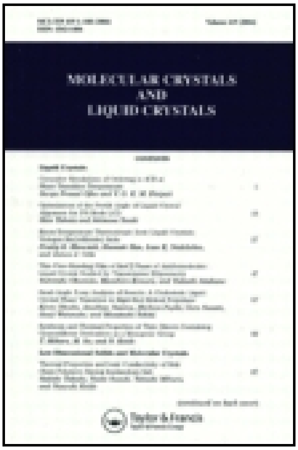

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The Photoluminescence Properties of Vinylcarbazole - Vinylimidazole Copolymer Thin Films

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The Photoluminescence Properties of Vinylcarbazole – Vinylimidazole Copolymer Thin Films

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In our work we obtained the white light emitting material by copolymerization of vinylcarbazole with vinylimidazole. The ratio of vinylcarbazole to vinylimidazole comers in the obtained copolymer (PVKI) was 4:3. This article is concerned with the photoluminescence (PL) study of PVKI thin films deposited on the glass substrate by the dip-coating method. The obtained results were compared with the photoluminescence of thin films of poly (N-vinylcarbazole) (PVK) and poly (N-vinylimidazole) (PVI) deposited by the same technique. All PL spectra have been measured under steady state excitation ($\lambda = 325\,nm$) in the temperature range from 13 K to 325 K.

Keywords: copolymer; photoluminescence; PVI; PVK; vinylcarbazole; vinylimidazole

INTRODUCTION

Polymers are attractive materials because of their potential applications in optoelectronic devices and therefore their optical and electrical properties are extensively studied. One of the most important advantages of these materials is an ease of modification of their optical features by substitution of side groups in polymers or copolymerization. The applicability of these compounds in optoelectronic devices such as polymer light emitting devices (PLED) depends on the emission properties. One of the most intensively studied materials, being the base of PLEDs, is poly (N-vinylcarbazole) (PVK) [1–7]. This polymer has many advantages such as good chemical and thermal stability

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as well as high efficiency of fluorescence [8]. However, the emission of light in the PVK is mainly in the blue light region (maximum at 380–410 nm) [9,10], therefore for some applications, it should be interesting to modify its optical features to obtain a white light emission [11]. One of the possibilities is the substitution of some elements such as Cl or Br in positions 3 and 6 of carbazole ring [1]. The other useful way is copolymerization of vinylcarbazole with different monomers [12]. Since polymers should be used in many applications as thin films, the research of them in this form is very important. Despite the wealth of studies in this field, the knowledge about photophysical properties of the polymer thin layers is still rather limited and many questions remain unanswered. The understanding of the fundamental processes occurring in the polymer thin layers is crucial for the improvement of their properties and the development of their applications.

In our work we obtained the white light emitting material (PVKI) by copolymerization of vinylcarbazole with vinylimidazole. We studied the photoluminescence properties of PVKI as well as PVK and poly (N-vinylimidazole) (PVI) thin layers deposited on the glass substrate. All measurements were carried out at the temperature range from 13 K to 325 K.

EXPERIMENTAL

The pure vinylcarbazole and vinylimidazole materials as well as PVK and PVI were purchased from Aldrich Chemical Co. and used as received. The vinylcarbazole – vinylimidazole copolymer (PVKI) was polymerized by using azo-iso-butyronitrile (AIBN) as an initiator. The vinylcarbazole (0.2 mol) and vinylimidazole (0.1 mol) were dissolved in 6 ml of benzene and poured in the glass flask with 120 ml of benzene at 78°C. After 20 min. the AIBN (1.55×10^{-3} mol) was introduced into the flask. The reaction was carried out under nitrogen atmosphere for 6 hour. The copolymer was precipitated from methanol and dried at 105°C. The pastelike product was collected and thoroughly washed with benzene and methanol. The chemical structure of the obtained copolymer was confirmed on the basis of ^{13}C-NMR and IR analysis. The obtained ratio of vinylcarbazole to vinylimidazole comers in the copolymer was equal 4:3. The chemical structures of all studied polymers are shown in Figure 1.

