Organic Electronics 13 (2012) 980–984

Contents lists available at SciVerse ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

OLED with a controlled molecular weight of the PVK (poly(9-vinylcarbazole)) formed by a reactive ink-jet process

Sung Il Ahn [a,*], Wan Kyu Kim [b], Si Hong Ryu [b], Kuk Joo Kim [c], Seong Eui Lee [c,*], Sung-Hoon Kim [a], Jung-Chul Park [a], Kyung Cheol Choi [c,*]

[a] Department of Engineering in Energy and Applied Chemistry, Center for Green Fusion Technology, Silla University, Busan 617-736, South Korea
[b] Department of Advanced Materials Engineering, Korea Polytechnic University, Shihung 429-793, South Korea
[c] Department of Electrical Engineering, KAIST, Daejeon 305-701, South Korea

ARTICLE INFO

Article history:
Received 8 October 2011
Received in revised form 3 February 2012
Accepted 21 February 2012
Available online 8 March 2012

Keywords:
OLED
Ink-jet
Reactive ink-jet
PVK

ABSTRACT

An ink-jet printing method was proposed to solve several conventional problems of ink jet process. PVK (poly(9-vinylcarbazole)) thin film was synthesized and simultaneously patterned by the reactive ink-jet process (RIP). Gel permeation chromatography shows a linear relationship between the molecular weight of the PVK and the reaction time. The as-synthesized PVK with a controlled molecular weight was applied to an OLED device. Most of the OLED with the RIP–PVK film performed better compared to the reference OLEDs. The luminance graphs indicated the existence of a proper molecular weight leading to the optimum structural conformity which was matched well to the modified OLED structure, showing a linear relationship with the reaction time in the turn-on threshold. This result implies that one can control the proper molecular weight of a polymer and thus the electrical properties of an OLED device via the RIP method.

1. Introduction

The ink-jet printing is one of most attractive patterning process due to the low process cost, and moderate degree of pattern precision [1–6]. The progress of ink-jet technology has allowed not only the creation of patterns on paper but also the construction of patterns within electronics parts such as printed circuits [6], thin film transistor [7], sensors [8], color filters [9], OLEDs (organic light emitting diodes) [4,5], and others. The authors have researched other usages of ink-jet printers, focusing on inks as a reactant that can cause reactions between ink droplets (or within one drop) and transform them as useful products in the form of a patterned film as described in Fig. 1. Unlike the conventional inkjet printing method, controlling the reaction temperature, catalyst, time, and additional treatment process can result in the creation of a specific molecule. For example, in the case of a monomer, we can expect a different molecular weight of the corresponding polymer by controlling the reaction parameters, producing either an oligomer (soluble in many solvents) or a molecule with a medium molecular weight (soluble in specific solvents) or a high molecular weight (scarcely soluble in any solvent). Consequently, designing a chemical reaction between inks (or in a single ink mixture) can result in a patterned material that is hardly etched or printed or that has a specific weight and specific band energy. In this paper, patterned PVK (poly(9-vinylcarbazole)) thin films were prepared using the reactive ink-jet process (RIP), and were applied to an OLED device to characterize its electrical performance in the device, as with PVK it is known that holes are the majority carriers when excited [10].

2. Experimental

For the RIP, 6 g of NVK (9-vinylcarbazole, Aldrich, 98%) and AIBN (2,2′-azobis(2-methylpropionitrile), Aldrich,

---

* Corresponding authors.
E-mail addresses: siahn@silla.ac.kr (S.I. Ahn), selee@kpu.ac.kr (S.E. Lee), kyungcc@ee.kaist.ac.kr (K.C. Choi).

1566-1199/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.orgel.2012.02.016

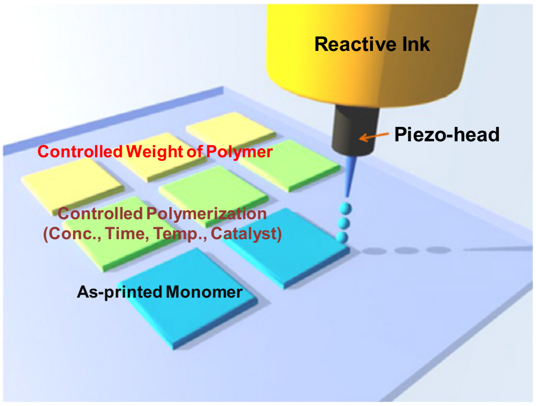


Fig. 1. Schematic diagram of the direct patterning method proposed as reactive ink-jet process.

