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A. Heim^a & G. Leising^a

^a Institut für Festkörperphysik, TU Graz A-8010
Graz, Petersgasse, 16, Austria

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PHOTOLUMINESCENCE OF POLY-(PARAPHENYLENE)

A.HEIM, G.LEISING
Institut für Festkörperphysik, TU Graz
A-8010 Graz, Petersgasse 16, Austria

Abstract We present photoluminescence spectra for Poly-(para-phenylene) (PPP), which is synthesized by basically two different methods. Yamamoto-PPP emits a strong blue-green structured fluorescence, whereas the fluorescence of the Kovacic-PPP is dominated by a structureless broad band in the red. The difference in the fluorescence spectra are discussed by means of polymerization induced defects.

1. EXPERIMENTAL

The PPP-samples were synthesized using the methods of YAMAMOTO (1) and KOVACIC (2). For the Kovacic preparation route (PPP-K) we used $AlCl_3$ - $CuCl_2$ as the catalyst-system. YAMAMOTO-PPP (PPP-Y) was prepared by polycondensation of a Grignard reagent (from p-dibromobenzene) using $NiCl_2$ (bpy) as a catalyst. The reaction products were carefully washed and heated (inert atmosphere) in order to achieve a pure polymer material. During the heating process of the pristine PPP-Y (250 °C, 30 h) about 60 weight-percent volatile products are removed.

For the steady excitation of the PPP-powder a monochromator JY H225 equipped with a 950 Watt xenon arc was used. The emission passing through a monochromator JY HRS2 was received by a PMT Hamamatsu R649. The spectra were corrected for the wavelength dependent influences of the measuring optical components. To improve the S/N-ratio a photon counting technique was applied.

2. RESULTS AND DISCUSSION

In Fig.1 the excitation and emission spectra of the PPP-samples at room temperature are compared to the fluorescence of p-terphenyl. The emission spectrum of PPP-Y with the maximum at 482 nm shows shoulders at about 408 nm, 431 nm, 461 nm and 520 nm, whereas PPP-K exhibits distinct bands at 433 nm and 459 nm and two shoulders at about 490 nm and 522 nm, dominated by a broad structureless band at about 700 nm.

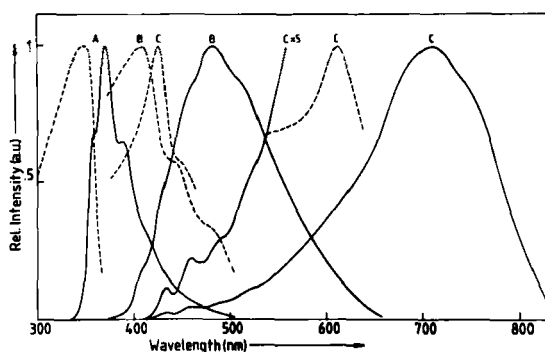


FIG.1

The excitation (---) and emission (—) spectra of

A: p-terphenyl	$\lambda_{em}=390$ nm,	$\lambda_{ex}=270$ nm
B: PPP-Y	$\lambda_{em}=535$ nm,	$\lambda_{ex}=325$ nm
C: PPP-K	$\lambda_{em}=535$ nm,	$\lambda_{ex}=330$ nm
	$\lambda_{em}=660$ nm	

The fluorescence of products removed by heating the PPP-Y is peaked at 403 nm and has shoulders at 380 nm, 388 nm, 397 nm and 425 nm (Fig.2). The position of the excitation edge depends on the monitored emission wavelength indicating that the volatile products of PPP-Y consist of several compounds with different chainlengths.

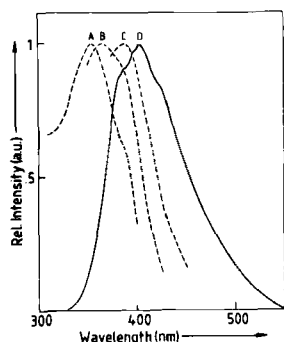


FIG.2

The excitation (---) and the emission (—) spectra of the volatile products of PPP-Y

A: $\lambda_{em}=425$ nm

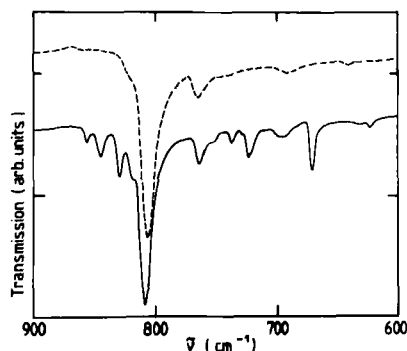
B: $\lambda_{em}=450$ nm

C: $\lambda_{em}=490$ nm

D: $\lambda_{ex}=270$ nm

FIG.3

IR-transmission (KBr-pellets) for PPP-Y (---) and the volatile product (—)



This is verified by infrared spectroscopy, where the position of the C-H-deformation mode for para-substituted benzene shifts to lower wavenumbers for an increasing number n of coupled benzene rings. For the volatile product this deformation mode is located at 808.6 cm^{-1} accompanied by well resolved peaks at higher wavenumbers (Fig.3), which arise from p-phenyl-oligomers ($n=2,3,4,\dots$). For PPP-Y the absorption-maximum occurs at 806.5 cm^{-1} and it is peaked at 805.4 cm^{-1} for PPP-K (Fig.3,4) (5).

The structured luminescence in the blue-green region emitted by both kinds of PPP is due to electronic transitions between vibrational states of the excited and the ground state. This is confirmed by comparison of the energy differences of these bands with Raman data

(3,4) for the skeletal frequencies and their combinations. Besides we found a shift of the absolute position of these bands to the red going from PPP-Y to PPP-K. Additional to the IR-spectra this shift is again an evidence of the higher degree of polymerisation for PPP-K.

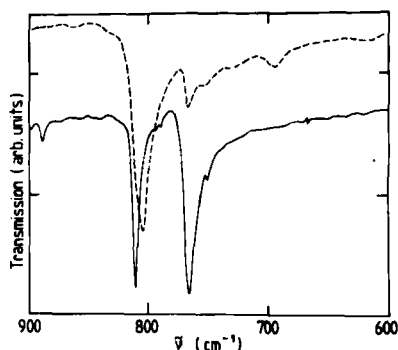


FIG.4
IR-transmission (KBr-pellets)
for PPP-K (---)
and perylene (—)

We assume that the broad red band representing the main difference in the fluorescence of PPP-K and PPP-Y, is due to defects on the chain (6). The chemical structure of these defects seems to be comparable to that of perylene (see IR-spectra Fig.4). Besides perylene exhibits a quite similar fluorescence spectrum but with different band positions. Since the polymerisation process described by YAMAMOTO favors only links in para-position, this defect cannot occur in the PPP-Y.

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