The PVK, PVI and PVKI layers were dip-coated on the glass substrates from the solution containing 10 mg of polymer (or copolymer) in 1 ml of chloroform. Then, the layers were dried at the room temperature under nitrogen atmosphere. Finally, the samples were heated at temperature which was 5°C higher than the boiling point of the solvent.

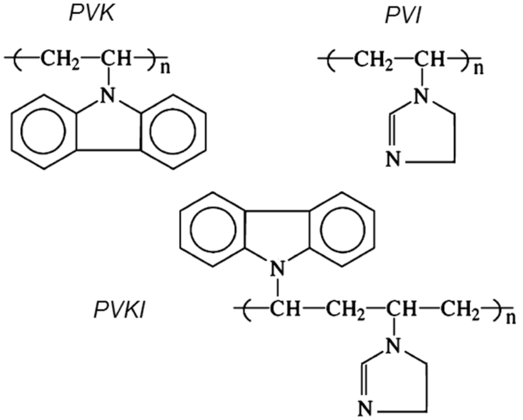

FIGURE 1 Chemical structure of the PVK, PVI and PVKI.

The photoluminescence (PL) spectra were measured using the Omnichrome He-Cd laser ($\lambda = 325$ nm, 42 mW) as an excitation source and the photomultiplier (R-928 HAMAMATSU) as a photodetector. The prism monochromator SPM-2 (Carl Zeiss Jena) was applied for spectral selection. The PL spectra of thin layers were measured in the temperature range from 13 K to 325 K using the helium refrigerator (Cryogenic Inc). The samples were placed in the closed cycle He cryostat (HC2-APD Cryogenics Inc.) and the temperature was controlled exact to 0.1 K. A more detailed description of PL experimental set-up is elsewhere [13].

RESULTS AND DISCUSSION

The PL spectrum of PVKI copolymer thin layer, measured at 300 K, is presented in Figure 2. This spectrum has the strong high-energy peak centred at 2.9 eV and the low-energy broad band positioned about 2.4 eV. These two bands result in the intense white emission. Such character of this spectrum is attributed to the carbazole and imidazole groups present in the PVKI chain. It is confirmed by comparison of the copolymer emission with the PL spectra of PVK and PVI thin films, which are also presented in Figure 2. The high-energy band of the PVKI spectrum and the main PVK peak (centred at 2.97 eV) are overlapped. Moreover, the position of the PVKI low-energy band is in agreement with the maximum of the PVI spectrum which is situated at 2.32 eV. Thus, the PVKI photoluminescence spectrum consists of the high-energy carbazole band and the low-energy imidazole band.

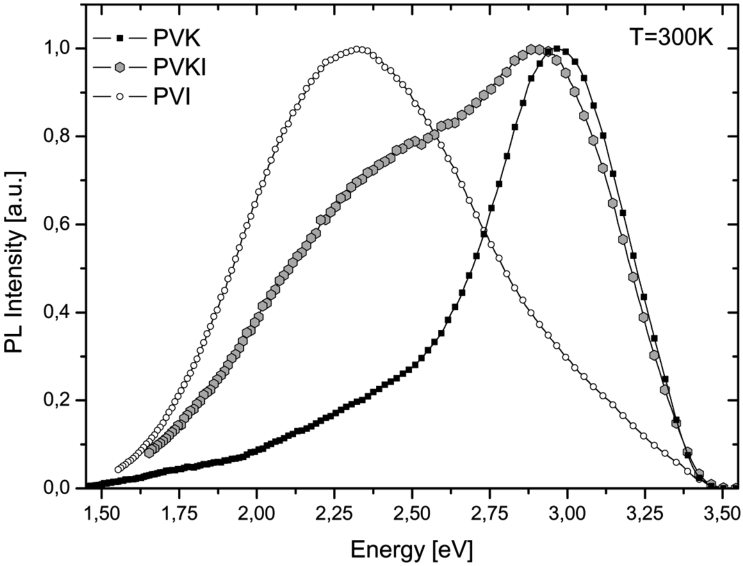

FIGURE 2 Photoluminescence spectra of PVKI (grey circle), PVK (square) and PVI (white circle) thin layers at room temperature (300 K).

