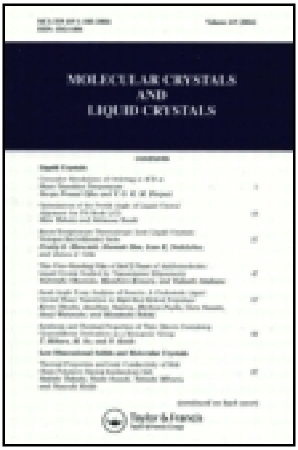

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 04 Oct 2006.

To cite this article: Yong-Joon Park , Jae-Gyoung Lee , Ha-Keun Hwang , Hyoung-Suk Kim , Byoungchoo Park , Hyung-Suk Woo , Tab-Wan Kim , Hye-Kyong Min & Eung-Ju Oh (1996): Photoluminescence of Oligomer and Polymer Blends, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 280:1, 385-390

To link to this article: http://dx.doi.org/10.1080/10587259608040360

Mol. Cryst. Liq. Cryst., 1996, Vol. 280, pp. 385–390
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PHOTOLUMINESCENCE OF OLIGOMER AND POLYMER BLENDS

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We have measured the photoluminescence(PL) of polymer and oligomer blends using partially converted poly-(*p*-phenylene vinylene) (PC-PPV) and a kind of *p*-phenylene vinylene oligomer, 1,4-distyrylbenzene in the solution of N-methyl-2-pyrrolidinone(NMP). The PL spectra of this blended material showed that the amounts of oscillator strength of oligomer peak at 2.79eV shifted to red, near 2.49eV, which is responsible for PC-PPV. This changing of oscillator strength results the enhancement of initially weak PL intensity of PC-PPV and eventually changing the color. In order to explain the excitonic migration effect occurring more seriously in blended system, as we believed, we compared this data to that of PC-PPV/oligomer multi-layered film as well as of oligomer itself. Those results will be also compared with that of another blended material, oligomer and polyaniline(PANI), and the differences will be discussed.

INTRODUCTION

Organic materials have attracted in recent years much interest, both fundamental and applied point of views, extending the possibility of applications to many electronic and opto-electronic devices including light emitting diode(LED).[1-2] After the first impressive results on LED based on poly(*p*-phenylene vinylene)(PPV)[1], many research groups demonstrated the possibility of LED fabrication with wide range of colors and remarkable improvement in efficiency using several kinds of organic materials, conjugated polymers and oligomers.[3-7]

The recent efforts of high efficiency electroluminescent emission at low bias voltage with tuning the color from red to blue have acted to focus especial attention on the neutral excitations in organic materials. In electroluminescent emission excited singlet exciton states, formed by injected charges, decay radiately. The photoexcitation across the $\pi - \pi^*$ energy gap is another way to exam the excited states that eventually contribute to non-radiative decay process, e.g. triplet exciton states, that limits the emission efficiency as well as the radiative decay.

Since excited states form their energy states just below the $\pi - \pi^*$ energy gap of conjugated polymers, the approach to color tuning is to choose polymer that have $\pi - \pi^*$ energy gap just above the energy for the desired emission. Many efforts to synthesize π–conjugated polymers with different energy gaps, their derivatives, and copolymers containing several segments with different kinds of conjugated polymers have been carried out. In recent years polymer blends have acted to focus especial attention on the color tuning and improvement of efficiency by carefully selecting the component polymers and controlling the fractions of polymers in blends.[8]

In this report, we present the optical absorption and PL of polymer and oligomer blends using PC-PPV with band gap around 2.58eV and a kind of *p*-phenylene vinylene oligomer, 1,4-distyrylbenzene with band gap energy near 2.91eV in the solution of NMP. We focused our attention to see the changing of oscillator strengths from pure oligomer PL peak to that of PC-PPV. In order to explain the excitonic migration effects occurring more seriously in blended system, as we believed, we compared PL data from blended material to those of PC-PPV/oligomer multi-layered film and another polymer blends, oligomer and PANI base which doesn't have radiative decay process.

