8–10].

In this work, we have investigated some optical properties of MEH-PPV deposited onto porous alumina substrates with different pore sizes. The use of the different diameters would give information on the critical size of the aligned polymer chains in the pores. Furthermore, we have also examined the effect of the solvent on the formation of the polymer chains inside the pores. The penetration of the chains of polymer films made with different solvents would provide information on the state of chains induced by the solvent nature.

2. Experimental

MEH-PPV was synthesized by a method described previously in the literature [3]. The polymer was dissolved in three different solvents: *p*-xylene (denoted as MEH-PPV/ X), toluene (denoted as MEH-PPV/T), and chloroform

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(denoted as MEH-PPV/C). The concentration of the solutions was identical for all solvents (8 mg· cm^{-3}).

The anodic alumina of different pore diameters is obtained by electrochemically oxidizing substrates of composition (Al–1% Mg) in different electrolytes at different temperatures and potentials. The pore morphology of the samples was checked by scanning electron microscopy and their diameters were in the range of 18–118 nm.

The polymer solutions were spin cast onto the cleaned alumina substrates using identical experimental conditions for obtaining samples with comparable geometrical parameters. Different speeds from 1000 to 5000 rpm were also used for varying the thickness of the spin-coated layer but it was found that the penetration of the polymer into the pores is independent of the rotation speed. PL measurements were first performed using a Fluorolog HORIBA spectrophotometer. Next the Raman spectra of the samples were recorded with a BRUKER RFS 100 apparatus. Both measurements were carried out on bulk reference polymer films and on alumina/polymer systems at room temperature and in air.

3. Results and discussion

Fig. 1 shows the PL spectra of reference MEH-PPV thin films obtained from solutions using chloroform, toluene and xylene as solvents. Apparently, no significant difference in the shape or in position of the PL peaks were observed in these polymers. A close inspection of the spectra indicated that a small blue shift of about 2 nm for the MEH-PPV/C
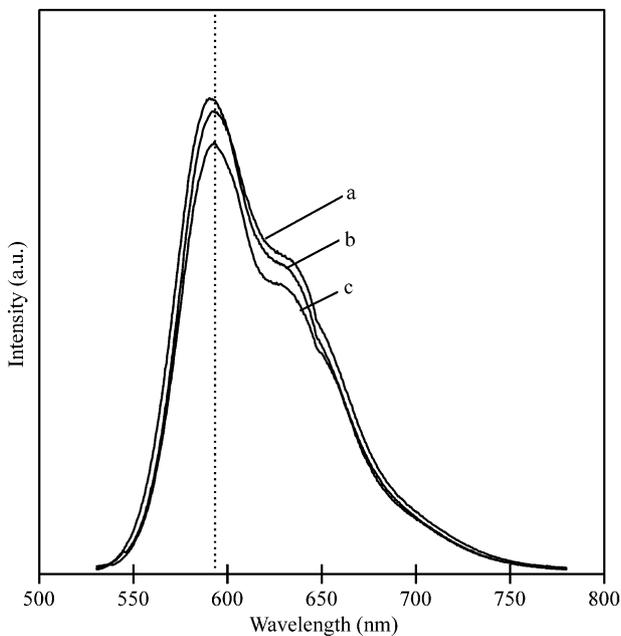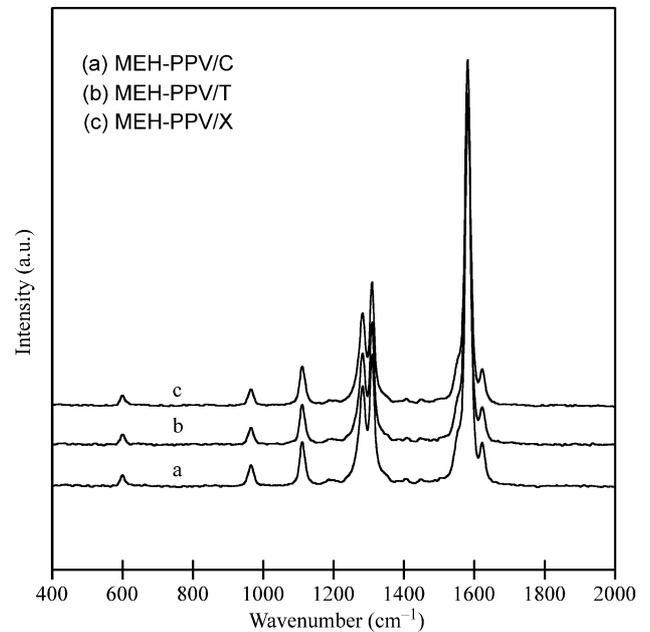
Fig. 2. Raman spectra of MEH-PPV thin films at $T = 300$ K, spin-coated from solutions using different solvents: (a) chloroform (MEH-PPV/C); (b) toluene (MEH-PPV/T); (c) xylene (MEH-PPV/X).

