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Notes

Effect of Controlled Stretching on the Luminescence of Poly[2-methoxy-5-(2′-ethylhexoxy)-*p*-phenylenevinylene] in Dilute Solution in Poly(vinyl chloride) and Poly(vinyl acetate)

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Introduction

A number of derivatives of poly(*p*-phenylenevinylene) (PPV) have been investigated as polymers that fluoresce and conduct electricity.[1−3] Much of the work has centered around poly[2-methoxy-5- (2′-ethylhexoxy)-*p*-phenylenevinylene) (MEH-PPV).[4−7] There is considerable literature with emphasis on the electrooptical properties. The present consensus is that an exciton is formed which migrates or delocalizes over 6−10 monomer units from excitation to emission.[8−10]

In a series of previous papers[11−13] we have presented the effect of pressure on the luminescence spectrum of MEH-PPV as a neat polymer and in dilute solution in a series of other polymers. The neat polymer has a spectrum that can be fit with three Gaussian bands. In solution in other polymers, in addition to the emission observed in the neat polymer, there is structured emission at higher energy which can be fit by three or four Gaussian bands. Since the fitting is empirical, we group the area of the three bands corresponding to the neat polymer as the low-energy band (LEB). The higher-energy bands are grouped as HEB.

The present paper presents the results of increasing tension on the emission spectra on MEH-PPV in PVCl and PVA. There have been a number of experiments reported in the literature on stretched PPV,[14−20] and a few refer to derivatives. Heeger and co-workers (e.g., refs 21 and 22) have done extensive studies of MEH-PPV and related derivatives in polyethylene oriented by stretching. Their technique is to perform a stretch usually at 110−120 °C and then to study the material at room temperature or down to liquid nitrogen temperature. These studies do not involve the observation of the spectra over a continuous range of stretches as in our experiments.

Experiment

To study the effect of stretching on the emission from MEH-PPV or similar polymers in dilute solution in various polymers, we have developed the device shown in Figure 1. All parts are stainless steel. The basic elements are two plates 29 mm by 19 mm by 9.5 mm thick held within a closely machined framework. One plate is fixed in position. The second is movable against two springs. It is moved by two rods 4.75 mm in diameter which come through the fixed plate. The rods are driven by a micrometer which can be controlled to 5 μm, although the stretches used in the experiments presented here are much larger. The plates have a section 9.5 mm square milled out to 3.2 mm depth. The sample is mounted as shown in Figure 2 and held in place by a plate with five screws. A padding of plain polymer is added under the plates to prevent slippage. At each increment of stretch the width of the polymer piece is measured under a microscope. It is then possible to calculate the relative number of units available for emission exposed to the laser at each stretch.

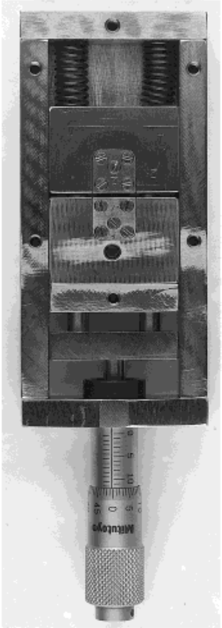

Figure 1. Photograph of the device for controlled stretching of emitting polymers.

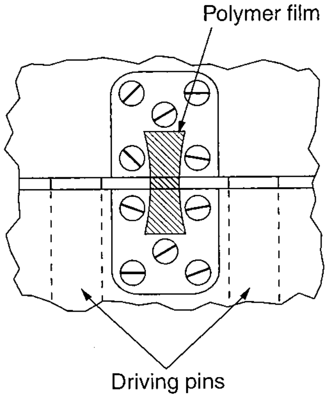

Figure 2. Detail of the polymer clamping mechanism.