The photoluminescence properties of PVKI were found to be strongly dependent on temperature from 13 to 325 K. A set of PL spectra of the PVKI thin layer as a function of temperature is presented in Figure 3. The spectrum at the lowest temperature (13 K) has the major maximum centred at 3.13 eV and the tail extending to 1.6 eV. Moreover the small peak at 2.02 eV was observed. Since this peak is relatively narrow and shifted to lower energy relative to the main band, we suppose that it is attributed to the defect state created in the thin film. It is commonly known that such narrow lines, connected with defects, appear usually at low temperatures in various organic solids [14]. At higher temperatures this line merges with other stronger band appearing above 150 K. It is clearly visible in Figure 3 that the PL intensity of the carbazole band is quenched when the temperature increases from 13 to 80 K. Next the emission in the whole investigated spectral range rises up to 250 K. In this range the broad imidazole band appears distinctly at 175 K. Above 250 K the intensity of the whole spectrum diminishes again. These changes are clearly visible in the inset of Figure 3 where the overall intensity versus temperature is shown. The other feature of the PL temperature evolution (see Fig. 3) is the red-shift of the carbazole band. It is illustrated in Figure 4 where the normalized PL spectra of PVKI, measured at 13 K

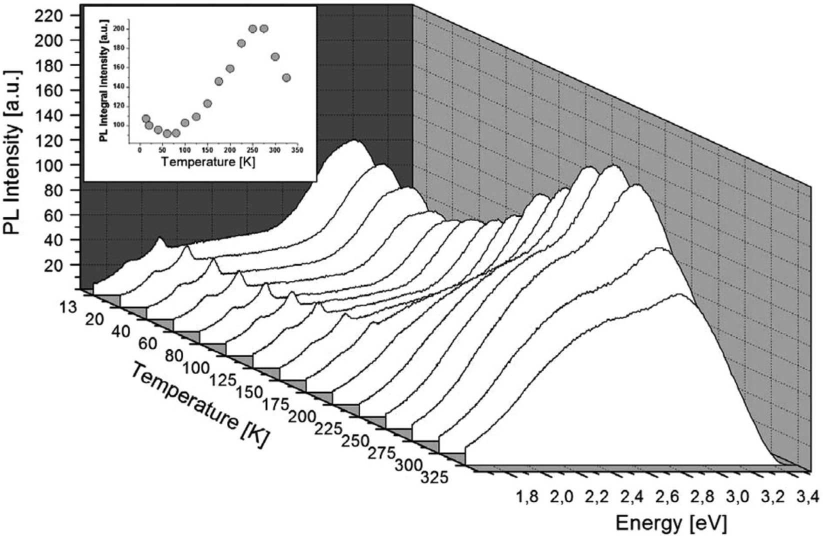

FIGURE 3 Photoluminescence spectra of PVKI thin layer at various temperature from 13 K to 325 K and the temperature dependence of PL integral intensity (in the inset).