98%) from 0.05 wt.% to 0.8 wt.% to NVK were dissolved in 40 ml of BCA (2-(2-butoxyethoxy)ethyl acetate, Aldrich, 99%) solvent. Each reactant mixture was inserted into one of the cartridges of EPSON Stylus Photo R290 inkjet printer and then printed onto a silicon wafer and a patterned ITO glass. The printed films were treated in a convection oven for 30 min at various temperatures (100, 120, 140, and 160 °C) and at constant temperature of 120 °C for various reaction times (30, 60, 90, and 120 min). Finally, as a reference for the modified OLED device, 2 wt.% of PVK (Mn = 25,000–50,000, Aldrich) in toluene was coated onto various substrates and then dried in a convection oven for 30 min at 120 °C.

Glass substrates (25 mm × 25 mm, thickness of 0.5 cm) with four patterned ITO (2 mm × 2 mm) were prepared. As mentioned in the previous section, the reaction mixtures were printed on the patterned ITO and then reacted for various reaction times (30, 60, 90, and 120 min; marked as D30, D60, D90, and D120, respectively) at 120 °C. 30 nm of Alq3 (tris(8-hydroxyquinolinato)aluminum) doped with 1% C545T (10-(2-benzothiazolyl)-2,3,6,7-tetrahydro-1,1,7,7-tetramethyl-1H,5H,11H-(1)-benzopyropyrano(6,7-8-i,j)quinolizin-11-one) and 30 nm of Alq3 were sequentially deposited on the synthesized PVK films by the RIP method. Finally, LiF (0.5 nm)/Al (100 nm) film was thermally deposited on the Alq3. A reference OLED device with PVK (Ref.) and an OLED with the as-synthesized PVK via spin-coating (S30) were fabricated at the same manner.

3. Results and discussion

Polymerization of NVK from spin-coating or by a RIP method is identified by a GPC (gel permission chromatography) analysis as shown in Table 1. Most RIP samples indicate the existence of polymers with a similar number averaged molecular weight (Mn) of around 1600 g at a constant reaction time of 30 min regardless of the AIBN content except one case. Increasing the reaction time resulted in a gradual increase in the Mn of the as-synthesized PVKs.

IR characterizations were carried out with the as-synthesized PVK films by a drop-coating method using the RIP ink due to the thickness of the as-synthesized PVK, which was about 60 nm via RIP method and which led to an extremely low intensity of the IR spectrum. The authors assumed that the as-synthesized PVKs synthesized by the RIP method would have vibration modes similar to that of a sample created with the drop-coating method at the molecular level. Fig. 2a shows the IR spectra obtained from the as-synthesized PVK at 120 °C for 30 min, a reference PVK sample, and an NVK sample. The specific peaks in NVK are located at 1665 & 1640 cm^{-1} ($C{=}C$ stretching of the vinyl group), and 1370 cm^{-1} ($CH{=}CH_2$ in-plane deformation) [11,12]. The disappearance of these peaks, as shown in Fig. 2 (a′) & (a″), confirms the formation of the PVK from the drop-coated mixture of NVK and AIBN (0.1 wt.% to NVK) on the Si wafer at 120 °C.

To find a proper concentration of AIBN to NVK for the ink-jet printing process, the authors prepared as-synthesized PVKs using a spin-coating method that depended on various conditions, as shown in Fig. 2b–d. Many reports have proposed that configuration differences in PVK results in two different PL peaks; a totally eclipsed configuration sandwiched by two carbazole groups as shown in Fig. 3 is responsible for the low-energy emission band, whereas a result of it being partially overlapped by only one eclipsed carbazole group is responsible for the high-energy emission band [13–15]. The PL in Fig. 2c shows the increase in high-energy emissions as the reaction time increases. Because the two peaks are related to the degree of polymerization of the NVK as shown in Table 1, this result indicates that the more polymerized PVK has a less sandwiched form in terms of the aforementioned ratio.

The surface roughness of the RIP PVKs was measured by AFM, as shown in Fig. 4. The as-synthesized PVK appears to be rougher than the spin-coated PVK with a 1.7 nm RMS roughness. However, considering that the acceptable roughness of any coated film is generally between 10%

Table 1
GPC results of the average molecular weight of the as-synthesized PVK depending on the reaction time and the AIBN content.

