

Investigation of photoluminescence in poly(paraphenylene)

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The photoinduced luminescence spectra of poly(paraphenylene) (PPP) are impurity quenching studies in Er^{3+} -implanted PPP were investigated. We have measured the transient luminescence spectrum distributions from PPP and the lifetimes of the luminescence in the nanosecond time regime. The experimental results show that the transient luminescence spectra with sharp luminescence bands centred at 4340, 4332 and 4318 Å are well resolved; Fe^{3+} quenches intensely the luminescence from Er^{3+} -implanted PPP. We have also discussed luminescence mechanism with the polaron model and the theory of lattice relaxation.

1. Introduction

For several years, studies of electrical and optical properties in PPP have been the object of great attention because the PPP chain has a broken symmetry and a nondegenerate ground state. Special photoexcited states of PPP have recently attracted considerable interest in view of the possibility of photoexcitation of polaron states. The experimental studies include luminescence, photoconductivity, infrared spectra and photoinduced optical absorption changes [1-5]. Previous studies have theoretically found that the polaron defect state in PPP leads to confinement of the photo-generated carriers and to the observed recombination luminescence [6]. However, very few luminescence studies of PPP have been reported only until now. In this paper, we present some new luminescence properties of PPP polymerized by the Kovacic route and impurity quenching studies in Er^{3+} -implanted PPP and the decay kinetics of PPP are investigated in the nanosecond time regime for the first time. We discuss also further the origins of the luminescent property with the polaron model and the lattice relaxation theory.

2. Experimental

PPP samples studied in this work were produced using the Kovacic method. The details of the sample preparation are discussed in ref. [7]. Infrared spectrometric (FTIR) analysis shows the presence of bands which confirms the formation of linear chains, linked in para positions. This is in agreement with IR spectra previously observed for PPP obtained by Kovacic and electrochemical method. We find an average number of 12-14 phenyl rings in the polymer chains of our PPP samples.

In optical absorption measurements were made using a Varian Carry 2300 in the visible and near IR region. The spectrum measurements of the PPP samples were performed by using Jobin-Yvon Ramanon HG2S type double monochromator with holographic gratings and an AsGa photomultiplier (RCA) equipped with an Apple II computer and a photon counting system was applied. Laser lines were provided by either an argon (12 W) or a krypton (12 W) CW Laser, Spectra-Physis (USA). Spectra were recorded at room temperature and liquid nitrogen temperature and liquid helium temperature. The transient lumines-

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cence measurements were carried out using a model EMG102 excimer laser with a boxcar detector and a cryogenic refrigeration system and a test laser pulse with a duration of about 10 ns. The fluorescence life of the sample was measured with SP70/80NS fluorescence spectrometer.

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3. Results and discussion

3.1. Optical absorption spectrum

Optical absorption spectra of pressed samples of PPP were recorded over the energy range 1.4-4.2 eV as a function of temperature. The optical absorption spectra of PPP are characterized by the main peaks at 350 nm (300 K) and 345 nm (78 K) due to the $\pi-\pi^*$ transition for the conjugated π electron system. The peak observed at 520 nm on the absorption curve is very small and the shoulder observed at 420 nm is not obvious. In the 600-900 nm region, an absorption peak is not observed.

The peak of absorption shifts a small amount to high energy as the temperature is decreased to 78 K.

3.2. Comparison between steady state and transient spectrum

Figure 1 shows the luminescence spectra measured coincident with the pulsed excitation at 308 nm (curve A), with an R562 photomultiplier tube (Japan) and cw argon laser excitation at 413 nm (curve B). Under the pulsed excitation, the luminescence spectra of PPP are characterized by the main peaks at 429.6 and 452.6 nm. The luminescence intensity is very weak in the 500-600 nm region (curve A). Under steady state excitation, the luminescence intensity is very strong in the same region (curve B). Obviously, the spectral resolution of curve A is better than that of curve B. Therefore, the luminescence spectra will be discussed by using the lattice relaxation process easily.

