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Emission Enhancement, Photooxidative Stability, and Fluorescence Image Patterning of Conjugated Polymer Film via *in Situ* Hybridization with UV-Curable Acrylate Monomers

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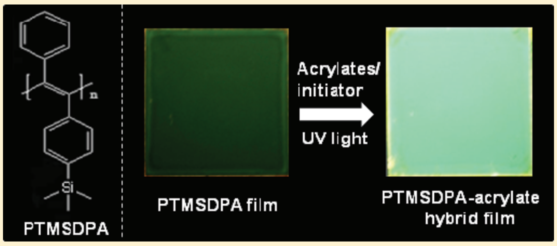
Supporting Information



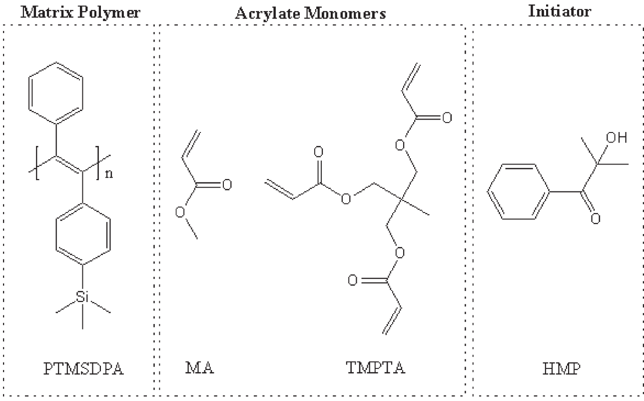
ABSTRACT: An acetylene−acrylate polymer hybrid film with enhanced emission, chemical resistance, and photooxidative stability was successfully prepared by the photopolymerization of acrylates *in situ* in poly[1-phenyl-2-(*p*-trimethylsilyl)phenylacetylene] (PTMSDPA) film. An acrylate mixture of methyl acrylate (MA) and trimethylol propanetriacrylate (TMPTA) easily diffused into PTMSDPA film, and simultaneously, the emission of the PTMSDPA film significantly increased. Subsequently, when the acrylate-deposited PTMSDPA film was irradiated by UV light at the appropriate irradiation power, the acrylate monomers were readily polymerized *in situ* in PTMSDPA film. The hybrid film still retained enhanced emission after the photopolymerization. Moreover, the hybrid film hardly dissolved in toluene even after immersing for several minutes, whereas the PTMSDPA film immediately dissolved in toluene. The hybrid film also showed photooxidative stability in air, as compared to the PTMSDPA film, due to the oxygen-blocking effect of the acrylate components. Photomasked UV irradiation of the acrylate-deposited PTMSDPA film led to a highly resolved, fluorescent image pattern on the hybrid film.

1. INTRODUCTION

Conjugated polymers are very useful materials for organic photoelectronic device applications such as light-emitting diodes (LEDs), photovoltaic cells, field-effect transistors (FETs), and optical sensors. For practical applications of these organic polymers, high chemical resistance and photooxidative stability as well as high emission quantum yields are intensively required. Among many conjugated polymers, poly[1-phenyl-2-(*p*-trimethylsilyl)phenylacetylene] [PTMSDPA in Chart 1][1] is well-known as a fluorescent conjugated polymer with an extremely large fractional free volume (FFV)[2] of about 0.26 in film.[3]

In previous studies, we found that this polymer allows various kinds of liquid chemicals, such as alcohols, hydrocarbons, silicon oils, and alkoxysilanes, to easily diffuse into its film through microvoids.[4] The diffusion of these common liquid chemicals leads to relaxation of the intramolecular π-stack structure of the side phenyl rings, which remarkably enhances fluorescence (FL) emission via swelling-induced quenching site degeneration. Especially, when utilizing sol−gel reaction of alkoxysilanes *in situ* in PTMSDPA film, nano-ordered PTMSDPA−silica hybrid films can be successfully developed.[4c,e] In this method, polymer chains in the hybrid film are locked up and left swollen out during the *in situ* sol−gel reaction, and thus enhanced emission is firmly retained. Moreover, the chemical resistance of the PTMSDPA film is significantly enhanced by the solvent-blocking effects of the silica gel components incorporated into the polymer film.