Reaction time (min, at 120 °C, 0.1 wt.%)	30	60	90	120
Mn (g/mol)[a]	1637	3186	5152	11,293
Mw (g/mol)[b]	1789	3336	12,940	12,635
AIBN content (wt.%, at 120 °C, 30 min)	0.01	0.05	0.1	0.2
Mn (g/mol)[a]	1989	1578	1637	1550
Mw (g/mol)[b]	3949	1703	1789	1664

[a] Number averaged molecular weight.
[b] Weight averaged molecular weight.

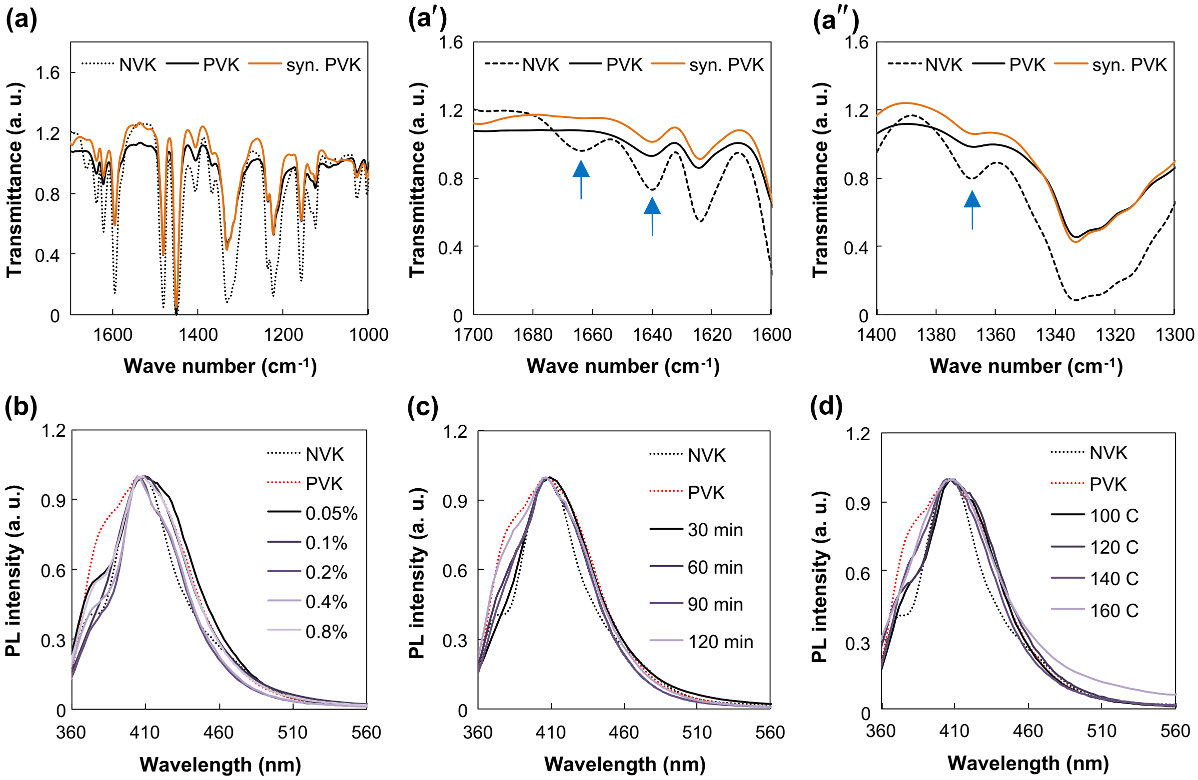


Fig. 2. (a) IR spectra of the NVK, reference PVK (Aldrich) and the as-synthesized PVK samples created via spin-coating at 120 °C for 30 min, (a′) & (a″) enlarged spectra of (a) (the arrows indicate specific peaks of NVK at 1370, 1640, and 1665 cm^{-1}); PL spectra of the as-synthesized PVKs using a spin-coating method depending on (b) the concentration of AIBN (wt.%), (c) the reaction time at constant AIBN of 0.1 wt.%, and (d) the reaction temperature with a constant AIBN concentration of 0.1 wt.%. Note that all PL spectra are normalized.

