Bull. Chem. Soc. Jpn., 66, 948—954 (1993) [Vol. 66, No. 3

Preparation and Luminescence Properties of Organic Thin Films Obtained by Vacuum Deposition of Poly(*p*-phenylene) Synthesized by Various Chemical Methods

Naoki TOSHIMA* and Toshihide ASAKURA
Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

(Received October 12, 1992)

Various organic thin films were obtained by vacuum deposition of poly(*p*-phenylene) (PPP) synthesized by three different methods: Grignard coupling of *p*-dibromobenzene (PPP-Y), and two kinds of oxidative cationic polymerization of benzene (PPP-K by a $CuCl_2$–$AlCl_3$ system and PPP-T by a CuCl–$AlCl_3$–O_2 system). The IR absorption band at 760 cm^{-1}, which is attributed to a mono-substituted benzene ring, was stronger for the PPP thin films than that for the original PPP. The deposited thin films were partially soluble in THF and chloroform. The electronic absorption spectra of the PPP-K and the PPP-T thin film solutions had shoulders near 410 nm, while that of the PPP-Y film did not. The emission spectra had a peak at 375 nm for the PPP-K and the PPP-Y solutions. In contrast, the PPP-T solution had emission peaks at 465 and ca. 500 nm in addition to a peak at 380 nm, and the excitation spectrum for the peak at 465 nm was quite different from that for the peak at 380 nm. As for thin films, the PPP-K and the PPP-Y had emission peaks at 400—500 nm, while the PPP-T had an emission peak at 615 nm in addition to the peaks at 400—500 nm. The difference in the emission spectra is discussed in terms of the difference in contaminating by-products in the corresponding PPP.

Recently, conducting polymers such as poly(acetylene), poly(*p*-phenylene), poly(pyrrole), poly(thiophene), and poly(aniline) have attracted considerable attention as one of the organic materials for electronics. These are useful as the materials for secondary batteries, electronic devices, indicative elements, chemical sensors, functional electrodes, etc.[1]

Poly(*p*-phenylene) (PPP), one of the conducting polymers, has superior heat resistibility and high electrical conductivity upon doping (500 S cm^{-1}, as doped by AsF_5).[2] The methods used to synthesize PPP can be roughly classified into two groups, i.e., chemical[3—5] and electrochemical methods.[6] The benefit of the chemical method is that PPP is easy to synthesize on a large scale. Especially, in the method which the present authors have recently developed, PPP can be obtained on a large scale by using a smaller amount of catalyst than the conventional method.[3] The PPP synthesized by the chamical methods, however, is hard to handle. It is dufficult to take advantage of the properties of PPP as a macromolecule because PPP is usually obtained in the form of insoluble and unprocessable powder by the chemical methods. On the other hand, PPP which is synthesized by the electrochemical method is obtained in the form of a film. In this method, however, it is not easy to synthesize PPP on a large scale by the ordinary way. A specially-designed technique is required to obtain PPP electrochemically on a large scale.

A vacuum deposition method to obtain inorganic thin films by a dry process has made progress with the development of semiconducting devices in the past twenty years. The preparation of organic thin films by a dry process has been investigated from the viewpoint of application to devices. The organic thin film made by the vacuum deposition method is suitable for manufacturing electronic devices. Organic thin films of polymers,[7] especilly of PPP which was synthesized by chemical methods,[8,9] was already obtained by this method. In the latter reports, it was proposed that the PPP molecules in the thin film are oriented perpendicularly to the surface of a substrate. The physical properties of the thin film, however, have not been reported yet.

Compared with the film synthesized by an electrochemical wet process, the organic thin film obtained by the vacuum deposition dry process is expected to have great advantages in the production of electronic devices. Because of the potential conjugation of benzene rings, PPP is also expected to have special physical properties. Thus, it is very important to obtain precise information on the physical properties of a PPP thin film. For example, the photoluminescence property of PPP powder was already reported.[10] However, the same property of a PPP thin film has not been reported yet to the best of our knowledge.

In this paper, organic thin films were obtained by vacuum deposition from three kinds of PPP powder, which were synthesized by three different chemical methods. The IR spectra of the obtained thin films imply that the molecular weight of the PPP, of which the thin films consist, is lower than that of the source materials. Further, it was revealed that the existence of by-products in the PPP powder affects the luminescent behavior of the thin film obtained from the powder. The luminescent behavior of the thin film also depends upon the synthetic method of the source material.