In operation the gap is initially set at 0.5 mm, the retaining plates are screwed in place, and a spectrum or decay curve is

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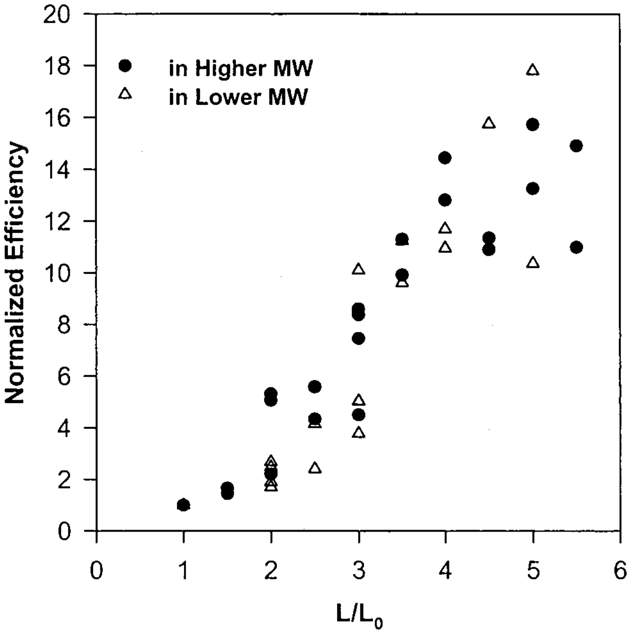

Figure 3. Change in normalized emission efficiency vs L/L_0 for MEH-PPV in PVCl.

measured. The gap is then increased by 0.25 or 0.5 mm and a second measurement made. This process is continued, usually to a gap of 3.0 mm unless the sample breaks before that. The occasional load extended to 4.0 mm. The sources of the materials used and their processing are as in refs 11–13. The spectroscopic techniques are described in refs 11–13 and 23–25 in detail.

Recently we added a device to the bottom of the holder which permits moving the whole apparatus up by 1 or 2 mm. At the larger gaps this permits us to obtain spectra at different parts of the stretched polymer.

Results

The steady-state results fall into two categories: the change in total emission efficiency per molecule and the ratio of emission associated with the LEB to that for the HEB (both defined above).

In Figure 3 we present the change in total efficiency as a function of increment of stretch for MEH-PPV at 0.0063% concentration in lower molecular weight (LMWt, $M_n \sim 22\,000$) and higher molecular weight (HMWt, $M_n \sim 58\,000$) PVCl. In both cases there is a dramatic increase in efficiency with stretch, by a factor of 15 ± 3 over a stretch to 5 times the original length. The numbers shown are corrected for the change in length and width as discussed above. At a stretch by a factor of 5 the multiplier is 3.5–3.6. It should be mentioned that one stretch load was made with MEH-PPV at a concentration of 0.025% in the HMWt PVCl. No significant difference is behavior from the more dilute sample was found. There was negligible effect of raising the device in the laser beam.

The efficiency results for PVA are in marked contrast. As shown in Figure 4, at stretches of more than a factor of 2 the total efficiency drops off significantly. In Figure 5 we display the area fraction of the low-energy band (LEB) as a function of stretch. In all cases the relative amount of LEB decreases.

The time dependence was measured at several wavelengths. The initial values were as reported in refs 11–13, and the changes with stretch are not over 10–20%.

The changes introduced by stretching did not reverse easily, but after several days the spectra had returned significantly (~50%) to their original shape and intensity.

