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LETTER TO THE EDITOR

Photoluminescence of poly(3-alkylthiophene) under hydrostatic pressure

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Abstract. Photoluminescence of poly(3-alkylthiophene) in the liquid state is very noticeably enhanced under hydrostatic pressure. However, at high pressures above the liquid–solid transition, the luminescence intensity decreases and the emission peak shifts to a lower energy. These results are tentatively explained in terms of a change of the torsion angle at the bond between thiophene rings and the resulting change of effective conjugation length under pressure.

Recently poly(3-alkylthiophene) has attracted much interest from both fundamental and practical viewpoints as the first fusible conducting polymer (Yoshino *et al* 1987a, b). Anomalous temperature dependences of absorption spectra and photoluminescence have also been observed in the pre-melting region (Yoshino *et al* 1988a, b). It is also found that the phase transition temperature between solid and liquid states is strongly influenced by hydrostatic pressure.

In this Letter a remarkable pressure dependence of photoluminescence in poly(3-alkylthiophene) is studied and discussed in terms of the pressure effect on molecular conformation.

Poly(3-alkylthiophene)s with long alkyl side chains such as poly(3-octylthiophene), poly(3-dodecylthiophene) and poly(3-docosylthiophene) were prepared by the chemical polymerisation method utilising FeCl_3 as catalyst. Details of the preparation method and procedure have already been reported (Yoshino *et al* 1986). In this Letter, it is mainly poly(3-dodecylthiophene) that is discussed.

These poly(3-alkylthiophene)s can be dissolved in various conventional solvents such as chloroform (Sato *et al* 1986, Elsenbaumer *et al* 1986, Sugimoto *et al* 1986). Films were prepared by dissolving them and then casting the solution onto a glass substrate. Free-standing films were obtained by peeling off the substrate. The absorption spectrum was measured with a Hitachi 330 spectrophotometer. Each sample was set in the pressure chamber with optical windows and brought up to a pressure of 10 kbar by an oil-press method. The luminescence from the sample in the chamber was measured using an Ar-ion laser (2.539 eV) as an excitation light source, a spectrometer CT-50 and a photomultiplier (Hamamatsu Photonics Co. Ltd, R649) with a multi-alkali cathode

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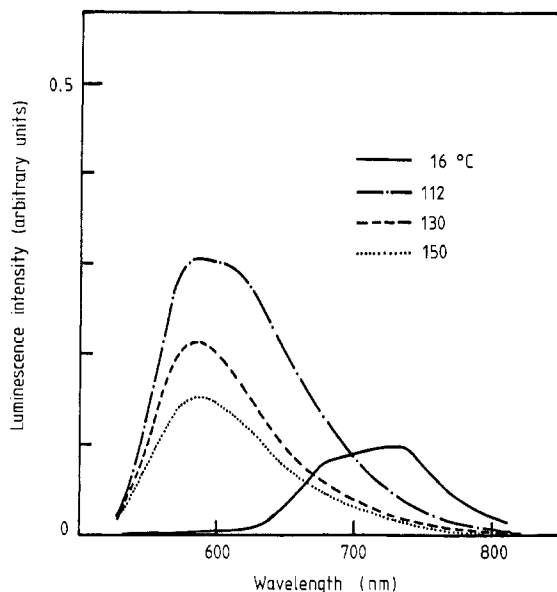


Figure 1. Temperature dependence of photoluminescence in poly(3-dodecylthiophene) at ambient pressure (1 bar) in the range covering both solid and liquid phases.

connected to a microcomputer (NEC PC-9801VX21). A lock-in amplifier system was also used to obtain a good signal-to-noise ratio.

Figure 1 indicates the temperature dependence of the photoluminescence in poly(3-dodecylthiophene) at an ambient pressure (1 bar) in the range covering both solid and liquid phases. As is evident from this figure, the luminescence peak shifted to higher energy with increasing temperature. The luminescence intensity in the solid phase increased with increasing temperature; however, at higher temperatures beyond the melting point (117 °C) the luminescence intensity is again suppressed.

A blue shift to the higher-energy side of the absorption peak had already been reported for poly(3-alkylthiophene) (Yoshino *et al* 1988a, b) and has been explained in terms of an increased band gap at higher temperature due to the decrease of effective conjugation length on account of the introduction of torsions at bonds between neighbouring thiophene rings. The increase of photoluminescence in the solid phase with temperature can also be explained by the introduction of torsions. That is, photoexcited species (such as electrons and holes, or negative and positive polarons) should be confined in the narrow excited region due to the decrease of effective conjugation length, resulting in the enhancement of recombination luminescence. On the other hand, the increased suppression of luminescence with increasing temperature in the liquid phase in which the torsion angle is considered to be markedly independent of temperature can be explained by the increased non-radiative decay of excited species.