Chart 1. Chemical Structures of PTMSDPA, Acrylates, and Initiator Used in This Study



This *in situ* hybridization of the conjugated polymer film via immobilization of silane sol compounds would be a very useful technique for multilayer lamination and higher luminescence efficiency in polymer light-emitting diode (PLED) device

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fabrications. However, silane sols suitable for the preparation of a transparent PTMSDPA−silica hybrid film without phase separation are highly limited.[4c,e] Indeed, only a few silane sol compounds with high boiling points, water solubility, and miscibility were suitable for this purpose. Further, in order to obtain a higher quality hybrid film, silane-deposited film required thermal post-treatment at high temperature for a prolonged time period.

Recently, we have focused on identifying more convenient and simpler hybridization methods than the sol−gel reaction. Acrylate monomers can be easily polymerized by UV irradiation with the aid of a photoinitiator.[5] This photopolymerization method is very useful for film fabrication and photolithography in the microphotonics and microelectronics industries. Also, this typical photoirradiation reaction is applicable to fluorescence image patterning for the fabrication of photonic/electronic/sensory devices.[6] In this study, we examined photopolymerization of acrylates *in situ* in PTMSDPA film. Eventually, a nicely featured PTMSDPA−acrylate polymer hybrid film was obtained. The FL emission, chemical resistance, and photooxidative stability of the hybrid film were significantly enhanced as compared to PTMSDPA film. Further, photomasked UV irradiation of the hybrid film during the process of photopolymerization produced a finely resolved FL image pattern on the hybrid film. We herein describe the details of the preparation method, FL emission properties, photooxidative stability, and FL image patterning of the PTMSDPA−acrylate polymer hybrid film.

2. EXPERIMENTAL SECTION

2.1. Materials. The PTMSDPA polymer was donated from NOF Co., Ltd., Japan. The acrylate monomers of methyl acrylate (MA) and trimethylol propanetriacrylate (TMPTA), along with the photoinitiator of 2-hydroxy-2-methylpropiophenone (HMP), were purchased from Aldrich. Their chemical structures are shown in Chart 1. These all were dried by nitrogen gas before use.

2.2. Measurements. The weight-average molecular weight (M_w) and number-average molecular weight (M_n) of PTMSDPA were determined by gel permeation chromatography [Shimadzu A10 instruments (Kyoto, Japan), Polymer Laboratories (Shropshire, UK), a PLgel Mixed-B column 300 mm in length, and HPLC-grade tetrahydrofuran were used as an eluent at 40 °C], based on calibration using polystyrene standards. The FT-IR spectra were recorded on a JASCO 620 spectrometer. The Ar ion sputtering XPS (X-ray photoelectron spectroscopy) measurement was conducted using a PHI Quantera SXM (ULVAC-PHI, Inc.) with an Al Kα X-ray source at 15 kV and 25 W. The Ar ion gun was accelerated at 2 kV, corresponding to a sputter rate of 5.0 nm min^{-1} for a SiO_2 standard. The emission angle of the photoelectrons, θ, was kept constant at 45°. The fluorescence emission spectra were recorded on a JASCO ETC-273 spectrofluorometer at an excitation wavelength of 420 nm and a scanning rate of 100 nm/min at room temperature (excitation light source: xenon lamp; excitation light power: 1.73 μW/cm^2). The time-resolved fluorescence emission spectra and the integral fluorescence intensity were recorded at an excitation wavelength of 365 nm and a scanning rate of 10 dots/s at room temperature using an Ocean Optics HR4000 UV−NIR high-resolution spectrofluorometer attached to a Nikon Eclipse E400 fluorescence microscope equipped with a superhigh-pressure 100 W Hg lamp (OSRAM, HBO103W/2). The fluorescence intensities were collected at 520 nm. The UV-irradiation power was controlled using several neutral-density (ND) filters and was monitored by a UV-light meter (Lutron, YK-34UV). The fluorescence CCD images were also recorded on the same fluorescence microscope equipped with a Nikon DS-Fi1 digital camera.

