6840 *Macromolecules* **2009**, *42*, 6840–6843
DOI: 10.1021/ma9013884

Macromolecules
COMMUNICATION TO THE EDITOR

Vinyl-Type Polynorbornenes with Triarylamine Side Groups: A New Class of Soluble Hole-Transporting Materials for OLEDs

Jun Ha Park,[†] Changhun Yun,[‡] Myung Hwan Park,[†] Youngkyu Do,*[,†] Seunghyup Yoo,*[,‡] and Min Hyung Lee*[,§]

[†]*Department of Chemistry, KAIST, Daejeon 305-701, Republic of Korea,* [‡]*Department of Electrical Engineering, KAIST, Daejeon 305-701, Republic of Korea, and* [§]*Department of Chemistry, University of Ulsan, Ulsan 680-749, Republic of Korea*

Received June 30, 2009
Revised Manuscript Received August 13, 2009

Polymers bearing triarylamine derivatives are receiving considerable interest as ideal hole-transporting materials (HTMs) in various optoelectronic device applications such as organic light-emitting diodes (OLEDs) and photovoltaic cells due to the excellent hole-transporting/injecting properties of triarylamine derivatives and due to their solution processability and good film-forming properties,[1,2] which render them suitable for the fabrication of large-area and flexible OLEDs based on spin-coating and inkjet printing.[3] Various examples of the polymeric HTMs in which triarylamine moieties are incorporated either in the conjugated main chain[2,4] or in the side chain[5,6] of their polymer backbones have thus been reported so far. Among them, side-chain polymers are regarded as attractive because their intrinsic properties, such as physical/mechanical and rheological properties, can be easily tuned by varying the nature of their polymer backbones while retaining the hole-transporting properties that are inherited primarily from the pendant triarylamine moieties. A proper choice of a polymer backbone possessing a high thermal stability and good film-forming properties, in particular, may provide an effective route to achieve efficient optoelectronic devices with improved durability as well as easy processability for low-cost and scalable fabrication.

In such regards, vinyl-type polynorbornenes bearing triarylamine side groups can be considered promising polymeric HTMs in optoelectronic devices since the parent polynorbornenes are known to have excellent thermal properties with high T_g (> 370 °C), low moisture absorption, and good optical properties such as high optical transparency and low birefringence, all of which are highly desirable for HTMs used in many optoelectronic applications including OLEDs. Although polynorbornenes with pendant triarylamines produced via ring-opening metathesis polymerization (ROMP) have been investigated as HTMs by Weck, Marder, and co-workers,[7] these types of polymers exhibit moderate T_gs (typically below 100 °C) and could suffer from thermo-oxidative instability due to the presence of unsaturation along the polymer backbone. However, there has been no report so far on the use of vinyl addition polymerization of norbornene with a triarylamine group that yields a completely saturated polymer backbone comprising bicyclic structural units. In this report, we set out to explore the vinyl addition polymerization of norbornene bearing triarylamine side groups with the help of palladium(II) catalyst by noting that late transition metal catalytic systems based on nickel(II) or palladium(II) are effective for the preparation of vinyl-type polynorbornenes due to their high activity and, moreover, due to their high tendency to result in soluble polynorbornenes and their high level of tolerance toward the functionality of a monomer.[8,9]

Triarylamine-functionalized norbornene monomers, **M1** and **M2**, were designed and prepared according to Scheme 1. As triarylamine moieties, *N*,*N*′-bis(naphthalene-1-yl)-*N*,*N*′-bis(phenyl)-benzidine (**NPB**),[10] the well-known molecular HTM in OLEDs, and its monoamine analogue were introduced for **M2** and **M1**, respectively. The reactions of 5-norbornene-2-pentyl bromide[11] with the lithium salt generated in situ from 4-bromotriarylamine starting materials (**1** and **2**) and *t*-BuLi afforded the monomers in high yields (82% for **M1** and 72% for **M2**). The analysis of the ^{1}H NMR spectra further confirms that the monomers consist of a mixture of *endo* and *exo* isomers (ca. 2:1 ratio) following the composition of 5-norbornene-2-pentyl bromide.