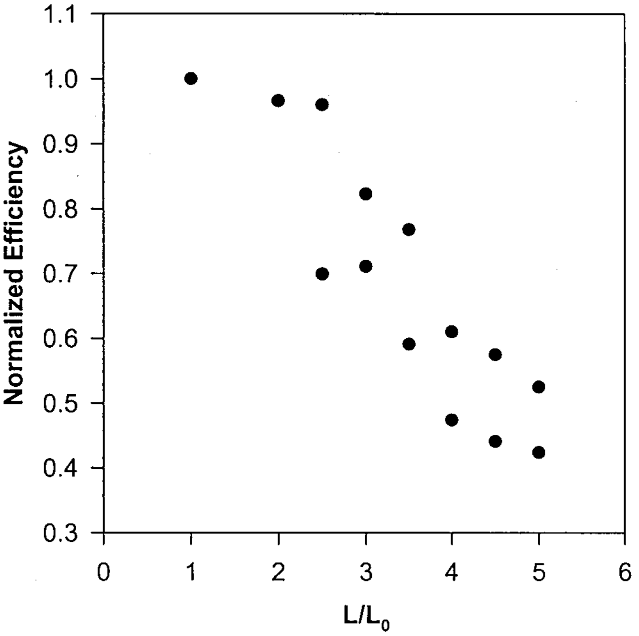

Figure 4. Change in normalized emission efficiency vs L/L_0 for MEH-PPV in PVA.

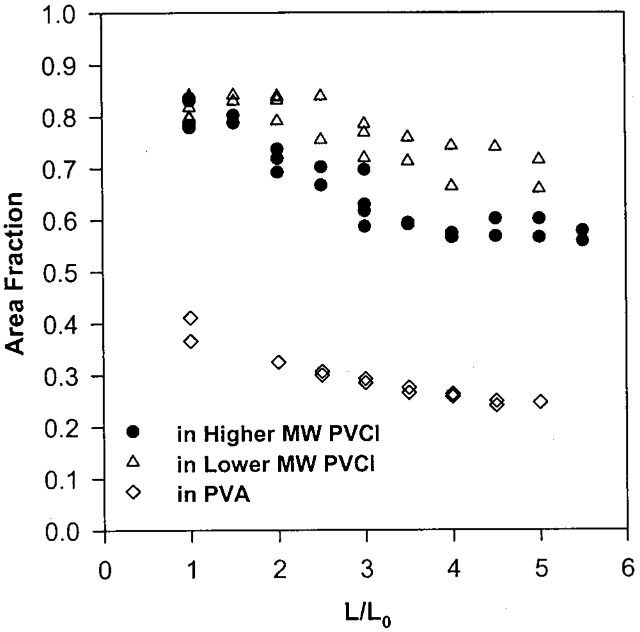

Figure 5. LEB area fraction vs L/L_0 for MEH-PPV in PVCl and PVA.

Discussion

It is generally assumed that one step in the process is an excitation transfer along several monomer units. If the MEH-PPV molecule is curled up, there can be frequent abrupt changes in conformation, “kinks”, which interfere with the excitation transfer process. A straightening of the chain by stretching could greatly reduce the kinks and increase strongly the number of emitting entities available per polymer molecule. We believe this is the major source of the very large intensity increase in PVCl. The molecular weight of the MEH-PPV is estimated to be ~700 000,[21–26] which provides 2500–2600 monomer units. The two PVCl base polymers used contained ∼350 and 900 monomer units so that there is likely to be considerable entanglement of emitting polymer with the blending PVCl.

At 1 atm $T_g = 30-40$ °C for PVA so the material is quite pliable and can deform to minimize repulsion. Evidently the stretching of the PVA molecules stiffens the matrix and causes the MEH-PPV to ball up further to minimize the area of contact with the more rigid PVA; i.e., the stiffening reduces the ability of the matrix to adjust to minimize the repulsion to the large MEH-PPV molecules with a consequent increase in quenching by long-range intramolecular excitation transfer.

The decrease in the fraction of the total energy associated with the low-energy band with increasing stretch which parallels the effect of increasing pressure[11−13] is of interest, but the interpretation is not yet clear.

Conclusions

The effect of stretching on the emission efficiency per MEH-PPV molecule in blends in PVCl and PVA is very different. In PVCl there is an increase in efficiency by a factor of 15 at $L/L_0 = 5$. At the same stretch the emission efficiency in PVA has dropped to ∼0.4 of its initial value. In PVCl the primary effect is the elongation of the MEH-PPV molecule providing more emitting entities. MEH-PPV is less compatible with PVA, and the stiffening of the PVA matrix with stretching causes the MEH-PPV to ball up further to minimize area of contact with subsequent internal quenching.