Figure 2 indicates emission spectra of poly(3-dodecylthiophene) under various pressures at 150 °C. It is clearly observable in this figure that the emission peak does not shift very noticeably but its intensity increases markedly with pressure up to 3 kbar. However, above 3 kbar luminescence intensity again decreases and the emission peak shifts to a lower energy.

These results can be tentatively explained as follows by taking the change of molecular conformation with pressure into consideration. With increasing pressure at 150 °C, a

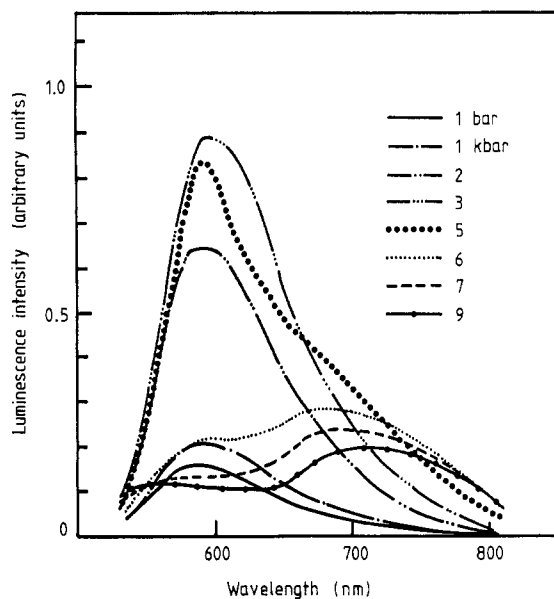


Figure 2. Photoluminescence spectra of poly(3-dodecylthiophene) under various pressures at 150 °C.

transition from the liquid phase into the solid phase was clearly observed at around 2.5 kbar (Yoshino *et al* 1989). This means that the enhancement of photoluminescence with pressure is a characteristic in the liquid phase. If the torsion angle decreased markedly with pressure in the liquid phase, the luminescence intensity should be enhanced contrary to observation. However, it should be noted that at higher pressure, the difference of temperature ($T_d = 150 - T_m$) from the melting point T_m markedly decreased. Molecular motion is expected to become more violent at larger T_d even if the mean torsion angle is kept nearly constant. In such a case non-radiative decay of photoexcited species should be more effective. Therefore, with increasing pressure, the luminescence can be enhanced.

On the other hand, figure 3 shows the effect of hydrostatic pressure on the absorption spectrum of poly(3-dodecylthiophene) at 45 °C. Only at high pressures does the absorption peak show a slight red shift. We have also confirmed that the effective conjugation length becomes longer with hydrostatic pressure as shown in figure 3 in the solid phase. This is considered to be due to the decrease of the torsion angle. This is also consistent with the present result. That is, even at 150 °C, above 2.5 kbar poly(3-dodecylthiophene) is in the solid phase. Therefore, with increasing pressure, the effective conjugation length should become shorter, which restricts the escape of the excited species from the excited region, resulting in the enhancement of the recombination luminescence. The shift of the absorption peak to lower energy can also be satisfactorily explained by the increased conjugation length.

Exactly the same behaviour was also observed in other poly(3-alkylthiophene)s with an alkyl chain longer than the butyl unit, although the temperature at which such effects become noticeable increases in the sample with shorter alkyl chains. The changes of the torsion angle between neighbouring thiophene rings are expected to be triggered by the conformation change of the side alkyl group—such as a gauche-trans change.

In summary, anomalous pressure dependence of photoluminescence was observed

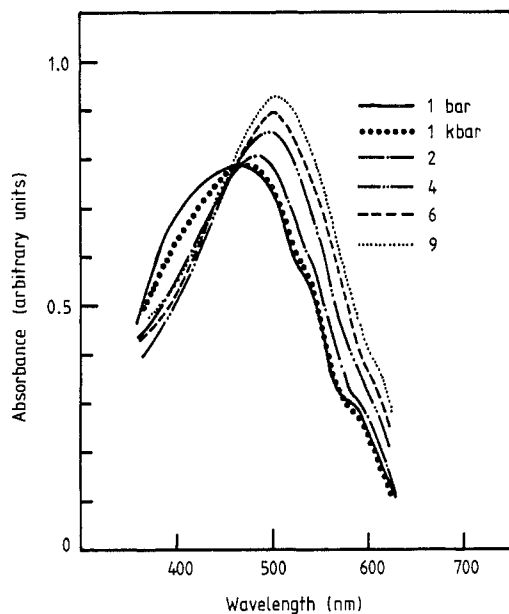


Figure 3. Absorption spectra of poly(3-dodecylthiophene) measured under various hydrostatic pressures at 45 °C.

in a poly(3-alkylthiophene) with a long alkyl chain, which can be explained qualitatively by the change of effective conjugation length due to the change of the torsion angle. Assuming non-radiative recombination was also necessary to interpret the dependence in the liquid phase. To confirm this interpretation, time dependence of the photoluminescence in the picosecond range, and Raman and infrared spectra measurements under pressure are necessary.

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