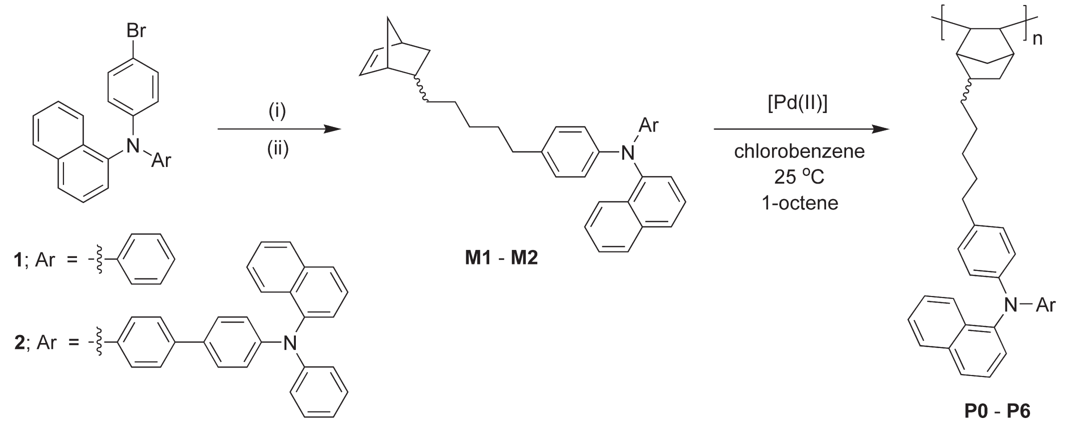
The homopolymerization reactions of **M1** were first investigated using a cationic Pd(II) catalyst derived from the in situ reaction of N-heterocyclic carbene (NHC; *N*,*N*′-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) complex, [(NHC)Pd(η^3-allyl)Cl],[12] and AgSbF$_6$ (Scheme 1). This catalytic system was chosen due to its high activity in the polymerization not only of functionalized norbornenes but also of *endo*-norbornenes.[8] The initial polymerization of **M1** with the Pd(II) catalyst resulted in high monomer conversion (71%), but it was found that the resulting polymer (**P0**) is almost insoluble in organic solvents even at elevated temperatures (Table 1). However, the polymerizations in the presence of 1-octene chain transfer agent (CTA)[13] efficiently led to the production of soluble polynorbornenes (**P1**−**P5**). The conversion gradually decreases with increasing 1-octene concentration from 0.2 to 20 mol %. On the other hand, the molecular weight of polynorbornene decreases rather sharply with increasing 1-octene concentration from 0.2 to 10 mol %. For a 1-octene feed larger than 10%, the decrease becomes relatively insignificant. The ^{1}H and ^{13}C NMR spectra of **P1**−**P5** exhibited the expected resonance features corresponding to the rigid polynorbornene backbone and triarylamine side groups with the peak broadening and disappearance of olefinic protons, as typically observed for vinyl-type polynorbornenes (Figure S3 in the Supporting Information). All the polymers **P1**−**P5** were highly soluble in common organic solvents such as chloroform, dichloromethane, THF, and chlorobenzene at ambient temperature. On the basis of these results, the polymerization of **M2** monomer bearing an **NPB** side group was carried out in the presence of 0.1 mol % of 1-octene. Although the conversion was rather lower than that of **M1** polymerization probably due to a steric reason, it was seen that the high-molecular-weight polynorbornene (**P6**) can readily be produced. The spectroscopic and elemental analysis data are also consistent with the formation of vinyl-type polynorbornene with pendant **NPB** groups.

Among the polymers prepared, **P5** and **P6** were selected for further analysis and OLED device fabrication. TGA measurements reveal that they possess high thermal stability with decomposition temperatures above 400 °C. In particular, the DSC analysis shows the high glass transition temperature (T_g) of 268 and 365 °C for **P5** and **P6**, respectively. The T_g value of **P5** is in fact in good agreement with those observed for polynorbornenes with a similar alkyl chain length.[14] In contrast, much higher value was observed for **P6**. This is regarded to result mainly from the additional rigidity supplemented by the **NPB** groups. We note that the molecular **NPB** itself has a relatively high T_g of ca. 95−100 °C.[10,15]

---

*Corresponding authors. E-mail: ykdo@kaist.ac.kr (Y.D.); syoo@ee.kaist.ac.kr (S.Y.); lmh74@ulsan.ac.kr (M.H.L.).

Scheme 1.[a]



[a] Conditions and reagents: (i) 2 *t*-BuLi, THF, −78 °C; (ii) 5-norbornene-2-pentyl bromide, THF, 0 °C; [Pd(II)] = [(NHC)Pd(η^3-allyl)][SbF$_6$].