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References and Notes

(1) Grem, G.; Leditzky, G.; Ullrich, B.; Leising, G. *Adv. Mater.* **1992**, *4*, 36.
(2) Berggren, M.; Granstrom, M.; Inganas, O.; Anderson, M. *Adv. Mater.* **1995**, *7*, 900.
(3) Tessler, N.; Denton, J.; Friend, R. H. *Nature (London)* **1996**, *382*, 695.
(4) Wudl, F.; Alleman, P. M.; Srdanov, G.; Ni, Z.; McBranch, D. *ACS Symp. Ser.* **1991**, *455*.
(5) Buroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature (London)* **1990**, *347*, 539.
(6) Nguyen, T.-Q.; Doan, V.; Schwartz, B. J. *J. Chem. Phys.* **1999**, *110*, 4068.
(7) Dogariu, A.; Vacar, D.; Heeger, A. J. *Phys. Rev. B* **1998**, *58*, 10218.
(8) Graham, S. C.; Bradley, D. D. C.; Friend, R. H.; Spangler, C. *Synth. Met.* **1991**, *41−43*, 1277.
(9) Rauscher, U.; Bassler, H.; Bradley, D. D. C.; Hennecke, M. *Phys. Rev. B* **1990**, *42*, 9830.
(10) Bassler, H.; Gailberger, M.; Mahrt, R. F.; Oberski, J. M.; Weiser, G. *Synth. Met.* **1992**, *49−50*, 341.
(11) Yang, G.; Li, Y.; White, J. O.; Drickamer, H. G. *J. Phys. Chem. B* **1999**, *103*, 5181.
(12) Yang, G.; Li, Y.; White, J. O.; Drickamer, H. G. *J. Phys. Chem. B* **1999**, *103*, 7853.
(13) Li, Y.; Yang, G.; Zhu, A.; Drickamer, H. G. *Chem. Phys. Lett.* **1999**, *310*, 259.
(14) Yan, M.; Rothberg, L.; Hsieh, B. R.; Alfano, R. R. *Phys. Rev. B* **1994**, *49*, 9419.
(15) Gagnon, D. R.; Karasz, F. E.; Thomas, E. L.; Lenz, R. W. *Synth. Met.* **1987**, *20*, 85.
(16) Heun, S.; Mahrt, R. F.; Greiner, A.; Lemmer, U.; Bässler, H.; Halliday, D. A.; Bradley, D. D. C.; Burn, P. L.; Holmes, A. B. *J. Phys.: Condens. Matter* **1993**, *5*, 247.
(17) Hayes, G. R.; Samuel, I. D. W.; Phillips, R. T. *Phys. Rev. B* **1997**, *56*, 3838.
(18) Machado, J. M.; Karaxz, F. E.; Lenz, R. W. *Polymer* **1988**, *29*, 1412.
(19) Murata, K.; Kuroda, S.; Shimoi, Y.; Abe, S.; Noguchi, T.; Ohnishi, T. *Synth. Met.* **1997**, *84*, 555.
(20) Furukawa, M.; Mizuno, K.; Matsui, A.; Rughooputh, S. D. D. M.; Walker, W. C. *J. Phys. Soc. Jpn.* **1989**, *58*, 2976.
(21) Hagler, T. W.; Pakbaz, K.; Voss, K. F.; Heeger, A. J. *Phys. Rev. B* **1991**, *44*, 8652.
(22) Hagler, T. W.; Pakbaz, K.; Heeger, A. J. *Phys. Rev B* **1995**, *51*, 199.
(23) Jurgensen, C. W.; Drickamer, H. G. *Phys. Rev. B* **1984**, *30*, 7202.
(24) Dreger, Z. A.; Lang, J. M.; Drickamer, H. G. *Chem. Phys. Lett.* **1991**, *185*, 184.
(25) Yang, G.; Dreger, Z. A; Drickamer, H. G. *J. Phys. Chem. B* **1997**, *101*, 4218.
(26) Helgeson, R., personal communication.

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