Experimental

Preparation of PPP. Three synthetic methods were used for the preparation of the PPP powder, which was

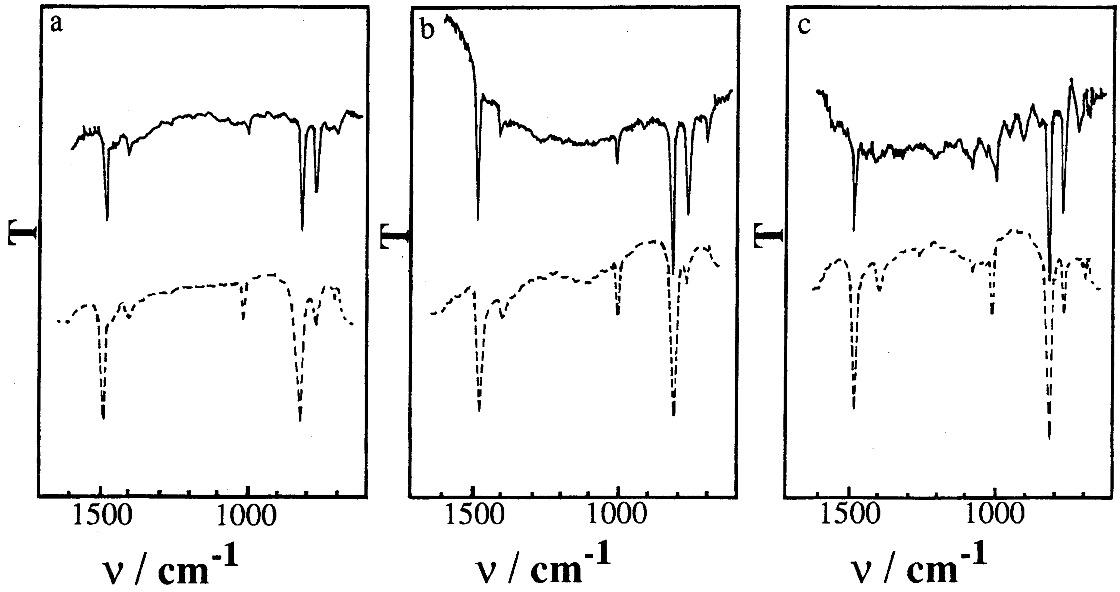

Fig. 1. The IR spectra of the powder (dashed lines) and the FT-IR spectra of the thin films (solid lines) of a) the PPP-T, b) the PPP-K, and c) the PPP-Y. The thin films are deposited on KBr cleaved surfaces.

the source material for thin film preparation. (a) The first method is commonly referred to as Kovacic's method;[3] $AlCl_3$ (33 g) was used as a catalyst and $CuCl_2$ (10 g) as an oxidant. A polymer (3.0 g) was synthesized from benzene (78 g) by an oxidative cationic polymerization. Hereafter, the polymer prepared by this method is referred to as PPP-K. (b) In the second method, which is referred to as Yamamoto's method,[4] p-dibromobenzene (11.2 g) was polycondensed in THF (60 cm^3) by a Grignard coupling reaction with a $NiCl_2$(2,2'-bipyridine) complex (50 mg) as a catalyst, resulting in a polymer (3.6 g) referred to as PPP-Y. (c) The last method has been recently developed by the present authors.[5] By a CuCl (5.0 g)–$AlCl_3$ (20 g)–O_2 catalytic system, benzene (78 g) was polymerized by oxidative cationic polymerization, resulting in a polymer (5.2 g) referred to as PPP-T.

Each PPP powder was purified by stirring in THF for 24 h to remove low-molecular-weight components which are soluble in organic solvents. These three kinds of polymers were characterized as PPP by comparing their IR spectra with the reported one.[11]

Vacuum Deposition. The apparatus used for vacuum deposition was a Shinku-kiko VPC-260F vacuum chamber. A cleaved KBr single crystal was used as a substrate for the preparation of a sample for FT-IR measurement, and nonfluorescent fused quartz was used as a substrate for other spectroscopic measurements. The substrates were held 11 cm above the molybdenum boat used as an evaporation source holder. When the pressure in the bell-jar reached 2×10^{-5} Torr (1 Torr=133.322 Pa) by evacuation, heating of the source was started. The boat was heated at a rate of 1 °C s^{-1} starting from room temperature. In the case of PPP-K and PPP-T, the depositing procedure was stopped when the temperature of the boat reached 680 °C because the vapor pressure decreased at that point and the deposition almost ceased. In the case of PPP-Y, heating was stopped at 480 °C. A PPP thin film of a few thousand Å in thickness was obtained from 50 mg of the source material. The film thickness was measured by an ULVAC CRTM1000 crystal oscillating thickness monitor.

Spectroscopic Measurement. A Shimadzu FTIR-4000 Fourier-transforming IR spectrometer, a Hitachi type 340 self-recording spectrometer, and a Hitachi MPF-4 fluorescent spectrometer were used for the measurement of FT-IR spectra, electronic absorption spectra, and luminescence and excitation spectra, respectively. The excitation spectra were corrected by using a spectrum corrective attachment and Rhodamine B as a photon counter. Each spectroscopic measurement was carried out at room temperature. Fluorescence-spectrum-grade chloroform supplied from Nacalai Tesque, Inc. was used as a solvent for luminescence measurements.