sample spectrum as compared to those of the other spectra, the main peak onset of these being located at 592 nm. The difference between the spectra is weak in thin films prepared with polar or non-polar solvents in contrast with results obtained in solutions [11] where the emission spectra were found to be significantly red-shifted when the polarity of the solvent increased. The Raman spectra (Fig. 2) of the samples show identical features indicating that the structure of the polymer does not depends on the nature of the solvent used. These spectra are mainly characterized by a strong vibrational band located at 1600 cm^{-1} and a doublet located at 1300 cm^{-1}.

When deposited onto alumina substrates, the PL spectra of the polymer were modified and the observed modifications depend on the nature of the solvent used. Fig. 3 shows the PL spectra of the alumina/MEH-PPV/C systems with different pore sizes. The spectrum of a polymer film is also shown for comparison. For the composite systems, we observe a blue shift of the PL spectra and an increase of their intensity as compared to those of bulk polymer films. In addition, the linewidth of the spectra of all systems was found to decrease.

The shift depends on the size of the alumina pores: it increases when the pore diameter decreases. The maximum shift obtained for 18 nm diameter pores is about 9 nm. As for the spectra intensity, the increase is maximum with a pore diameter of 78 nm. With smaller pores, the PL intensity increase is smaller, but is still higher than the that obtained in a bare polymer film. Similar results were obtained in alumina/MEH-PPV/T and alumina/MEH-PPV/X samples (Figs. 4 and 5). However, we note that for these systems, although the evolution trend is comparable to that of

Fig. 1. Photoluminescence spectra of MEH-PPV thin films at $T = 300$ K, spin-coated from solutions using different solvents: (a) chloroform (MEH-PPV/C); (b) toluene (MEH-PPV/T); (c) xylene (MEH-PPV/X).
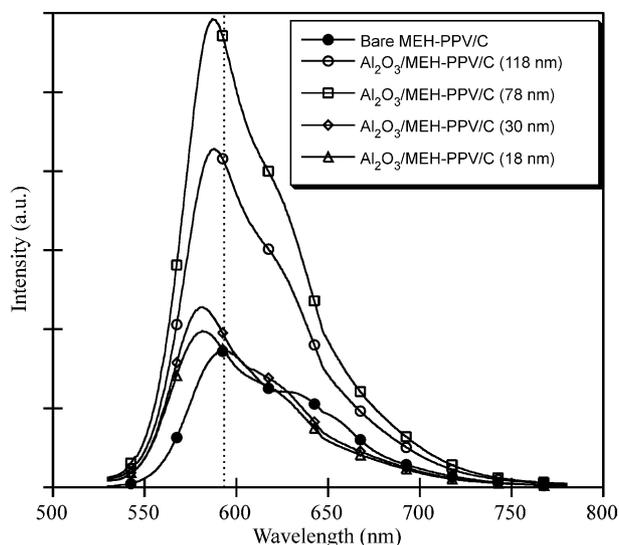
Fig. 3. Photoluminescence spectra of alumina/(MEH-PPV/C) composites at $T=300$ K with different alumina pore sizes.