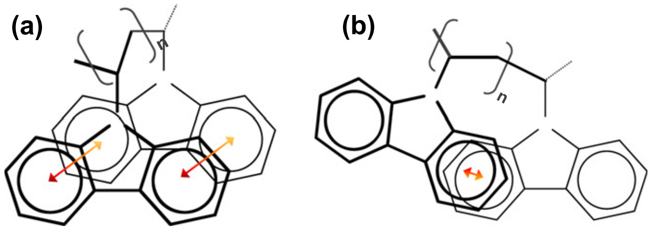
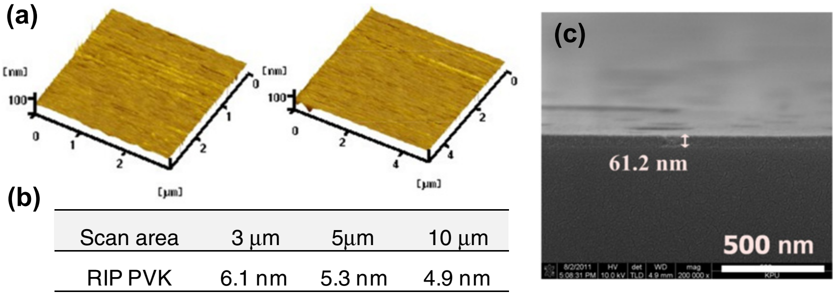


Fig. 3. Two different configurations in PVK [14]; (a) a totally eclipsed configuration sandwiched by two carbazole groups giving a low-energy emission band, (b) partially overlapped by only one eclipsed carbazole group giving a high-energy emission band. Note that the ratio of (a) & (b) can be changed by heating treatment and/or altering the molecular weight of PVK based on the PL results.



Scan area	3 μm	5μm	10 μm
RIP PVK	6.1 nm	5.3 nm	4.9 nm

Fig. 4. (a) Selected AFM images of the PVK as-synthesized via RIP method at 120 °C for 30 min, (b) RMS values of the surface roughness of the PVK film, (c) SEM image of the as-synthesized PVK films used in the AFM measurement.

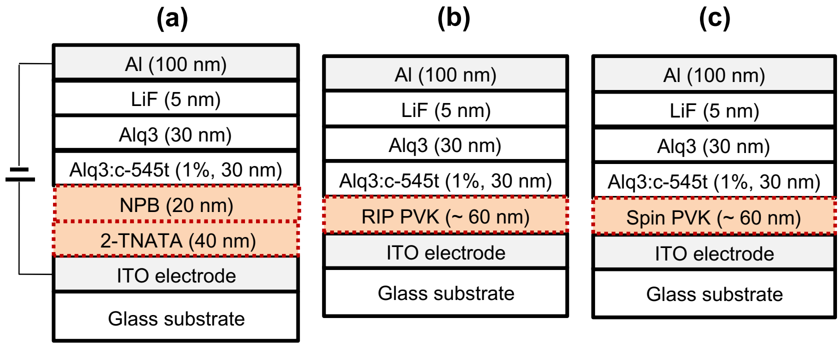


Fig. 5. Schematic diagrams of (a) one of the common OLED structures used in this experiment, (b) a modified OLED structure with an as-synthesized PVK film using the RIP method, (c) a modified OLED structure with an as-synthesized PVK film using the spin-coating method. In (b) & (c), note that the hole injection and transporting material (2-TNATA and NPB) are replaced with the as-synthesized or reference PVK.

and 15% for any manufacturing process, the RIP PVK has a reasonable roughness of less than 10% (based on the thickness of the as-synthesized PVK as judged from the SEM images given in Fig. 4c) for the fabrication of OLED devices.

One of the commonly adopted OLED structures in Fig. 5a was modified for a comparison of the as-synthesized PVKs created via the two different methods of RIP and spin-coating. As shown in Fig. 5b and c, the hole injection and transporting materials (respectively, 2-TNATA [4,4′,4″-tris(2-naphthylphenylamino)triphenylamine] and NPB (N,N′-di(naphthalene-1-yl)-N,N′-diphenyl-benzidine) in the reference device were replaced with the as-synthesized or reference PVK. Although PVK is not an ideal material to replace the two layers, the as-synthesized PVKs could be characterized via the characterization of the modified OLED.