Results

IR Spectra and Solubility of PPP Thin Films. Figure 1 shows the IR spectra of the three kinds of PPP, namely PPP-K, PPP-Y, and PPP-T, in the form of both powder and deposited thin films, respectively. The IR spectra of the thin films deposited on the surfaces of cleaved KBr single crystals showed specific absorption bands at 1480 (corresponding to the ring vibration of a benzene ring), 1000 (corresponding to the C–H in-plane deforming vibration of a benzene ring), and 810 cm^{-1} (corresponding to the C–H out-of-plane deforming vibration of a para-disubstituted benzene ring), which are attributed to PPP.[11] It was confirmed from the spectra that all kinds of PPP could be used as a source material to give an organic PPP thin film by the vacuum deposition technique.

By comparing the IR spectra of the thin films with those of the source powder, information on molecular weight is obtained. The intensity of the peak at 760

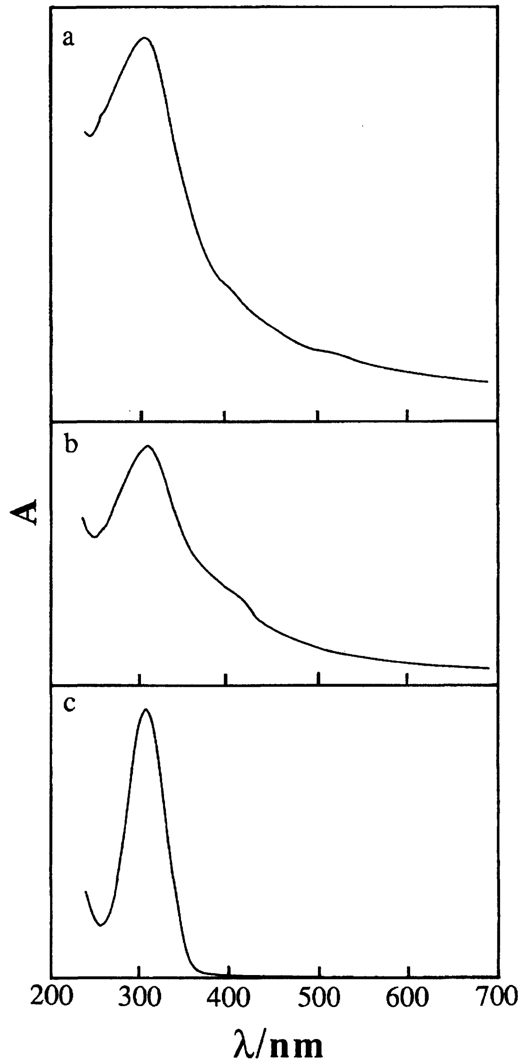

Fig. 2. The electronic absorption spectra of the solutions obtained from a) the PPP-T thin film, b) the PPP-K thin film, and c) the PPP-Y thin film, in chloroform at room temperature.

cm^{-1}, corresponding to the C–H out-of-plane deforming vibration of a mono-substituted benzene ring (the end group of the polymer chain), was compared with that of the peak at 810 cm^{-1}, corresponding to the same vibration of a para-disubstituted benzene ring (inner parts of the polymer chain), in both the thin film and the source powder. The relative intensity of the peak corresponding to the mono-substituent was much stronger in the case of the thin film than that in the case of the powder. In other words, the ratio of the benzene ring at the end of the polymer chain to that in the inner part was higher in the case of the thin film than that in the case of the powder. Therefore, it was supposed that only the components with a low degree of polymerization were evaporated and deposited, or deposition of polymer by heat resulted in a decrease in the degree of polymerization. This trend was observed in all three cases of PPP.

The source material was washed very well with THF and, therefore, contained few THF-soluble components. When the film deposited on a substrate was immersed in THF or chloroform, however, parts of the film could be removed from the substrate, resulting in dissolving in the solvent or forming precipitates in the solvent. This fact also supports our supposition that the deposited PPP contains low-molecular-weight PPP oligomers.

Spectra of the Solutions Obtained from PPP Thin Films. The vacuum-deposited PPP thin films were partially soluble in THF and chloroform, while the PPP powder used as source material was rarely soluble in organic solvents. Figure 2 shows the electronic spectra of chloroform solutions obtained from the three kinds of PPP thin films. In the case of the solution of the PPP-Y thin film, only one peak was observed at 310 nm. On the other hand, in the case of the solutions of the PPP-K and the PPP-T thin films, two shoulder peaks were observed near 410 and 530 nm in addition to the main peak at 310 nm.

The luminescence and the excitation spectra of the chloroform solutions of the PPP thin films are shown in Fig. 3. One peak was observed at 375 nm in the emission spectra of the solutions of the PPP-Y and the PPP-K thin films. The excitation peak for this emission was observed at 305 nm. This wavelength was almost equal to that of the absorption maximum of the solution of the corresponding PPP. On the contrary, the luminescence spectrum of the solution of the PPP-T thin film consisted of peaks at 465 and c.a. 500 nm in addition to that at 380 nm. The excitation peak corresponding to the emission peak at 380 nm was observed at 300 nm, while the excitation peaks for the emission at 465 nm were observed at 266, 338, and 416 nm, which was different from that at 380 nm. This situation was specific for the PPP-T thin film.