the alumina/MEH-PPV/C system, several different points are to be noted. First, the blue shift of the PL spectra is smaller in both MEH-PPV films deposited from solutions using toluene and xylene. The latter shows the smallest shift (~ 3 nm). Second, the PL increase in intensity is weaker in both systems than in alumina/MEH-PPV/C system. However, there is apparently no correlation between the absolute blue shift of the PL spectra and the variation of their intensity. It should be noted that the films are deposited on identical substrates, using the same deposition parameters, and their formation in alumina pores were expected to occur in an identical way. The difference in the PL behaviour observed from the measurements result therefore from the nature of the polymer films. It should be noted that
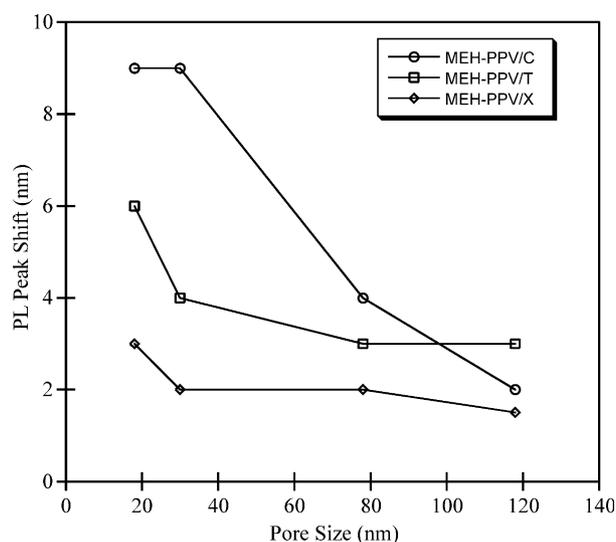

Fig. 4. Shift of the main photoluminescence peak in alumina/MEH-PPV composites as a function of the pore size for polymer spin-coated from solutions using different solvents. The shift is measured using the corresponding photoluminescence peak of the bare polymer as a reference.
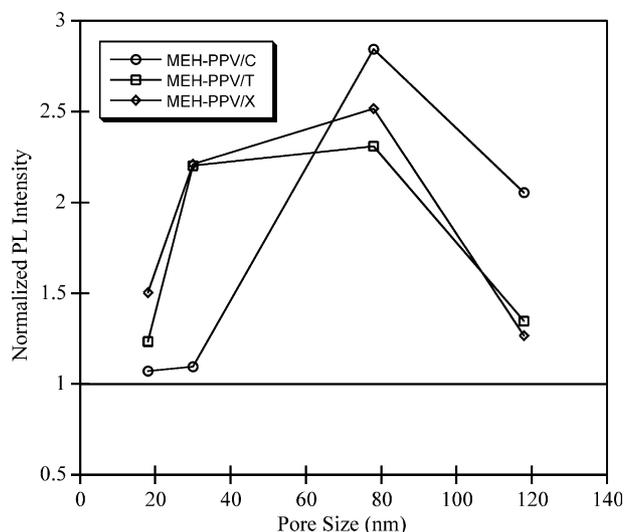

Fig. 5. Relative intensity variation of the main photoluminescence peak in alumina/MEH-PPV composites as a function of the pore size for polymer spin-coated from solutions using different solvents. The ratio is measured using the corresponding photoluminescence peak intensity of the bare polymer as a reference.

the Raman spectra recorded on the alumina/MEH-PPV systems (not shown) did not reveal strong differences as compared to that of a bare polymer film.

The effect of the solvent on the PL spectra of MEH-PPV in solutions has been studied by several groups [11–13]. It was demonstrated that the choice of the solvent and the polymer concentration in the solution have a strong influence on the chain conformation, which in turn, affects the PL yield [12]. It was also suggested that the use of a 'poor' solvent tends to red-shift the spectrum, and the decay process occurs with a longer lifetime [13]. The difference between "good" and poor solvents were not, however, clearly defined. Some authors classified the solvents into polar and non-polar categories [11] and suggested that polar solvents are better than non-polar ones to dissolve MEH-PPV. Others defined a good solvent as the one in which a polymer can dissolve fully in a short time (in contrast with a poor solvent which needs a longer time to dissolve). With the latter definition, we found that chloroform is a better solvent than toluene and xylene is the poorest one. The modifications of the PL spectra obtained in solution prepared with poor solvents were assigned to the formation of long and rigid conjugated chains, which tend to aggregate in these solvents. These effects are similar to those observed in solutions with a high polymer concentration, where the interactions between chains increase considerably. It was further suggested that the conformation effect resulted from the solvent used would be memorized in cast thin films, leading to changes of the PL spectra of solid thin films [12].

The results we obtained in MEH-PPV films using three solvents of various polarities do not show clearly a strong difference in the PL features, suggesting that the polarity of solvent has little or no influence on the optical properties of solid MEH-PPV thin films. Instead, the similarity of

the spectra suggests that the chains aggregation is almost similar in the films studied. This conclusion does not contradict the results obtained in MEH-PPV solutions, which have shown the influence of the solvent nature on the photophysical process. In particular, it is known that in non-polar solvents, the polymer chains tend to bend or twist by breaking the π conjugation, and form aggregates, while in polar solvents, these chains can move more easily in the solution [13]. However, when the film is formed by casting on a plane surface after evaporation of the solvent, the polymer chains seem to self organize in a favorable energetic configuration such that the difference in their original conformation in solution markedly decreases. This explains why the structure of the polymer films prepared with different solvents are identical from the Raman results.