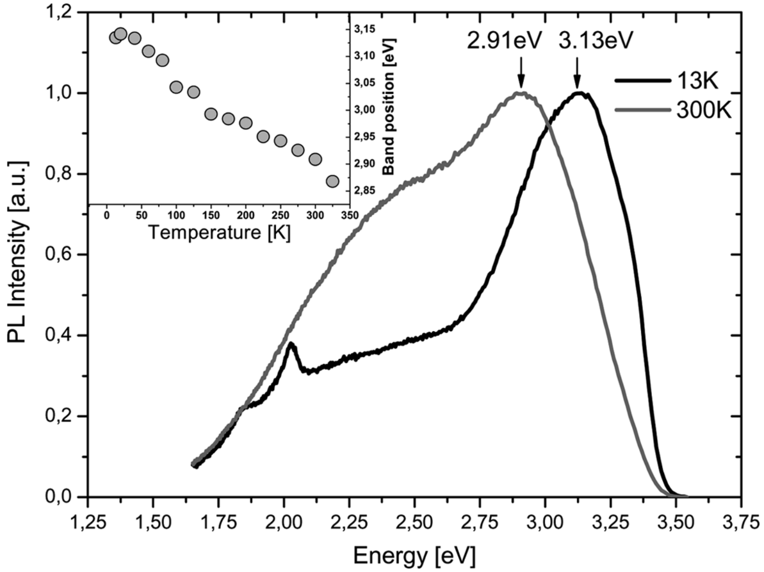

FIGURE 4 Normalized photoluminescence spectra of PVKI thin layer at 13 K and 300 K. In the inset is temperature dependence of PL maximum position.

and 300 K, are compared. The maximum of the carbazole peak relocates from 3.13 eV at 13 K to 2.91 eV at 300 K. This shift is separately shown in the inset of Figure 4. In order to explain the observed emission properties of PVKI at different temperatures, the corresponding spectra of the PVK and PVI thin layers deposited on the glass substrate were measured.

The PL spectra of PVK thin layer at different temperatures are shown in Figure 5. They are characterized by the broad peak which varies from 3.03 to 2.96 eV in the studied temperature range. This band originates from the low-energy intrachain excimer recombination [15,16]. The excimer state arises when two interacting carbazole pendant groups, one of which is electronically excited, achieve an overlapping and form a sandwichlike configuration [17]. It is evident from Figure 5 that the integral intensity of PVK spectra decreases monotonically when the temperature rises. This thermal quenching of luminescence is separately shown in the inset of Figure 5. The reduction of emission is mainly caused by the increase of nonradiative transitions probability at higher temperatures. Moreover, when the temperature increases, the red-shift of the main band is observed (see inset of Fig. 6). It is typical of many organic materials [14], where additional interactions at higher temperature cause the

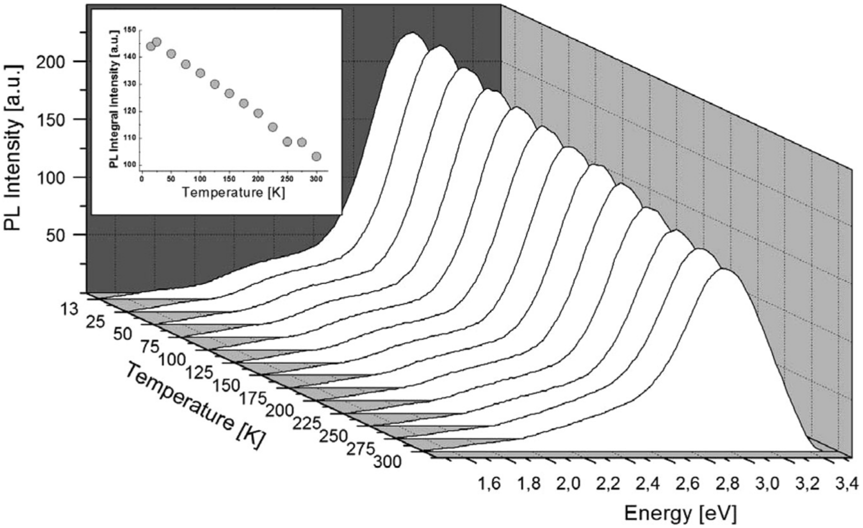

FIGURE 5 Photoluminescence spectra of PVK thin layer at various temperature from 13 K to 300 K and the temperature dependence of PL integral intensity (in the inset).