Electronic Absorption Spectra of PPP Thin Films. Figure 4 shows the electronic absorption spectra of the PPP-T(a), the PPP-K(b), and the PPP-Y(c) thin films deposited on fused quartz substrates. The electronic spectra of the PPP-T and the PPP-K thin films were quite similar to each other, and mainly consisted of two peaks at ca. 210 and ca. 330 nm. In addition to the main peaks, shoulder peaks were observed at ca. 290 and ca. 410 nm in the spectrum of the PPP-K thin film and ca. 410, ca. 460, and ca. 520 nm for the PPP-T thin film. In the case of the PPP-T, there may have been an additional peak near 290 nm, although it was hidden by the shorter side of the main peak at ca. 330 nm.

The spectrum of the PPP-Y thin film differed a little from the above spectra, consisting of main peaks at 220 and 280 nm. The peak at about 330 nm was unclear. No shoulder peak was observed at wavelenghts longer than 400 nm.

Luminescence and Excitation Spectra of PPP Thin Films. Figure 5 shows the luminescence and the excitation spectra of the three kinds of PPP thin films. Although the emission spectrum of the PPP-T thin film was clear as shown in Fig. 5a, the emission of the PPP-T powder was so weak in intensity that its measurement was rather difficult. Thus, the emission maximum of the PPP-T powder was detected to be at 670 nm with very weak bands at ca. 430 and ca. 470 nm. The luminescence spectrum of the PPP-T thin film resembled that of the powder and consisted of the maximum at 615 nm. Much weaker bands were also observed at 437 and 466 nm as in the case of the powder. Two peaks were observed at ca. 270 and ca. 320 nm in the excitation spectrum.

The emission spectrum of the PPP-K powder consisted of a maximum peak at 600 nm, peaks with medium intensity at 435 and 458 nm, and shoulders at ca. 490 and ca. 520 nm. This spectrum was quite similar to that already reported,[10] although the maximum wavelength was a little shorter in the present case than in the reported case. On the other hand, in the luminescence spectrum of the PPP-K thin film shown in Fig. 5b, a maximum at 488 nm and shoulders at 425 and 453 nm were observed. Surprisingly, no peak was detected at 600 nm in the case of the thin film. The excitation spectrum consisted of peaks at ca. 270 and ca. 340 nm. The excitation spectrum of the PPP-T thin film (corresponding to the emission at 645 nm) and that of the PPP-K thin film (corresponding to the emission at 488 nm) resembled each other in spite of the difference in the emission wavelength.

The emission spectrum of the PPP-Y powder consisted of peaks at 456 and 484 nm, and shoulders at ca. 430 and ca. 520 nm. This spectrum was similar to that already reported.[10] In the emission spectrum of the PPP-Y thin film shown in Fig. 5c, two peaks were observed at 425 and 452 nm. The emission maximum of the thin film was different in wavelengh from that of the powder, and the emission intensity of the thin film was stronger than that of the powder. The excitation spectrum of the PPP-Y thin film consisted of peaks at 235 and 277 nm, and a shoulder at ca. 370 nm.

Discussion

Decrease of Molecular Weight by Vacuum Depositon. It has been proposed that the C–C bond of an organic polymer is cleaved by heat to form corresponding oligomers with lower molecular weight than the original polymer, and the resulting oligomers then evaporate by vacuum to deposit on a substrate.[7] Another possibility is that a polymer dissociates by bond cleavages into monomers, which evaporate and re-polym erize on a substrate to form a thin film of the polymer. The fact that a tacticity change is not observed in vacuum deposition of polystyrene,[12] however, implies that the polystyrene does not dissociate into monomers but into oligomers, which evaporate to produce the thin film of the polystyrene.