One test device had four OLED cells, all of which were tested in the same manner. The authors selected one cell based on its turn-on voltage from four cells of the OLED device and then compared this to a reference OLED. The energy band of the modified devices indicates that PVK can act as an electron-blocking layer. The HOMO (the highest occupied molecular orbital) level of PVK (5.8 eV) [16], however, increases the energy necessary to inject the hole from ITO into PVK due to the large difference in the band energy gap of about 1 eV between the PVK and ITO, which

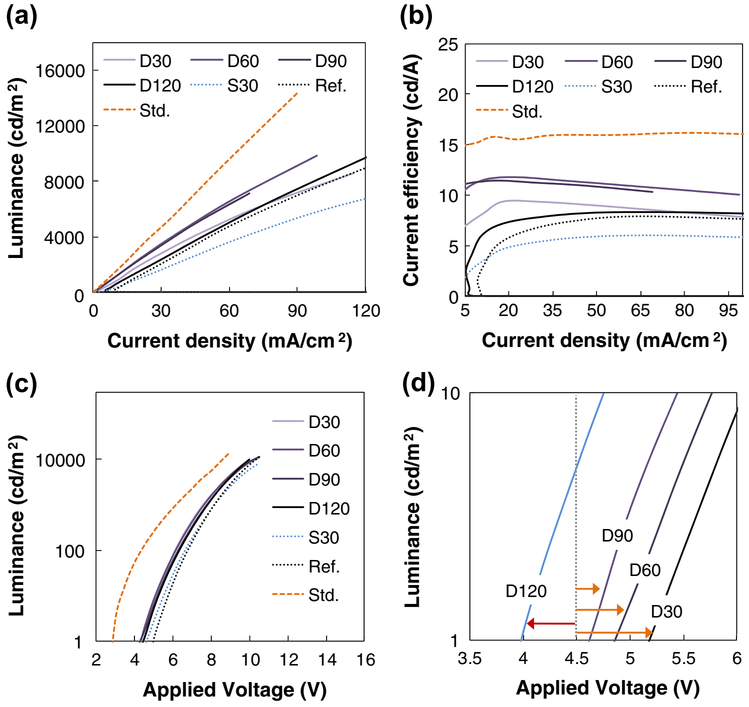


Fig. 6. (a) Luminance vs. current density graphs of the OLED devices depending on the reaction time of the reactive ink (for 30 min (D30), 60 min (D60), 90 min (D90), and 120 min (D120)), by spin-coating (for 30 min (S30)) (b) current efficiency vs. current density graphs of OLEDs. (c) Luminance vs. voltage graphs of the modified OLEDs. (d) Luminance vs. voltage graphs showing the turn-on voltage deviations compared to the (c); the arrows indicate the degree of deviations. Note that the std. indicates a common OLED device with a hole injection (2-TNATA) and transporting material (NPB).

is also responsible for the high turn-on voltage of the modified OLED compared to the standard OLED used in this study.

Fig. 6 presents graphs from two types of OLED devices modified by the as-synthesized PVKs created by the RIP and spin-coating methods. The luminance vs. current density graphs and the current efficiency vs. current density graphs shown respectively, in Fig. 6a and b, indicate that most of the modified devices perform more poorly compared to the std. (standard) OLED with a hole injection and transfer layer. Considering that the PVK is not an ideal material as a hole injection and/or transfer layer for the selected OLED structure, the performance of the modified OLEDs proves that the RIP method has high potential for use in direct patterning processes.

The current efficiency of the modified OLED shown in Fig. 6b reaches a maximum of 11.7 cd/A for RIP–PVK, 5.7 cd/A for spin-coating PVK, and 10 cd/A for the reference PVK. Compared to the OLED with RIP PVKs having a threshold voltage of around 4.5 V, the OLED with the reference PVK has a little higher threshold voltage of approximately 0.5 V. From the other three OLED cells, one cell, which had the largest difference in the turn-on voltage, was selected and compared to the cell having turn-on voltage of 4.5 V as shown in Fig. 6d. Looking closely the graphs, one can note an interesting result of the linear dependency of the turn-on voltage as the reaction time increases. The D30 set gives the highest turn-on voltage with a range of 4.5–5.2 V, whereas the D120 set shows the lowest turn-on with a range of 4–4.5 V. We can consider one major reason for this turn-on threshold trend. In this study, it was necessary to consider the glass transition temperature (T_g) of the as-synthesized PVK because the reaction occurred within a very thin layer of around 60 nm on the ITO substrate. The T_g value of the as-synthesized PVK is expected to be much lower T_g value due to the PVKs low molecular weight. This may lead to a change of the structural conformity of the as-synthesized PVK films when we increase the reaction time. According to one report, the T_g value of PVK is linearly dependent at 1/Mn and reaches theoretically 227 °C at the maximum Mn [17]. In addition, the molecular weight of the PVK, which is dependent on the reaction time, may yield a proper molecular weight that will influences the hole injection and mobility of the as-synthesized PVK film due to structural conformity. According to the PL experiments, there are two different major peaks that indicate the two different energy levels of the PVK film, as shown in Fig. 3. The PVK is a non-conjugated polymer, which means that the change of energy level, which is dependent on its molecular weight, is negligible compared to that of the conjugated polymer. On the contrary, the energy difference between the two conformational structures of PVK, which is dependent on the reaction time and/or the molecular weight is about 0.24 eV, which is enough energy to change the threshold of the OLEDs with the as-synthesized PVK films.