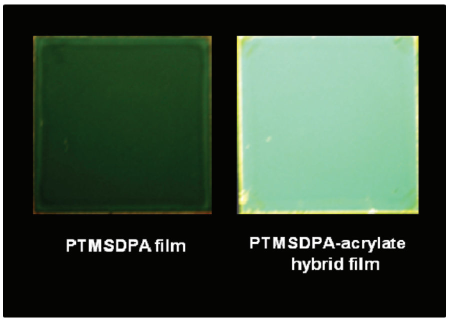

Figure 1. FL photographs of the PTMSDPA film (prepared by spin-casting method, film thickness ∼160 nm) and the PTMSDPA−acrylate polymer hybrid film (film thickness ∼300 nm) (excited at >365 nm). The same PTMSDPA film was used for the hybridization.

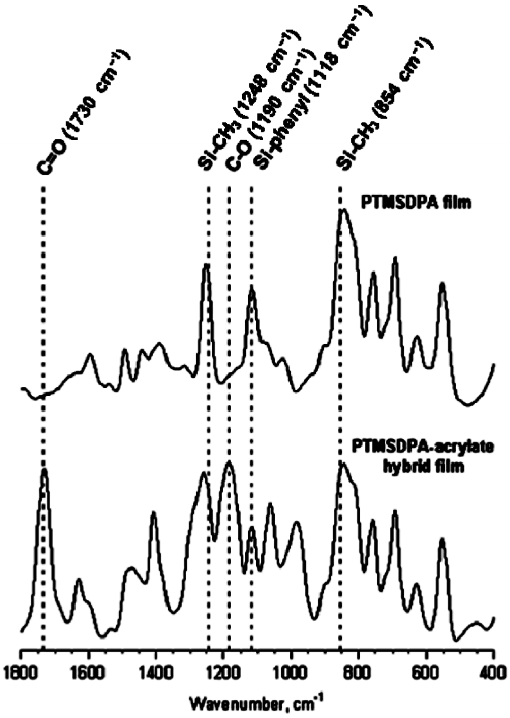

Figure 2. IR absorption spectra of the PTMSDPA film and the PTMSDPA−acrylate polymer hybrid film.

3. RESULTS AND DISCUSSION

The ultimate goal of this study was to develop a well-defined PTMSDPA−acrylate polymer hybrid film with enhanced emission via the immobilization of acrylate components into a PTMSDPA film (Chart 1). For this purpose, we examined the photopolymerization of a mixture of two acrylate monomers, MA and TMPTA with a photoinitiator of HMP (Chart 1), *in situ* in PTMSDPA film. The PTMSDPA used in this study had a high M_w of 5.2×10^6 g/mol and a polydispersity index (PDI = M_w/M_n) of 3.2. The liquid acrylate mixture of MA and TMPTA (volume ratio, 80:20) containing a small amount of HMP (0.5 vol %) was deposited onto the PTMSDPA thin film (prepared by the spin-casting method) without diluting. Then, excess residues of the acrylates were removed by spinning the film at a high speed of over 1000 rpm. Observation by the naked eye recognized that emission from the PTMSDPA film significantly increased after

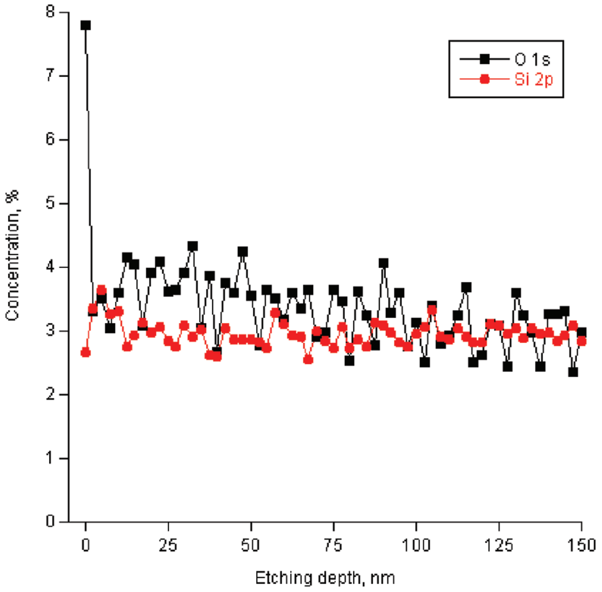

Figure 3. Depth profile of the PTMSDPA−acrylate polymer hybrid film as evaluated by Ar ion sputtering XPS measurement.