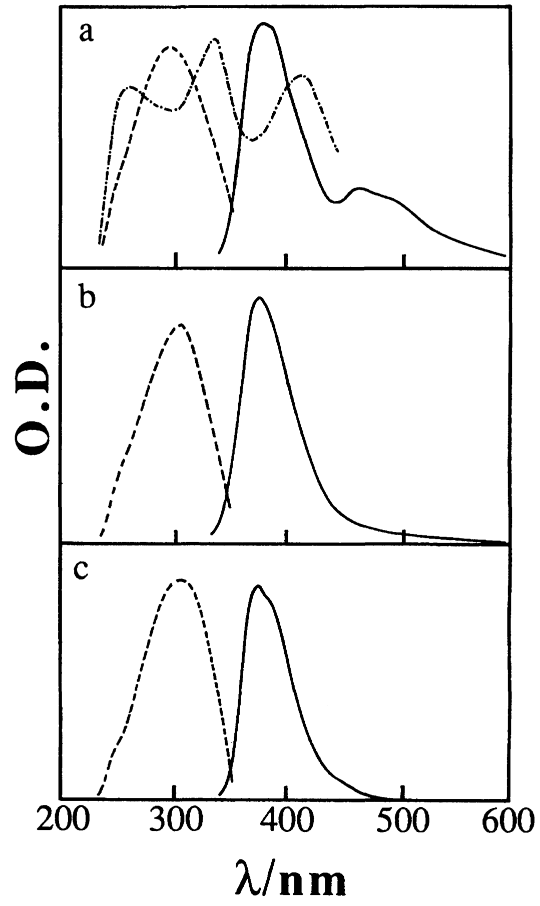

Fig. 3. The photoluminescence spectra (solid lines) and their excitation spectra (dashed lines) of the solutions obtained from a) the PPP-T thin film ($\lambda_{\mathrm{ex}}=300$ nm, $\lambda_{\mathrm{em}}(---)=380$ nm, $\lambda_{\mathrm{em}}(-\cdot-)=465$ nm), b) the PPP-K thin film ($\lambda_{\mathrm{ex}}=305$ nm, $\lambda_{\mathrm{em}}=375$ nm), and c) the PPP-Y thin film ($\lambda_{\mathrm{ex}}=305$ nm, $\lambda_{\mathrm{em}}=375$ nm) in chloroform at room temperature.

In the present case of PPP, the source material is estimated not to be contaminated with low molecular weight components, which have been removed by washing the source material with THF. Therefore, the fact that the thin film becomes partially soluble in organic solvents clearly demonstrates the bond cleavage by vacuum deposition, resulting in a decrease in molecular weight.

Furthermore, an increase in the spin density of PPP by vacuum deposition also supports the above consideration. The ESR spectra of PPP-Y, PPP-K, and PPP-T, in both the thin film and the powder forms, were measured by using a JEOL JES-PE-1 ESR spectrometer. 2,2-Diphenyl-1-picrylhydrazyl (DPPH) was used as a standard for spin density. By assuming the linearity of the height in the ESR signal to the number of radicals, the spin density of the PPP was roughly estimated. In the case of PPP-Y, the spin density of the source powder is low at 1.3×10^{15} spins/g, which in-

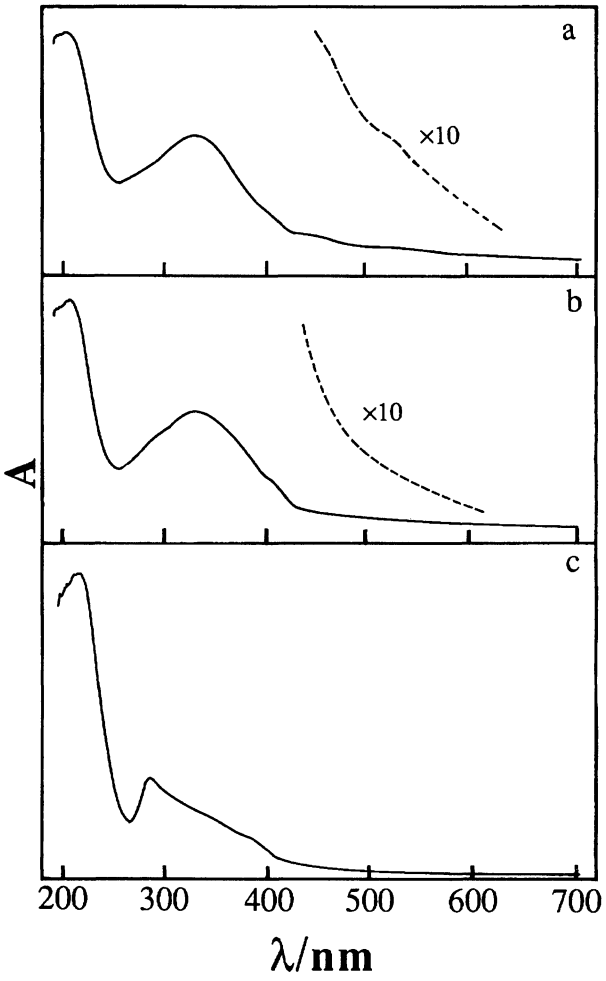

Fig. 4. The electronic absorption spectra of a) the PPP-T thin film, b) the PPP-K thin film, and c) the PPP-Y thin film deposited on fused quartz substrates at room temperature. The dashed lines show the 10-times-enlarged spectra.

creases to 5.1×10^{16} spins/g for the thin film. This fact suggests that the number of radicals increases by bond cleavege, which supports the above concepts of the decrease in molecular weight by bond dissociation. On the other hand, the spin density values of the two thin films obtained from PPP-K and PPP-T, whose original values are high at 6.3×10^{17} and 2.1×10^{18} spins/g for PPP-K and PPP-T, respectively, decrease to 1.2×10^{17} and 4.1×10^{17} spins/g, respectively. Even if this seems to be contrary to the above concept, it can also be explained by bond dissociation as follows. PPP-K and PPP-T originally have a large number of radicals. If the bonds cleave and the chain length of the molecule becomes shorter, then the radicals become unstable and form bonds by coupling to each other, resulting in a decrease in the spin density.