EXPERIMENTAL

PPV was synthesized according to the well known "precursor route". Sulphonium monomer salt was obtained by reacting the *p*-dichloroxylene with tetrahydrothiophene and methanol at the temperature 55℃ under the stream of N_2 gas. This salt was resolved in H_2O maintaining the temperature at 0℃ to react with NaOH solution and PPV precursor was finally obtained after dialyzing with 1N-HCl and water. In the case of oligomer, the salt was obtained from the starting materials, *p*-xylenedichloride and triphenylphosphin. Oligomer sample, 1,4-distylbenzene, was synthesized from this salt together with benzaldehyde under the reaction with lithium ethoxide and ethanol. Figure 1 shows the molecular structure of the 1,4-distylbenzene and PPV precursor.

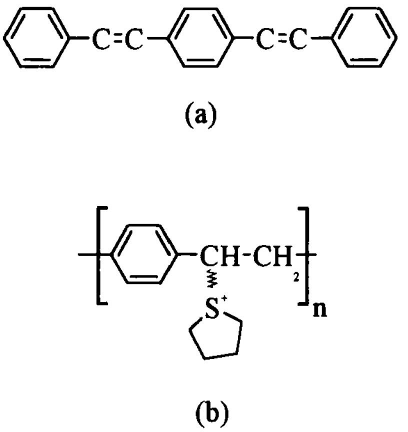

Figure 1. Molecular structure of (a) 1,4-distylbenzene and (b) PPV precursor.

In blended material, PPV precursor was mixed with oligomer in NMP solution with 1:1 mixing ratio(by weight). This polymer blend was spin coated on to the optical quartz substrate with thickness about 100 nm after 30 minutes of spinning at 1200 r.p.m. before the thermal elimination was performed, which converts the PPV precursor to partially converted PPV under the condition of the temperature at 100℃ during about 1 hour in vacuum chamber. This partial elimination was necessary in order to prevent the evaporation of oligomer itself. The PC-PPV/oligomer multi-layered film and another polymer blends, oligomer and PANI, were prepared in similar manner. The PL data were measured through the Monk-Gilicson type monochromator with gated photomultiplier detector, exciting the sample with Xenon discharge lamp equivalent to 20 KW for 8 μsec duration with pulse width at half peak height less than 10 μsec.

RESULTS AND DISCUSSION

Figure 2 shows the PL spectra of polymer blends(PC-PPV and PANI blended with oligomer) and PC-PPV/oligomer layered film as well as the oligomer itself. As shown in Figure 2(a), oligomer has its strong PL peaks at 2.79 eV and at 2.65 eV with relatively weak peak at 2.50 eV. It is clear, comparing with Figure 2(a), that spectra from Figure 2(b) and (c) show combined PL for both oligomer and PC-PPV with peaks appearing at 2.79eV, 2.65eV for oligomer and at 2.49eV for PC-PPV. In PC-PPV blend, the shifting of oscillator strength from 2.79eV to 2.49eV is bigger than that of PC-PPV/oligomer layered film. This changing of oscillator strength, however, is not shown in PANI blend as expected. In order to obtain the oscillator strength at peaks 2.79eV and 2.49 eV, we first fitted data to the Lorentzian line shape from where the oscillator strength of each peak was determined by integrating of the line shape over the spectrum band. According to this calculation, the fractional ratio of oscillator strength of two bands peaked at 2.79eV and 2.49 eV were given by 5.37 for blended film and 2.05 for layered film respectively, indicating greater red shift of oligomer peak in blended material.

The PL in organic materials is originated from the radiative recombination of singlet exciton, especially singlet polaron-exciton in PPV and its derivatives. It is generally true that the emission spectrum has much better resolved structure than is seen in the absorption spectrum. This implies that spectral diffusion occurs following photoexcitation, but prior to emission. Spectral diffusion involves exciton migration through the polymer with the exci-