Table 1. Polymerization Results of M1 and M2 with Pd(II) Catalyst[a]

polymer	monomer	CTA (mol %)[b]	conv (%)	$10^{-3}M_w$[c]	M_w/M_n[c]	T_g[d] (°C)	T_{d5}[e] (°C)
P0	**M1**	0	71	[g]			
P1	**M1**	20	28	15.5	2.36		
P2	**M1**	10	35	17.5	1.93		
P3	**M1**	5	43	24.9	2.31		
P4	**M1**	1	48	77.6	3.54		
P5	**M1**	0.2	55	158.4	2.79	268	401
P6[f]	**M2**	0.1	51	260.3	2.91	365	449

[a] Conditions: catalyst = [(NHC)Pd(η^3-allyl)Cl]/AgSbF$_6$; [Pd]/[AgSbF$_6$] = 1/1.5; [Pd] = 2.2 μmol; [Mon.]/[Pd] = 1,000; solvent: 25 mL of chlorobenzene; T_p = 25 °C; t_p = 20 h. [b] Molar ratio of chain transfer agent (1-octene) to monomer. [c] Determined by GPC. [d] Determined by DSC. [e] Determined by TGA at 5% weight loss. [f] [Pd] = 1.3 μmol; solvent: 15 mL of chlorobenzene. [g] Not determined.

Table 2. UV−vis, PL, and Electrochemical Data of P5 and P6

polymer	λ_{abs} (nm) (log ε)[a]	λ_{em} (nm)[b]	E_g (eV)[c]	$E_{1/2}^{ox}$ (eV)[d]	HOMO[e]/LUMO[f] (eV)
P5	293 (4.25), 351 (3.73)	442	3.08	0.55	−5.35/−2.27
P6	341 (4.50)	464	3.00	0.31/0.53[g]	−5.11/−2.11
NPB	341 (4.73)	466	3.02	0.29/0.56[g]	−5.09/−2.07

[a] Absorption measured in CH$_2$Cl$_2$ (2.0×10^{-5} M). [b] Acquired using a 2.0×10^{-6} M solution. [c] Estimated from the absorption edge. [d] The first half-oxidation potential vs a Fc/Fc$^+$ couple. [e] Calculated from the $E_{1/2}^{ox}$. [f] Estimated from the HOMO and band gap (E_g) energies. [g] The second half-oxidation potential.

The UV−vis absorption and PL spectra of **P5** and **P6** display almost no change from those observed for **M1** and **M2** monomers, indicating that the possible low-energy aggregation or excimer formation between the neighboring triarylamine moieties in **P5** and **P6** does not take place. Cyclic voltammetry measurements show that both **P5** and **P6** undergo a completely reversible oxidation process, reflecting high oxidational stability, similar to that observed for molecular **NPB**.[10] It can also be seen that the first oxidation of **P6** is more facile than that of **P5** owing to the electron-donating effect of the remaining amine group that stabilizes the cationic radical species. From the optical and electrochemical data, the HOMO and LUMO levels are calculated to be ca. −5.4 to −5.1 and −2.3 to −2.1 eV, respectively, which are appropriate for HTMs (Table 2). Particularly, the HOMO and LUMO levels of **P6** are found to be nearly identical to those of **M2** and molecular **NPB** (Figure S8).[10]

In order to test the hole-transporting capability of the polymers being studied, OLED devices were constructed in a nitrogen environment using tris(8-hydroxyquinolinolato)aluminum (Alq$_3$) as emitting layers (EMLs) and the polymers as hole-transporting layers (HTLs) in the following configuration: ITO/**P5** or **P6** (50 nm)/Alq$_3$ (40 nm)/LiF (1 nm)/Al (100 nm) (devices **I** and **II**). The polymer was spin-coated onto a plasma-treated ITO/glass substrate from a 1 wt % of chlorobenzene solution at 3000 rpm and then dried at 80 °C for 30 min. For comparison, a device having the same configuration based on the molecular **NPB** was fabricated by vacuum deposition (device **III**). The successive depositions of Alq$_3$, LiF, and Al layers in devices **I**−**III** were carried out on top of each HTLs (**P5**, **P6**, and **NPB**) at the same time. As shown in Figure 1, all the devices emitted a green light typical of Alq$_3$-based OLEDs featuring the electroluminescence (EL) spectra with an emission maximum λ_{em} of 528 nm. This result indicates that the spin-coated **P5** and **P6** layers function properly as HTLs for the green emission of Alq$_3$.