4. Conclusions

An inkjet printing method was proposed to solve several conventional problems of ink jet process. As an example study, PVK thin film was synthesized and simultaneously patterned by the RIP method. The polymerization of NVK using the RIP method is easily identified by a GPC analysis, which shows a linear relationship between the molecular weight of the PVK and the reaction time. The RIP–PVK films had worse surface roughness than that of spin-PVK film. Considering that the acceptable roughness of any coated film is generally between 10% and 15% for the general manufacturing process, however, the RIP PVK has a reasonable roughness of less than 10%. The as-synthesized PVK film was applied to an OLED device in order to evaluate its electrical performance. Most of the modified devices performed more poorly compared to the std. OLED with a hole injection and transfer layer, but performed better than the reference OLED or the spin-PVK OLED proving that the RIP method has high potential for use in direct patterning processes.

Conclusively, despite the requirement of more precise experiments than this study on the RIP method, the experimetal results imply that one can control the proper molecular weight of a polymer and thus the electrical properties of an OLED device via a simple experiment. The authors believe that the RIP method can become not only one of least expensive methods of fabricating devices but also one of the most convenient methods with which to study and develop highly efficient devices.

Acknowledgment

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (No. R11-2007-045-02001-0 and 2009-0073189).

References

[1] M. Singh, H.M. Haverinen, P. Dhagat, G.E. Jabbour, Adv. Mater. 22 (2010) 673–685.
[2] P. Calvert, Chem. Mater. 13 (2001) 3299–3305.
[3] B.-J. de Gans, P.C. Duineveld, U.S. Schubert, Adv. Mater. 16 (2004) 203–213.
[4] Z. Ding, R. Xing, Q. Fu, D. Ma, Y. Han, Org. Electron. 12 (2011) 703–709.
[5] S.C. Chang, J. Liu, J. Bharathan, Y. Yang, J. Onohara, J. Kido, Adv. Mater. 11 (1999) 734–737.
[6] H. Sirringhaus, T. Kawase, R.H. Friend, T. Shimoda, M. Inbasekaran, W. Wu, E.P. Woo, Science 290 (2000) 2123–2126.
[7] E.Y. Park, J.S. Park, T.-D. Kim, K.-S. Lee, H.S. Lim, J.S. Lim, C. Lee, Org. Electron. 10 (2009) 1028–1031.
[8] L.L. Lavery, G.L. Whiting, A.C. Arias, Org. Electron. 12 (2011) 682–685.
[9] H.S. Koo, P.C. Pan, T. Kawai, M. Chen, F.M. Wu, Y.T. Liu, S. Chang, Appl. Phys. Lett. 88 (2006) (1910) 111908–111911.
[10] W.D. Gill, J. Appl. Phys. 43 (1972) 5033–5040.
[11] M. Inoue, H. Morita, Y. Takai, T. Mizutani, M. Ieda, Jpn. J. Appl. Phys. 25 (1986) 1495–1499.
[12] S. McKinley, J.V. Crawford, C.-H. Wang, J. Org. Chem. 31 (1966) 1963–1964.
[13] A. Itaya, K. Okamoto, S. Kusabayashi, Bull. Chem. Soc. Jpn. 49 (1976) 2082–2088.
[14] F. Evers, K. Kobs, R. Memming, D.R. Terrell, J. Am. Chem. Soc. 105 (1983) 5988–5995.
[15] P. de Sainte Claire, J. Phys. Chem. B 110 (2006) 7334–7343.
[16] Y. Xu, J. Peng, J. Jiang, W. Xu, W. Yang, Y. Cao, Appl. Phys. Lett. 87 (2005) 193502–193504.
[17] C.H. Griffiths, A.V. Laeken, J. Polym. Sci. Polym. Phys. Ed. 14 (1976) 1433–1449.