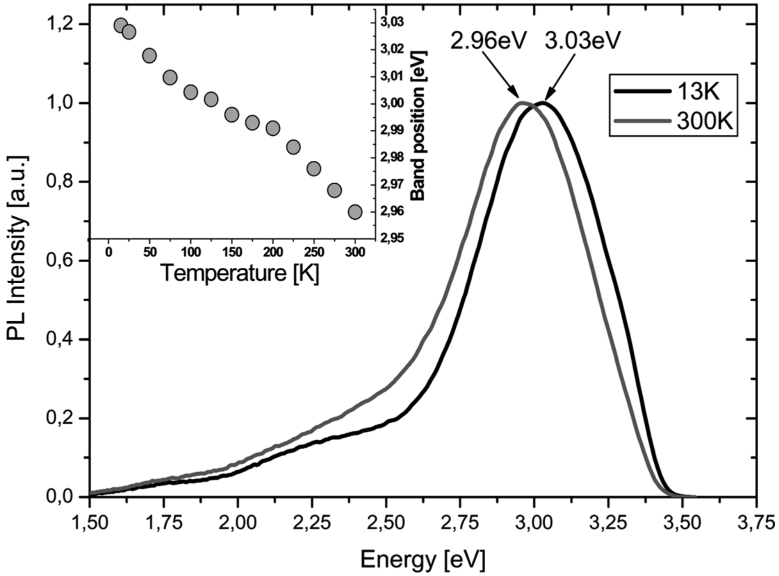

FIGURE 6 Normalized photoluminescence spectra of PVK thin layer at 13 K and 300 K. In the inset is temperature dependence of PL maximum position.

decrease in optical gap. In spite of the observed changes of intensity and position, the shape of PVK emission is invariable in the whole temperature range. This claim is confirmed by the fact that the normalized PL spectra at 13 K and 300 K are very similar (see Fig. 6). Thus, the mechanism of PVK emission stays unchanged in the measured temperature range.

The different temperature dependences were observed in the PVI thin layers. The very broad unstructured spectrum observed at all temperatures (see Fig. 7) shows that the PVI emission is probably connected with the excimers formation from the interacting neighbouring imidazole groups similarly to the carbazole excimers in PVK. However, the shape of the PVI spectrum changes when temperature rises in contrast to the PVK film. It is clearly seen in Figure 8 where the normalized photoluminescence spectra of PVI thin layer at 13 and 300 K are compared. We found that the high-energy part of spectrum is quenched at room temperature whereas the low-energy band is relatively enhanced. Such behaviour can be explained by the existence of two types of imidazole excimers with the different geometrical conformation. At the lowest temperatures the emission is mainly attributed to the high-energy excimer

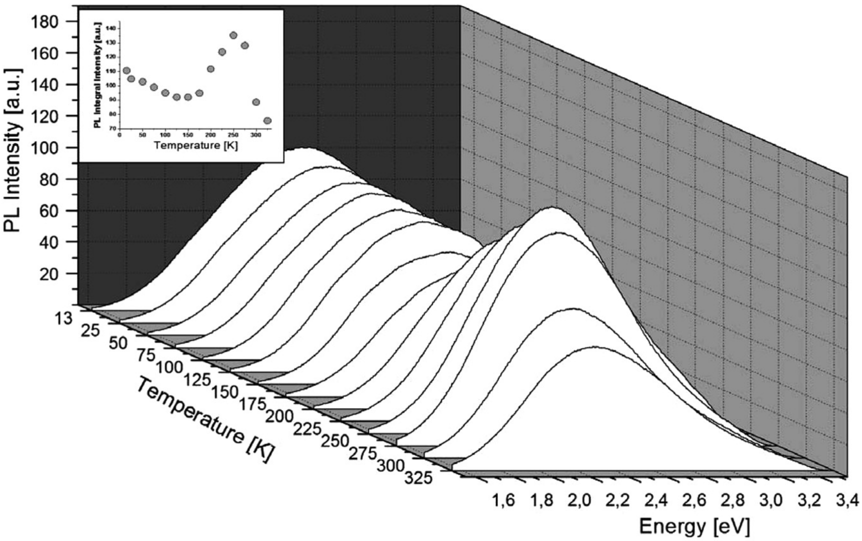

FIGURE 7 Photoluminescence spectra of PVI thin layer at various temperature from 13 K to 325 K and the temperature dependence of PL integral intensity (in the inset).