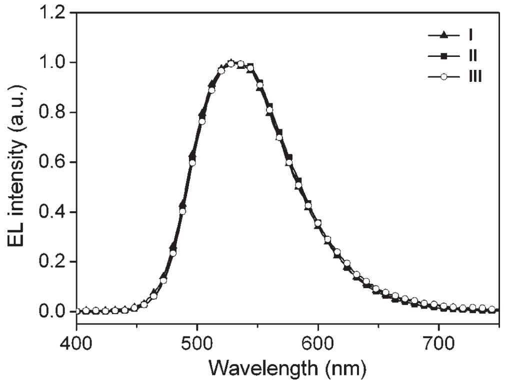


Figure 1. EL spectra of the devices (**I**−**III**) incorporating **P5**, **P6**, and **NPB** as HTL and Alq$_3$ as EML.

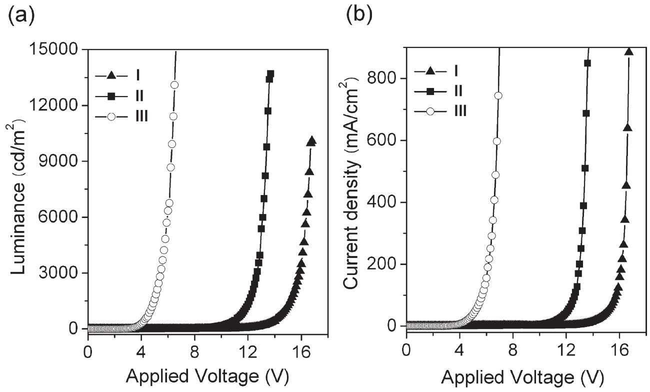


Figure 2. (a) Luminance vs voltage ($L-V$) and (b) current density vs voltage ($J-V$) characteristics for the devices (**I**–**III**).

Table 3. Performance of Electroluminescence Devices I–III

device	I	II	III
HTL	**P5**	**P6**	**NPB**
turn-on voltage (V)[a]	8.6	4.1	2.6
max luminance (cd/m^2)	10 100 at 16.8 V	13 700 at 13.7 V	30 300 at 7.0 V
luminance (cd/m^2)[b]	2800	3090	4220
η_{EQE} (%)[b,c]	0.89	0.98	1.42
η_{L} (cd/A)[b,d]	2.6	2.9	4.1

[a] Recorded at 1 cd/m^2. [b] Taken at 100 mA/cm^2. [c] External quantum efficiency. [d] Luminous efficiency.

The current density–voltage–luminance ($J-V-L$) characteristics for the devices are displayed in Figure 2, and the key parameters are listed in Table 3. While devices **I** and **II** based on polymeric HTLs exhibited higher turn-on voltages than that of device **III** based on a regular molecular **NPB**, the turn-on voltage of device **II** was lower than that of device **I**, indicating facile hole injection from the anode via **P6** into the emitting layer. This result is in parallel with the location of the HOMO level of **P6**, which is closer to the work function of ITO (-4.7 to -4.8 eV) than that of **P5**. With the increasing applied voltage, both devices **I** and **II** showed a high level of current density and luminance with a maximum brightness ($L_{\max}$) of 10 100 cd/m^2 at 16.8 V and 13 700 cd/m^2 at 13.7 V, respectively. Higher luminous efficiency (η_{L}) and external quantum efficiency (η_{EQE}) (Figure S9) were also observed for device **II** in a wide range of current densities, indicating that a device containing **P6** consistently performs better than one containing **P5**. Although the overall performances of device **II** in terms of $L_{\max}$, η_{L}, and η_{EQE} are rather lower than those of device **III** (Table 3), we find that device **II** shows high performance comparable to those of the reported Alq$_3$-based OLED devices with a similar structure incorporating polymeric HTMs.[6,16] For example, the maximum η_{EQE} and L values are reported in the range of 0.76–2.5% and 8600 – 18 000 cd/m^2, respectively. Therefore, the results shown here suggest that the polynorbornene bearing side-chain triarylamine moieties may have great potential as HTMs in OLEDs with a good cost-performance balance in some low-end display applications such as signage and smart electronic labels that are likely to receive the greatest benefits from the high-throughput solution processing such as printing.

In conclusion, we have demonstrated that soluble polynorbornenes bearing triarylamine side groups can be efficiently produced by the vinyl addition polymerization of norbornene monomers with Pd(II) catalyst in combination with the chain transfer agent. The polymers possess a high glass transition temperature and display a particularly outstanding hole-transporting/injecting ability when incorporated into OLED devices through solution process. The methodology shown here may further be extended to the synthesis of soluble analogues of various functional small molecules so that solution-processed devices can achieve a performance level comparable to that of vacuum-deposited counterparts.