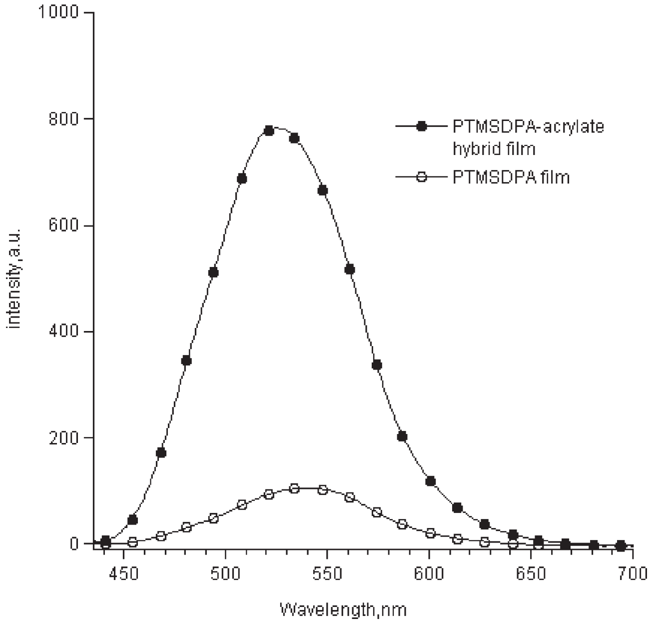

Figure 4. FL emission spectra of the PTMSDPA film and the PTMSDPA−acrylate polymer hybrid film (excited at 420 nm).

the deposition of acrylates. Subsequently, the acrylate-deposited PTMSDPA film was irradiated by UV light at an irradiation power of 0.207 mW/cm^2 for 10 min. This UV-cured hybrid film still retained enhanced emission and high optical transparency without any loss of film clarity after photopolymerization. Finally, a very nicely featured hybrid film was obtained as shown in Figure 1 (Figure S1 in Supporting Information for UV−vis spectra). Film thickness increased about 2 times from 160 to 300 nm after photopolymerization.

Figure 2 shows the IR spectra of the PTMSDPA−acrylate polymer hybrid film in comparison with the virgin PTMSDPA film. The hybrid film displayed absorption peaks characteristic of ester groups (1730 cm^{-1} due to C−O double bond; 1190 cm^{-1} due to C−O single bond) in addition to absorption peaks characteristic of Si−CH$_3$ (1248, 854 cm^{-1}) and Si−phenyl (1118 cm^{-1}) groups. This indicates that the acrylate monomers were polymerized *in situ* in the PTMSDPA film and became tightly immobilized in the PTMSDPA film.

The X-ray photoelectron spectroscopy (XPS) of the hybrid film clearly showed Si 2p (101.0 eV) and O 1s (532.0 eV) peaks ascribed to PTMSDPA and acrylate polymer, respectively (Figure S2 in Supporting Information). The dispersion state of acrylate components in the hybrid film was investigated by Ar ion sputtering XPS measurement.

Figure 3 shows the elemental concentration of Si 2p and O 1s at various depths within the hybrid film. The relatively higher O concentration (O/Si ratio ∼2.9) at the surface region was probably due to the surface adsorption of carbon dioxide and other oxygen-containing impurities. In a bulk region, although the O concentration slightly decreased with an increase in depth, showing a small concentration gradient, the acrylate component was well dispersed all around the hybrid film (Table S1 in Supporting Information).

Figure 4 shows the FL emission spectra of the PTMSDPA film before and after the photopolymerization of acrylates *in situ* in the film. After photopolymerization, the FL intensity at 541 nm increased about 7.4 times, and simultaneously, the FL maximum band shifted to blue by 17 to 524 nm. This emission enhancement is ascribed to degeneration of the quenching sites via swelling-induced relaxation of the intramolecular π-stack structure of the side phenyl rings. This FL response mechanism, so-called swelling-induced emission enhancement (SIEE), has already been well explained in our previous papers.[4a,d,f] Moreover, the chemical resistance of PTMSDPA film was significantly enhanced via *in situ* hybridization with the acrylates. The PTMSDPA−acrylate polymer hybrid film hardly dissolved in toluene even after immersing for several minutes, whereas the PTMSDPA film immediately dissolved in toluene (Figure S3 in Supporting Information). This indicates that the polymer chains of PTMSDPA in the hybrid film were tightly locked up and left swollen out after the photopolymerization of acrylates. According to our previous study, however, intense UV light irradiation for a prolonged time can induce FL quenching of the PTMSDPA film due to photooxidation.[7] Therefore, in this study, photopolymerization was carefully conducted using relatively weak UV light with an irradiation power of 0.207 mW/cm^2 in a nitrogen atmosphere. Actually, both the virgin and the acrylates-deposited PTMSDPA films were neither bleached nor FL-quenched under this condition even though it was exposed to UV light for several 10 min (Figure S4 in Supporting Information).