The PL characteristics of the alumina/MEH-PPV systems clearly show that different states of the polymer have been formed inside the pores, depending on the solvent used. These states differ from the corresponding bulk films by a more or less important shift of the emission peak. Previous studies of MEH-PPV incorporated in aligned silica [7,14] have suggested that the polymer is isolated in the pores and the chains are oriented in the aligned pores, giving rise to a strong polarization anisotropy in the PL characteristics. A large blue shift of the PL spectrum of oriented MEH-PPV was obtained ($\sim$30 nm), but the size of the silica pores was not given [11]. In our experiments, the maximum blue shift was observed in systems filled with MEH-PPV/C, the shift increases with the decreasing pore size. Similar results are obtained in MEH-PPV/T and MEH-PPV/X with smaller shifts, however. These results indicate that the pores were all filled with polymer, but the filling process depends on the nature of the solvent. They suggest that the conformation of the polymer chain in different solutions is different, which explains the fact that the blue shift varies with the polymer preparation. In fact, a large blue shift obtained in small pore sizes shows that the polymer chains have completely penetrated into these pores, while a small shift is indicative of a incomplete process with stronger interactions between molecular chains. If we refer to the polarity of the solvents used here, chloroform has a higher value ($\sim$3.9) than toluene ($\sim$2.4) and xylene ($\sim$2.3). Therefore, the conformation of the polymer chains should be more favorable for the pore penetration in MEH-PPV/C than in MEH-PPV/T and MEH-PPV/X. We cannot, however, rule out the possible, even probable, formation of polymer chains outside the pores [7], which contribute to the overall PL spectra. This consideration may explain the relative small shifts obtained in this work as compared to that observed in Ref. [14]. Nevertheless, the shift clearly indicates the formation of polymer inside the pores as previously reported in porous silicon/PPV composites [15]. The narrower spectra obtained in all composite samples are consistent with this result since they reflect a higher order of the polymer chains inside the pores [5].

The second interesting observation from the PL spectra in the alumina/MEH-PPV systems is the intensity increase compared to that of a bare polymer film. The increase can be attributed to two different processes. First, the PL intensity increase may result from a loose packing of the polymer film, which can be understood when the chains are inserted in the alumina pores. The packing is then less compact than in a bare film, and the emission of the chains will be stronger because less interactions are involved. However, in this hypothesis, the increase in the emission intensity would be higher in smaller pores. This was not experimentally observed. Instead, the highest increase was obtained for the 78 nm pores for all systems. The second possibility for the increase of the PL intensity is the film thickness formed inside the pores. In fact, the thickness of the alumina pores is about 1 μm but they may not be completely filled in all their thickness. The 78 nm size would correspond to a critical filled thickness but we cannot provide a plausible explanation for this value in the frame of the experiments carried out here. Finally, it is also possible to consider the interactions between the polymer chains with the internal walls of the pores, which provides an argument for the decrease of the PL intensity when using smaller pore sizes. In fact, in these pores the contact between the chains and the walls is expected to be more favorable than in larger pores, and hence the higher energy transfer would reduce the emission. However, this process is also unable to explain the maximum intensity obtained in the 78 nm pore size systems.

4. Conclusion

We have examined the possibility of filling alumina pores of different sizes, from 18 to 118 nm, by MEH-PPV polymer solutions prepared with different solvents. Using photoluminescence and Raman spectroscopy, we have demonstrated that solid polymer thin films have almost the same optical properties whatever the solvent used. This result contradicts the hypothesis on the conformation memory in solid polymer films suggested in Ref. [12]. Alumina pores were filled with polymer solutions then studied after the solvents have been evaporated. The polymer was found to fill all the pores, whatever their size but the filling process depends on the polymer solution. It was suggested that the effect of the solvent on the chain conformation plays a key role in the penetration of the polymer into the pores. The filling process and the chain formation in the pores are, however, complex and several questions on the PL characteristics remain unanswered. Further investigations using different polymers, different solvents and different pore substrates and sizes are needed to fully understand these processes.

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