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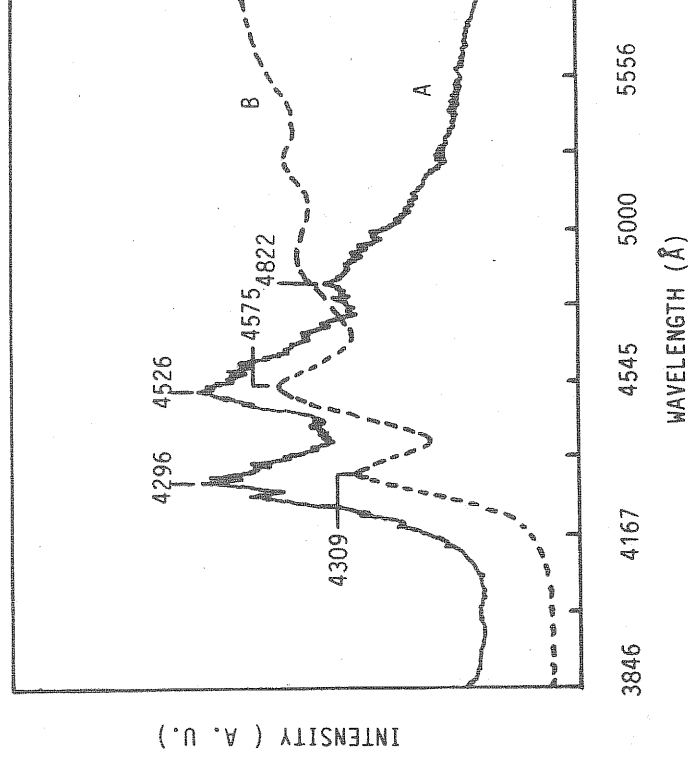


Fig. 1. Luminescence spectra of PPP at room temperature. A: pulsed excitation, $\lambda_{ex} = 308$ nm; B: cw Ar⁺ laser excitation, $\lambda_{ex} = 413$ nm.

3.3. Transient luminescence of PPP

Under the pulsed excitation at 308 nm, the variations of the luminescence spectra from PPP with temperature are shown in fig. 2. The results indicate that the luminescence spectra are well resolved. The peaks are rather sharp and located at 434 and 460 nm at 100 K. From fig. 2 and our experimental data, it is clear that the peaks are shifted slightly and the luminescence intensities are decreased step-wise as the temperature changes from 8.5 to 275 K.

3.4. Impurity quenching of photoluminescence of PPP

In Er³⁺-implanted PPP samples it is observed that the red luminescence is very much increased compared to that induced by the same sample

without Er³⁺ implant after preparation. The extrinsic part of the luminescence is now very intense with three apparent maxima 614 nm, 666 nm and 746 nm.

Doping of Er³⁺-doped PPP sample was performed in a solution of FeCl₃ but with low concentration. After 2 h doping, the luminescence spectrum was recorded under same excitation (406.7 nm) and temperature conditions (*T* = 5 K). The result shows that most of the luminescence has been quenched. The signal is very weak and composed of two bands at 500 and 535 nm.

The experimental results seem clear that two different contributions are observed: one extrinsic and one intrinsic. Er³⁺ increases the luminescence intensity of PPP in intrinsic part. On the contrary, Fe³⁺ quenches the luminescence of Er³⁺ doped PPP in the intrinsic and extrinsic part. Er³⁺ and Fe³⁺ intervene the pristine PPP ring chains as well

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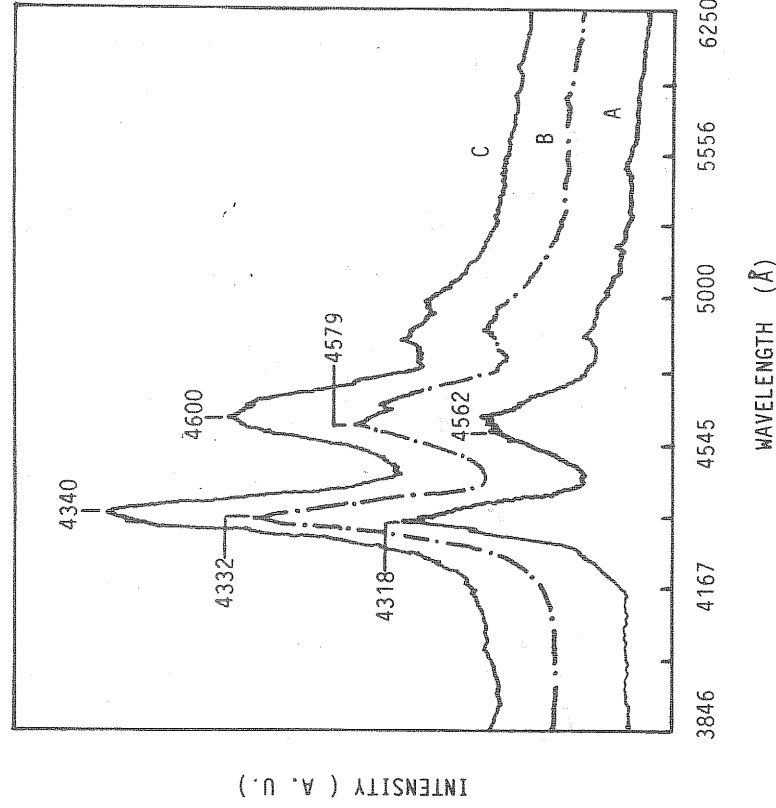