Acknowledgment. Financial support from the Korea Science and Engineering Foundation (KOSEF) (R01-2007-000-20299-0) and from the ERC program of the KOSEF (No. R11-2007-045-01001-0) funded by the Korea Ministry of Education, Science and Technology is gratefully acknowledged.

Supporting Information Available: Text describing the synthesis and measurements and the analysis data for the polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Shirota, Y.; Kageyama, H. *Chem. Rev.* **2007**, *107*, 953–1010.
(2) Thelakkat, M. *Macromol. Mater. Eng.* **2002**, *287*, 442–461.
(3) Sirringhaus, H.; Kawase, T.; Friend, R. H.; Shimoda, T.; Inbasekaran, M.; Wu, W.; Woo, E. P. *Science* **2000**, *290*, 2123–2126. Gustafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature* **1992**, *357*, 477–479.
(4) Lee, S. K.; Ahn, T.; Cho, N. S.; Lee, J.-I.; Jung, Y. K.; Lee, J.; Shim, H. K. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 1199–1209. Lim, E.; Jung, B.-J.; Shim, H.-K. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 243–253. Vak, D.; Jo, J.; Ghim, J.; Chun, C.; Lim, B.; Heeger, A. J.; Kim, D.-Y. *Macromolecules* **2006**, *39*, 6433–6439. Kim, Y.-H.; Zhao, Q.; Kwon, S.-K. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 172–182. Liou, G.-S.; Hsiao, S.-H.; Chen, W.-C.; Yen, H.-J. *Macromolecules* **2006**, *39*, 6036–6045. Jung, M.-S.; Lee, T.-W.; Hyeon-Lee, J.; Sohn, B. H.; Jung, I.-S. *Polymer* **2006**, *47*, 2670–2676. Xiao, H.; Leng, B.; Tian, H. *Polymer* **2005**, *46*, 5707–5713. Zhang, Y.; Hu, Y.; Li, H.; Wang, L.; Jing, X.; Wang, F.; Ma, D. *J. Mater. Chem.* **2003**, *13*, 773–777. Ego, C.; Grimsdale, A. C.; Uckert, F.; Yu, G.; Srdanov, G.; Müllen, K. *Adv. Mater.* **2002**, *14*, 809–811.
(5) Park, M. H.; Huh, J. O.; Do, Y.; Lee, M. H. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 5816–5825. Deng, L.; Furuta, P. T.; Garon, S.; Li, J.; Kavulak, D.; Thompson, M. E.; Fréchet, J. M. J. *Chem. Mater.* **2006**, *18*, 386–395. Bacher, E.; Bayerl, M.; Rudati, P.; Reckefuss, N.; Müller, C. D.; Meerholz, K.; Nuyken, O. *Macromolecules* **2005**, *38*, 1640–1647. Lee, T. H.; Tong, K. L.; So, S. K.; Leung, L. M.-L. *Jpn. J. Appl. Phys.* **2005**, *44*, 543–545. Peter, K.; Thelakkat, M. *Macromolecules* **2003**, *36*, 1779–1785. Mutaguchi, D.; Okumoto, K.; Ohsedo, Y.; Moriwaki, K.; Shirota, Y. *Org. Electron.* **2003**, *4*, 49–59. Jiang, X. Z.; Liu, S.; Liu, M. S.; Herguth, P.; Jen, A. K.-Y.; Fong, H.; Sarikaya, M. *Adv. Funct. Mater.* **2002**, *12*, 745–751. Bellmann, E.; Shaheen, S. E.; Grubbs, R. H.; Marder, S. R.; Kippelen, B.; Peyghambarian, N. *Chem. Mater.* **1999**, *11*, 399–407. Feast, W. J.; Peace, R. J.; Sage, I. C.; Wood, E. L. *Polym. Bull.* **1999**, *42*, 167–174.
(6) Ma, B.; Lauterwasser, F.; Deng, L.; Zonte, C. S.; Kim, B. J.; Fréchet, J. M. J.; Borek, C.; Thompson, M. E. *Chem. Mater.* **2007**, *19*, 4827–4832. Zhang, Y.-D.; Hreha, R. D.; Jabbour, G. E.; Kippelen, B.; Peyghambarian, N.; Marder, S. R. *J. Mater. Chem.* **2002**, *12*, 1703–1708.
(7) Kimyonok, A.; Domercq, B.; Haldi, A.; Cho, J.-Y.; Carlise, J. R.; Wang, X.-Y.; Hayden, L. E.; Jones, S. C.; Barlow, S.; Marder, S. R.; Kippelen, B.; Weck, M. *Chem. Mater.* **2007**, *19*, 5602–5608. Hreha, R. D.; Haldi, A.; Domercq, B.; Barlow, S.; Kippelen, B.; Marder, S. R. *Tetrahedron* **2004**, *60*, 7169–7176. Bellmann, E.; Shaheen, S. E.; Thayumanavan, S.; Barlow, S.; Grubbs, R. H.; Marder, S. R.; Kippelen, B.; Peyghambarian, N. *Chem. Mater.* **1998**, *10*, 1668–1676.
(8) Jung, I. G.; Seo, J.; Chung, Y. K.; Shin, D. M.; Chun, S.-H.; Son, S. U. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 3042–3052.
(9) Yamashita, M.; Takamiya, I.; Jin, K.; Nozaki, K. *Organometallics* **2006**, *25*, 4588–4595. Shin, B.-G.; Jang, M.-S.; Yoon, D. Y.; Heitz, W. *Macromol. Rapid Commun.* **2004**, *25*, 728–732. Park, K. H.; Twieg, R. J.; Ravikiran, R.; Rhodes, L. F.; Shick, R. A.; Yankelevich, D.; Knoesen, A. *Macromolecules* **2004**, *37*, 5163–5178. Barnes, D. A.; Benedikt, G. M.; Goodall, B. L.; Huang, S. S.; Kalamarides, H. A.; Lenhard, S.; McIntosh, L. H., III; Selvy, K. T.; Shick, R. A.; Rhodes, L. F. *Macromolecules* **2003**, *36*, 2623–2632. Kim, J.-M.; Shin, H.-Y.;