however at higher temperatures the small barrier between these two states can be overcome and the energy transfer to the low-energy excimer occurs. Thus, the observed red-shift of the whole spectrum is connected rather with this process than the move of the single excimer band like in PVK. Therefore, the position of PL maximum of PVI spectrum versus temperature, presented in the inset of Figure 8, exhibits somewhat different character than analogous one in PVK (see Fig. 6). Moreover, the integral PL intensity changes non-monotonically when the temperature increases. This fact is illustrated in Figure 7 where the PVI emission spectra measured at different temperatures are shown. In addition, the overall intensity versus temperature is drawn in the inset of Figure 7. It is evident that the intensity of the whole spectrum decreases from 13 K to 150 K. Next it increases up to 250 K and diminishes again with rising temperature. Such non-monotonic temperature dependence can be connected with the change of the excimer association probability. We suppose that the geometry of the polymer chains is conducive to the excimer association in certain temperature range (150 K–250 K) whereas this process can be inhibited at different temperatures (13 K–150 K). It is necessary to notice that the typical thermal

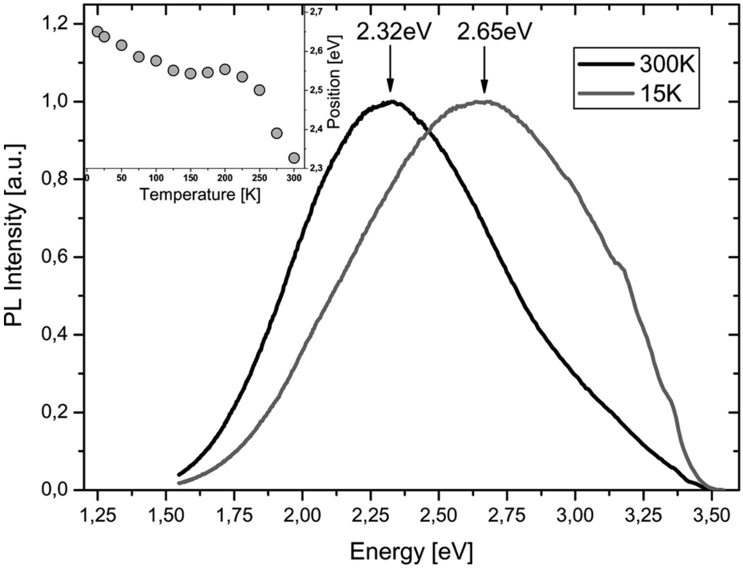

FIGURE 8 Normalized photoluminescence spectra of PVI thin layer at 13 K and 300 K. In the inset is temperature dependence of PL maximum position.

quenching, which was observed in the PVK layers, occurs also in the PVI films. However, its influence on the temperature dependence of PL intensity is not as significant as the conformational changes.

In the light of above results it is possible to propose the explanation of the PVKI copolymer emission properties. From Figure 3 and Figure 7 it is evident that the temperature dependence of the integral PL intensity for PVKI and PVI are very similar. Thus, we concluded that this feature of PVKI emission is mainly determined by the presence of the imidazole groups in the copolymer chain. It is interesting that the carbazole band of PVKI spectrum also exhibits the same behaviour when the temperature is changing, whereas this band, in case of PVK emission, diminishes monotonically with the increase of temperature. It just goes to show that the probability of the carbazole excimer association is strictly connected with the existence of the imidazole groups in the copolymer. On the other hand the red-shift of the carbazole excimer band, presented in the inset of Figure 6 is very similar to that observed for PVKI spectra (see Fig. 4). On this basis we are able to claim that the mechanism of the observed shift is attributed to changes occurring within the confines of the carbazole excimer and is not connected with the whole copolymer chain geometry.