The polymerization degrees of the PPP-K and the PPP-T powder used as source material are proposed to be 15[13] and a little lower than that,[5] respectively. The average degree of polymerization is calculated to be 16 for the PPP-Y powder from the C/Br ratio (49) in elemental analysis, assuming that unreacting Br atoms still remain at both ends of the polymer chain. Concerning the thin films, the polymerization degree is estimated to be about 10 comparing the intensity ratio in the IR spectra of the PPP thin films with that of the hexamer of benzene (*p*-sexiphenyl) as a standard. Therefore, the polymerization degree decreases from 15—16 to about 10 by vacuum deposition.

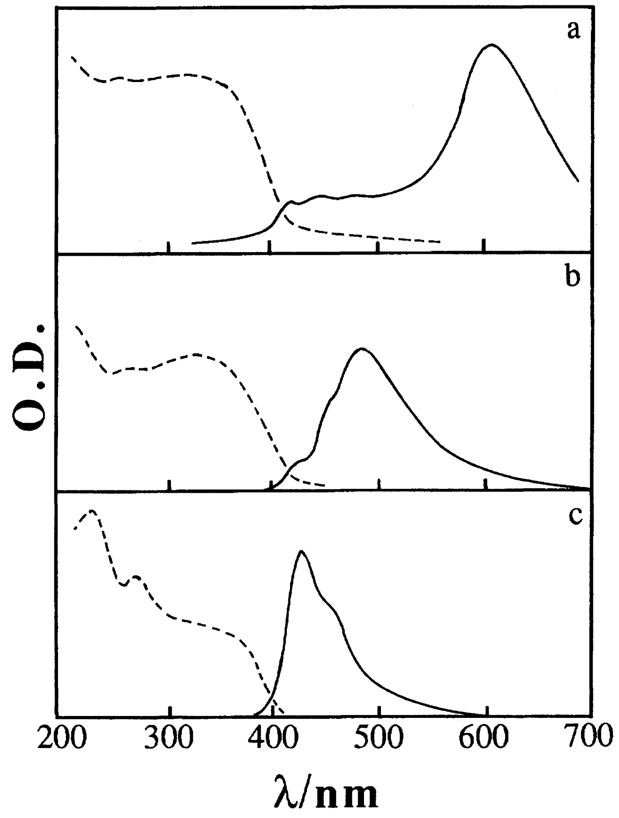

Fig. 5. The photoluminescence spectra (solid lines) and their excitation spectra (dashed lines) of a) the PPP-T thin film ($\lambda_{ex}=280$ nm, $\lambda_{em}=615$ nm), b) the PPP-K thin film ($\lambda_{ex}=280$ nm, $\lambda_{em}=488$ nm), and c) the PPP-Y thin film ($\lambda_{ex}=270$ nm, $\lambda_{em}=425$ nm) deposited on fused quartz substrates at room temperature.

Electronic Spectra of PPP Solutions. The three electronic spectra in Fig. 2 can be classified into two groups. The spectra of PPP-K and PPP-T resemble each other, while that of PPP-Y differs from both. The spectrum of the PPP-Y solution consists of a single peak at 310 nm. On the contrary, the peak at 310 nm becomes broader in the longer wavelength containing shoulder(s) at ca. 410 nm (PPP-K) and at ca. 410 and ca. 530 nm (PPP-T) in the spectra of the PPP-K and the PPP-T solutions, respectively.

The electronic spectra of some para-linked benzene oligomers have been reported.[14] For example, benzene, *p*-terphenyl, and *p*-quaterphenyl have absorption peaks at 254 (39300 cm^{-1}), 277 (35980 cm^{-1}), and 290 nm (34500 cm^{-1}), respectively. The maximum wavelength is shifted longer as the number of benzene rings increases. The band gap of a high polymer (PPP) is estimated to be 340 nm (3.5 eV) on the basis of quantum-chemical calculations.[15] This value is quite similar to the absorption edge of the peak at 310 nm. Based on the above considerations, the absorption spectrum implies that the PPP-Y solution has an ideal structure of PPP. On the contrary, the PPP-K and the PPP-T solutions seem to contain other components besides ideal PPP.

This difference in the electronic spectrum may be caused by a difference in the synthetic method between the two groups. PPP-Y is synthesized by the Grignard coupling reaction of *p*-dibromobenzene, and therefore, is presumed to be the ideal molecular structure of PPP which consists of 1,4-disubstituted benzene rings only. Thus, the peak at 310 nm is estimated to be the photo-absorption peak corresponding to the essential π–π^* electron transition of a PPP π-electron system.