Fig. 2. Variation of luminescence spectra with temperature. A: 8.5 K; B: 50 K; C: 100 K.

as PPP chain length and the original band gap will be changed, so that the photoinduced evolution states (polaron and bipolaron) can be effective quenching centers of photoluminescence. The mechanism of the quenching is being researched further. The Stokes shift of luminescence has been explained with a scheme involving a relaxation of an electron-hole pair to a polaron-exciton defect.

3.5. Luminescence life of PPP

The measurement of the luminescence life of PPP is shown in fig. 3. The luminescence decay curve (correspondent luminescence at 520.6 nm) of PPP is found to have a single exponential form with a lifetime of 2.26 ns. Therefore, the radiative recombination of polaron pairs would be expected to be very rapid in agreement with an interchain process. The decay kinetics was interpreted by the interchain recombination of photoexcited polaron pairs. A polaron pair is generated by photo-inducing on different chains and disappears with an interchain recombination rate, when they come to the nearest sites to each other on neighbouring chains after one-dimensional random walks.

The decay kinetics of photoinduced absorption between a few nanoseconds and a few microseconds is mainly due to the interchain recombination of the photoexcited polaron pairs and exhibits the radiative luminescence after relaxation. Similarly the Stokes shift of the luminescence (for example, absorption at 3.54 eV) at 429.6 nm (2.90 eV) with decreasing temperature can be explained by radiative decay from a polaron-exciton excited state [8,9].

As is known, in PPP, the nondegenerate ground state leads to confinement of the photogenerated carriers and to the observed recombination luminescence. According to the polaron model and the theory of lattice relaxation, we attempt to explain the mechanism of the luminescence of PPP. After the absorption of the photon and the creation of an e^-h^+ pair, which relaxes to a localized energy level, the radiative decay and the luminescence is observed. The different transitions between the localized energy levels correspond to the different luminescence band in PPP samples. Because of the temperature effect of the lattice relaxation [9] and the photogenerated carrier (polaron-exciton) recombination luminescence,

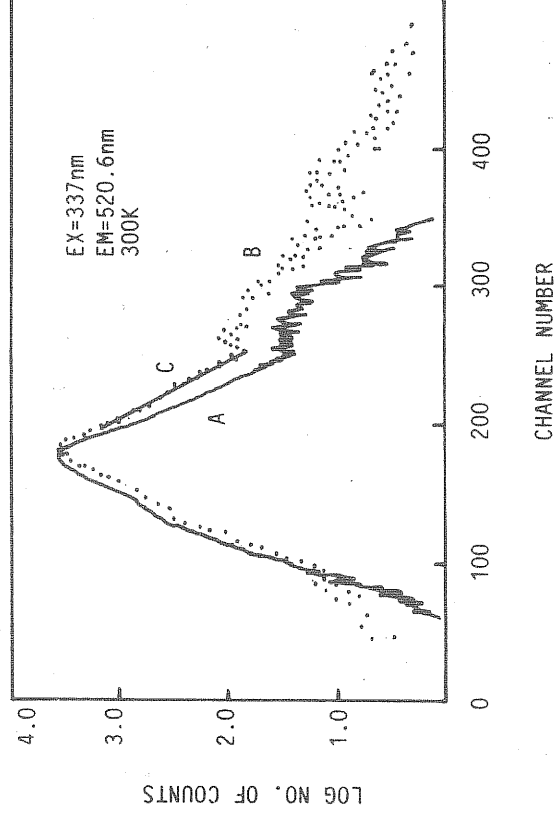


Fig. 3. Luminescence decay curve of PPP, fit with single exponential expression. A: pump; B: decay curve; C: fitted curve.

the relative shifts of the luminescence peaks from Kovacic PPP samples in the range of our measurements (410–600 nm) show obviously temperature dependences (a change of luminescence intensity and shift of peak). When temperature decreases, luminescence intensity changes strong and shifts slightly to red region.

Acknowledgements

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