SUMMARY

We presented the systematic study of photoluminescence properties of vinylcarbazole-vinylimidazole copolymer as well as poly(N-vinylcarbazole) and poly(N-vinylimidazole) thin layers deposited on the glass substrate. We observed that the obtained copolymer films exhibit the strong white emission at room temperature. This feature is the resultant recombination of the carbazole and imidazole excimers arising in the copolymer chains. It was found that the emission of PVKI layer is dependent on the temperature. We observed that the integral emission is especially affected by the temperature and reveals the non-monotonic character. On the basis of results obtained for corresponding PVK and PVI layers, we concluded that this feature is attributed to the imidazole groups in the copolymer, which significantly influence on the conformational properties of the chain and thereby determine the probability of carbazole and imidazole excimer association. On the other hand we found that the position of the carbazole band in PVKI spectrum is independent on the presence of the imidazole group and the observed red-shift is attributed to the change of interaction inside the carbazole physical dimer when the temperature increases.

REFERENCES

[1] Byun, H. Y., Chung, I. J., Shim, H. K., & Kim, C. Y. (2004). *Chem. Phys. Lett.* , *393*, 197.
[2] Kido, J., Shionaya H., & Nagai K. (1995). *Appl. Phys. Lett.*, *67*, 2281.
[3] Kusano, H., Shiraishi, N., Hosaka, S., Kuruma, I., Kitagawa, M., Ichino, K., & Kobayashi, H. (1997). *Synth. Met.*, *91*, 341.
[4] Morila, D., Kitagawa, M., Kusano, H., Kawakami, S., Isushima, T., Sawada, T., Hatano, K., Hirooka, K., & Kbayashi, H. (2000). *Synth. Met.*, *111–112*, 217.
[5] Sanetra, J., Bogdał, D., Nizioł, S., Armatys, P., & Pielichowski, J. (2001). *Synth. Met.*, *121*, 1731.
[6] Ouro Djobo, S., Bernede, J. C., & Marsillac, S. (2001). *Synth. Met.*, *122*, 131.
[7] Nam, N. P. H., Cha, S. W., Kim, B.-S., Choi, S.-H., Choi, D. S., & Jin, J.-I. (2002). *Synth. Met.*, *130*, 271.
[8] Kido, J., Hongawa, K., Okuyama, K., & Nagai, K. (1993). *Appl. Phys. Lett.*, *63*, 2627.
[9] Rębarz, M., Dalasiński, P., Bała, W., Łukasiak, Z., Wojdyła, M., & Kreja, L. (2005). *Opt. Appl.*, *35*(3), 407.
[10] Liang, C., Li, W., Hong, Z., Liu, X., Peng, J., Liu, L., Lu, Z., Xie, M., Liu, Z., Yu, J., & Zhao, D. (1997). *Synth. Met.*, *91*, 151.
[11] Thompson, J., Blyth, R. I. R., Mazzeo, M., Anni, M., Gigli, G., & Cingolani, R. (2001). *Appl. Phys. Lett.*, *79*(5), 560.
[12] Wang, D., Hong, Z., Ma, D., Zhao, X., Wang, L., Lu, S., Minami, N., Takada, N., Ichino Y., Yase, K., Jing, X., & Wang, F. (1999). *Synth. Met.*, *102*, 1132.
[13] Dalasiński, P., Łukasiak, Z., Rębarz, M., Wojdyła, M., Bratkowski, A., & Bała, W. (2004). *Opto-Electron. Rev.*, *12*, 429.

[14] Pope, M. & Swenberg, C. E. (1982). *Electronic Processes in Molecular Crystals*, Clarendon Press: Oxford, UK.

[15] Hoyle, C. E., Nemzek, T. L., Mar, A., & Guillet, J. E. (1978). *Macromolecules*, *11*, 429.

[16] Itaya, A., Okamoto, K., & Kusabayashi, S. (1976). *Bull. Chem. Soc. Jpn.*, *49*, 2082.

[17] Johnson, G. E. (1975). *J. Chem. Phys.*, *62*, 4697.