It should also be noted that the hybrid film showed remarkably improved photooxidative stability. Figure 5 shows the time-resolved FL intensity ratio of the hybrid film upon intense UV light irradiation at a power of 15.8 mW/cm^2 in comparison with the virgin PTMSDPA film. The FL quenching rate was much lower in the hybrid film than in the virgin film. The FL emission of the hybrid film decreased very slowly and lost only 7% of its initial value after 200 s, whereas that of the virgin film rapidly decreased to half of its original emission within the same time. In general, the photobleaching of conjugated polymers is assumed to be due to the formation of a charge transfer complex of polymer$^{\delta+}$−O$_2$$^{\delta-}$ in air.[8] Accordingly, the enhanced photooxidative stability of the hybrid film should be due to the oxygen-blocking effect of the acrylate components.

Next, we successfully obtained a finely resolved FL image pattern from the hybrid film without a chemical etching process

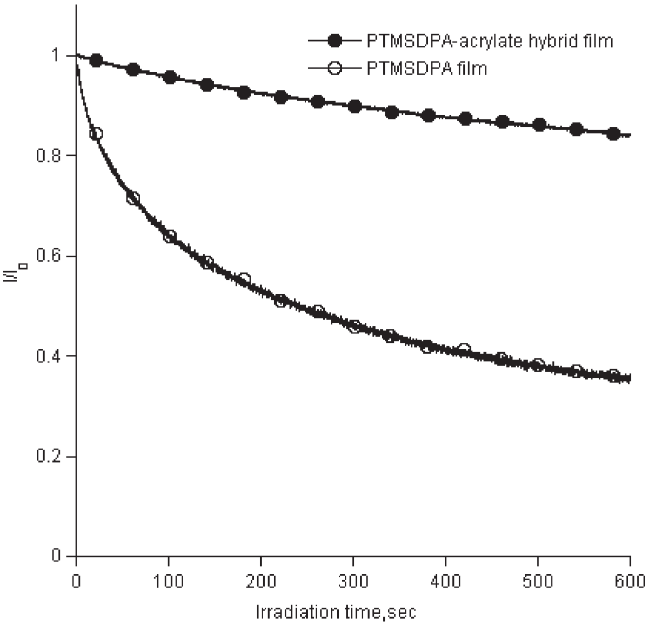

Figure 5. Variation in the time-resolved FL intensity of the PTMSDPA film and the PTMSDPA—acrylate polymer hybrid film upon UV light irradiation at a power of 15.8 mW/cm^2 (excited at 365 nm; scanning rate 10 dots/s).

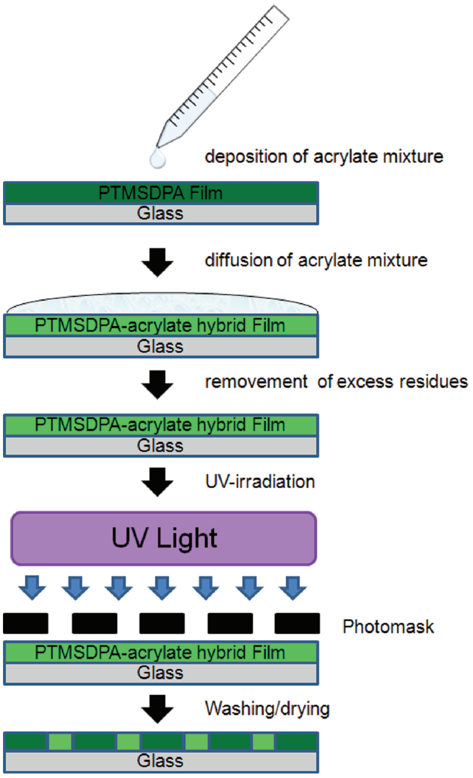

Figure 6. Procedure of FIP of the PTMSDPA—acrylate polymer hybrid film.

by utilizing photomasked UV irradiation in the hybridization process. Figure 6 shows the typical fluorescence image patterning (FIP) procedure. The acrylate-deposited PTMSDPA film was irradiated by UV light through a photomask for 10 min. Subsequently, the film was immersed in an excess of methanol to remove the unreacted acrylates on unexposed portions. Then, the film was dried in air.