In the case of PPP-T and PPP-K, the situation is different. Because the PPP-T and the PPP-K powders are synthesized by oxidative cationic polymerization of benzene, there is some possibility of forming 1,2-linkages in addition to 1,4-linkages, which leads to intramolecular cross-linkages and then formation of condensed ring structures.[16] Such structures are supposed to be also contained in the thin films obtained from these powders. Thus, the peaks at 410 and 530 nm are speculated to arise from the photo-absorption of such condensed ring molecules (CRM). For example, pyrene has a peak at 351 nm (28500 cm^{-1}) and tetracene at 471 nm (21200 cm^{-1}).[14] These differences in the absorption spectra will also bring about differences in the emission spectrum, which is discussed in the next section.

Luminescence Spectra of PPP Solutions. The luminescence spectra of the PPP thin film solutions, shown in Fig. 3, can be classified into two groups. In the case of the electronic spectrum, PPP-K and PPP-T resemble each other and PPP-Y differs from them. In the case of the luminescence spectrum, however, PPP-Y and PPP-K resemble each other, and PPP-T differs from them. The emission spectra of PPP-Y and PPP-K consist of a single peak at 375 nm, while that of PPP-T has two extra peaks at 465 and ca. 500 nm in addition to the main peak at 380 nm. The peak at 375 nm in the PPP-Y and the PPP-K spectra and that at 380 nm in the PPP-T spectrum are estimated to be essential for the emission of PPP.

The additional two peaks observed at 465 and ca. 500 nm for PPP-T are considered to arise from the CRM contaminating PPP-T. In fact, the excitation spectrum corresponding to the emission at 380 nm for PPP-T has a maximum at 300 nm, which is similar to the cases of PPP-Y and PPP-K. In contrast, a maximum at 416 nm is observed in the excitation spectrum corresponding to the emission peak at 465 nm. This wavelength is almost equal to that of the shoulder peak in the electronic absorption spectrum (cf. Fig. 2a).

It is estimated from the electronic spectrum that the CRM exists in the PPP-K solution, too. The emission spectrum of the PPP-K solution, however, does not contain such a peak as that observed in the emission spectrum of the PPP-T solution. The structure of the CRM of PPP-K is supposed to be so different from that of PPP-T that PPP-K does not give luminescence at longer wavelengths.

Spectra of PPP Thin Films and Powders. The luminescence spectrum of the PPP-Y thin film shown in Fig. 5c is similar to that of PPP-Y powder already reported.[10] In both the thin film and the powder, the luminescence of PPP-Y is speculated to be the emission accompanying the recombination of an electron-hole pair. The splitting of the emission peak is estimated to be due to the vibration of a benzene ring because the energy difference of the splitting peaks is in good agreement with the wavenumber of the IR peak corresponding to the ring vibration, 1480 cm^{-1}.

The luminescence spectrum of the PPP-T thin film (Fig. 5a) is quite different from that of the PPP-Y thin film (Fig. 5c). There is little difference in the luminescence spectrum of PPP-T between the thin film and the powder. The spectra mainly consist of a peak at a wavelength of 600 nm or longer. This peak near 600 nm is also observed in the emission spectrum of the PPP-K powder, which was already reported.[10] The emission spectrum of the PPP-K thin film, however, does not contain this long wavelength peak (Fig. 5b). The emission spectrum of an electrochemically-polymerized PPP film consists of a peak at ca. 600 nm in addition to structured peaks in the wavelength range from 400 to 500 nm, in which an edge excitation red-shift (EERS) effect is observed.[17] In this report, this long-wavelength emission is explained as an emission from a polaron-exciton defect in a PPP polymer chain, and also as the excimer-like emission of a PPP molecule with a variety of configurations to which the EERS effect is attributed.

On comparison of the present results of the luminescence spectra of PPP-Y, PPP-K and PPP-T in both the thin film and the powder forms, the short wavelength emissions in the wavelength range between 400 and 500 nm consisting of several peaks are common for the three kinds of PPP in both the powder and the thin film. It is supposed that the intensity ratio among these peaks varies from one to another depending upon the concentration of by-products, i.e. the CRM. Comparing the luminescence spectra of the PPP thin films, the strongest emission is observed at a short wavelength for PPP-Y, while the strongest is at a long wavelength for PPP-T. PPP-K has the strongest peak at an intermediate wavelength.

In the cases of the PPP-T powder, the PPP-T thin film, and the PPP-K powder, emission is observed at a longer wavelength than 600 nm, which can be attributed to the CRM by-products. PPP-Y does not contain such a by-product, because it is synthesized from *p*-dibromobenzene reacting only at a halogen-substituted position, while PPP-K and PPP-T contain the by-products.$^{5,16)}$ The formation of the by-products is most probable for PPP-T among the PPPs tested in the present investigation. If CRM moieties exist in a PPP polymer chain, then they may work as low energy defects, to which an excited electron transfers resulting in a long wavelength emission. To confirm the above mechanism, co-evaporation of naphthacene with PPP-K has been tried, and the emission spectrum of this thin film has been observed. Although the expected new emission was not observed (the emission spectrum was a mixture of those of naphthacene and PPP-K), the excitation spectrum, corresponding to the emission of naphthacene, was similar to that of PPP-K. Therefore, the energy transfer from PPP to naphthacene is confirmed by the naphthacene-contaminated PPP system.