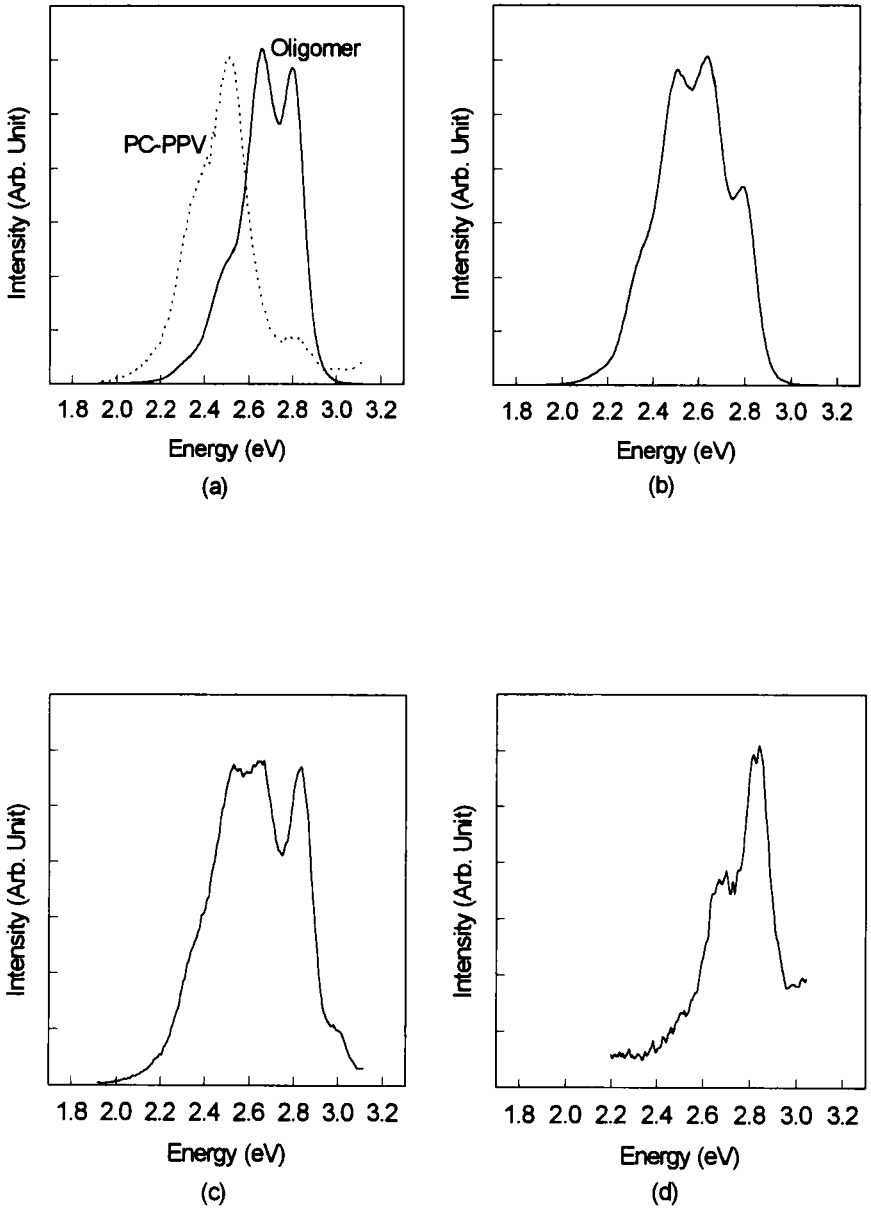

Figure 2. PL spectra of (a) oligomer and PC-PPV, (b) PC-PPV and oligomer blend, (c) PC-PPV/oligomer layer, and (d) PANI and oligomer blend

tons descending the potential gradient associated with the inhomogeneous distribution of conjugated chain segment energies.[9] In polymer blends, it is thus expected due to the bulk effect that this inhomogeneous distribution of different chain length has much higher order of degree than that of layered structure where only the surface effect between two materials is dominant. As we expected, however, for the case of PANI blend(Figure 2(d)), the oscillator strength of oligomer at 2.79 eV doesn't change much except relatively lowering of peak intensity at 2.65eV. Since PANI doesn't support the exciton level inside the energy gap(thus no PL), we propose this as non-exciton migration effect due to absence of potential gradient in PANI and oligomer blend.

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