Park, K. H.; Kim, T.-H.; Ju, S. Y.; Han, D. K.; Ahn, K.-D. *Macromolecules* **2001**, *34*, 4291–4293. Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460–462.

(10) Van Slyke, S. A.; Chen, C. H.; Tang, C. W. *Appl. Phys. Lett.* **1996**, *69*, 2160–2162.

(11) Gabert, A. J.; Verploegen, E.; Hammond, P. T.; Schrock, R. R. *Macromolecules* **2006**, *39*, 3993–4000. Stubbs, L. P.; Weck, M. *Chem.—Eur. J.* **2003**, *9*, 992–999.

(12) Viciu, M. S.; Navarro, O.; Germaneau, R. F.; Kelly, R. A., III; Sommer, W.; Marion, N.; Stevens, E. D.; Cavallo, L.; Nolan, S. P. *Organometallics* **2004**, *23*, 1629–1635.

(13) Lipian, J.; Mimna, R. A.; Fondran, J. C.; Yandulov, D.; Shick, R. A.; Goodall, B. L.; Rhodes, L. F.; Huffman, J. C. *Macromolecules* **2002**, *35*, 8969–8977.

(14) Müller, K.; Kreiling, S.; Dehnicke, K.; Allgaier, J.; Richter, D.; Fetters, L. J.; Jung, Y.; Yoon, D. Y.; Greiner, A. *Macromol. Chem. Phys.* **2006**, *207*, 193–200. Grove, N. R.; Kohl, P. A.; Allen, S. A. B.; Jayaraman, S.; Shick, R. *J. Polym. Sci., Part B: Polym. Phys.* **1999**, *37*, 3003–3010.

(15) O'Brien, D. F.; Burrows, P. E.; Forrest, S. R.; Koene, B. E.; Loy, D. E.; Thompson, M. E. *Adv. Mater.* **1998**, *10*, 1108–1112. Koene, B. E.; Loy, D. E.; Thompson, M. E. *Chem. Mater.* **1998**, *10*, 2235–2250.

(16) Domercq, B.; Hreha, R. D.; Zhang, Y.-D.; Larribeau, N.; Haddock, J. N.; Schultz, C.; Marder, S. R.; Kippelen, B. *Chem. Mater.* **2003**, *15*, 1491–1496. Jiang, X.; Liu, S.; Liu, M. S.; Ma, H.; Jen, A. K. Y. *Appl. Phys. Lett.* **2000**, *76*, 2985–2987. Shaheen, S. E.; Jabbour, G. E.; Kippelen, B.; Peyghambarian, N.; Anderson, J. D.; Marder, S. R.; Armstrong, N. R.; Bellmann, E.; Grubbs, R. H. *Appl. Phys. Lett.* **1999**, *74*, 3212–3214.