On the contrary, the PPP-K thin film has no long wavelength emission. This is probably because the original PPP-K powder contains less by-products like CRM than the PPP-T powder, and these molecules will be scattered out in the course of vacuum deposition resulting in their absence in the thin film. The intensity ratio of the short-wavelength emission to the long-wavelength emission implies that the PPP-K powder contains less by-products tnan the PPP-T.

The absence of an EERS effect in the spectra of the PPP-Y, the PPP-K, and the PPP-T thin films as well as the similarity of the excitation spectra to the absorption spectra also supports the mechanism described above.

Conclusion

1. The polymerization degree of PPP in the thin film is estimated to be about 10, which is lower than that of the source materials. This decrease is attributed to the C–C bond cleavage in the polymer, which occurs by heat treatment in the course of vacuum deposition.

2. The luminescence spectra of the PPP-Y and the PPP-K solutions consist of a peak at 376 nm, while that of the PPP-T solution contains peaks at 465 and ca. 500 nm in addition to the main peak at 380 nm. In the form of the thin film, in contrast, PPP-Y and PPP-K have emission peaks at 400—500 nm, while PPP-T has a long-wavelength (longer than 600 nm) emission peak besides the peaks at 400—500 nm.

3. The absorption spectra as well as the luminescence and the excitation spectra in the PPP-K and the PPP-T thin films reveal the presence of by-products such as condensed ring molecules (CRM) which are produced in the course of the PPP synthetic procedure. The by-products contained in the PPP-T thin film have luminescent properties, while those in the PPP-K thin film do not.

4. The long-wavelength luminescence, which is specific to the PPP-T thin film, can be explained as the emission from the defects, which are produced by by-products like CRM, and into which the electron could transfer from the excited state of PPP.

5. Under the above concept, a new disign principle of a thin film can be developed. Co-evaporation of PPP and another luminescent material, which has a longer wavelength emission than PPP, can give a thin film with a new emission spectrum, which differs from either that of PPP or that of the co-evaporating material. Here, the bulk of PPP functions as a light-absorbing matrix, and the energy transfers from the excited PPP molecule to the defect produced by the co-existing material. Then, the photo-emission from this defect may give a new emission spectrum.

References

1) For example: N. C. Billingham and P. D. Calvert, “Conducting Polymers/Molecular Recognition (Advances in Polymer Science 90),” Springer-Verlag, Berlin (1989), pp. 85—89; G. Grem, G. Leditzky, B. Ullrich, and G. Leising, *Adv. Mater.*, **4**, 36 (1992).

2) D. M. Ivory, G. G. Miller, J. M. Sowa, L. W. Shacklette, R. R. Chance, and R. H. Baughmann, *J. Chem. Phys.*, **71**, 1506 (1979).

3) P. Kovacic and A. Kyryakis, *J. Am. Chem. Soc.*, **85**, 454 (1963).

4) T. Yamamoto and A. Yamamoto, *Chem. Lett.*, **1977**, 353.

5) N. Toshima, K. Kanaka, A. Koshirai, and H. Hirai, *Bull. Chem. Soc. Jpn.*, **61**, 2551 (1988).

6) M. Satoh, M. Tabata, K. Kaneto, and K. Yoshino, *J. Electroanal. Chem. Interfacial Electrochem.*, **195**, 203 (1985).

7) M. Ashida, Y. Ueda, and T. Watanabe, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 179 (1978).

8) M. Komakine, T. Namikawa, and Y. Yamazaki, *Makromol. Chem., Rapid. Commun.*, **7**, 139 (1986).

9) T. Yamamoto, T. Kanbara, and C. Mori, *Chem. Lett.*, **1990**, 1211.

10) A. Heim, G. Leising, and H. Kahlert, *J. Lumin.*, **31—32**, 573 (1984).

11) R. C. Doss and P. W. Solomon, *J. Org. Chem.*, **29**, 1567 (1964).

12) S. Tanishima, Thesis for Masters Degree of the Faculty of Engineering, The University of Tokyo, 1989.

13) M. B. Jones, P. Kovacic, and D. Lanska, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 89 (1981).

14) J. B. Birks, “Photophysics of Aromatic Molecules,” in “Wiley Monographs in Chemical Physics,” Wiley & Sons, Ltd., New York (1970), pp. 70—75.

15) J. L. Brédas, R. R. Chance, R. Shilbey, G. Nicolas, and Ph. Durand, *J. Chem. Phys.*, **77**, 371 (1982).

16) C. E. Brown, P. Kovacic, C. A. Wilkie, R. B. Cody, Jr., and J. A. Kinsinger, *J. Polym. Sci., Polym. Lett. Ed.*, **23**, 453 (1985).

17) J. J. Aaron, S. Aeiyach, and P. C. Lacaze, *J. Lumin.*, **42**, 57 (1988).