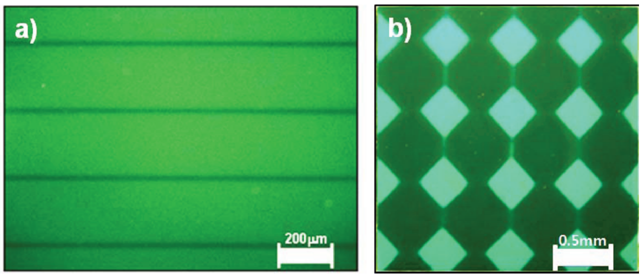

Figure 7. Representative features of the PTMSDPA—acrylate polymer hybrid films obtained from the FIP (excited at 365 nm, UV irradiation at energy of 12.4 J/cm^2).

The patterned FL images of the hybrid film obtained from the modified photolithography method are shown in Figure 7. Photomasked UV irradiation led to a finely resolved patterned FL image at a micrometer scale, as shown in Figure 7a. The UV-exposed portions appeared bright while the unexposed portions appeared dark with high contrast. Figure 7b shows a larger-scale FL image.

4. CONCLUSION

We successfully developed a nicely featured PTMSDPA—acrylate polymer hybrid film with enhanced emission by means of the photopolymerization of acrylates *in situ* in PTMSDPA film. The acrylates easily diffused into the PTMSDPA film and, simultaneously, the emission of the PTMSDPA film significantly increased. Subsequently, when the acrylate-deposited PTMSDPA film was irradiated by UV light at an appropriate irradiation power, the acrylate monomers were readily polymerized *in situ* in the PTMSDPA film. Enhanced emission was semipermanently retained. Further, this hybrid film showed enhanced photooxidative stability in addition to excellent chemical resistance. Photomasked UV irradiation successfully produced highly resolved FL image patterns on PTMSDPA—acrylate polymer hybrid films. This *in situ* hybridization of the conjugated polymer film via photopolymerization of UV-curable acrylate monomers is expected to be a very useful and facile technique for fabrication of optoelectronic, organic thin-film devices with high luminescence efficiency and photooxidative stability.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** UV—vis spectra and photographs (Figure S1), XPS data (Figure S2 and Table S1), FL photographs (Figure S3), and time-resolved FL emission plot (Figure S4). This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) (a) Tsuchihara, K.; Masuda, T.; Higashimura, T. *J. Am. Chem. Soc.* **1991**, *113*, 8548. (b) Tsuchihara, K.; Masuda, T.; Higashimura, T. *Macromolecules* **1992**, *25*, 5816.

(2) Toy, L. G.; Nagai, K.; Freeman, B. D.; Pinnau, I.; He, Z.; Masuda, T.; Teraguchi, M.; Yampolskii, Y. P. *Macromolecules* **2000**, *33*, 2516.

(3) (a) Shukla, A.; Ghosh, H.; Mazumdar, S. *Synth. Met.* **2001**, *116*, 87. (b) Hidayat, R.; Fujii, A.; Ozaki, M.; Teraguchi, M.; Masuda, T.; Yoshino, K. *Synth. Met.* **2001**, *119*, 597. (c) Fujii, A.; Hidayat, R.; Sonoda, T.; Fujisawa, T.; Ozaki, M.; Vardeny, Z. V.; Teraguchi, M.; Masuda, T.; Yoshino, K. *Synth. Met.* **2001**, *116*, 95. (d) Shukla, A. *Chem. Phys.* **2004**, *300*, 177.

(4) (a) Kwak, G.; Lee, W.-E.; Jeong, H.; Sakaguchi, T.; Fujiki, M. *Macromolecules* **2009**, *42*, 20. (b) Kwak, G.; Lee, W.-E.; Kim, W.-H.; Lee, H. *Chem. Commun.* **2009**, *16*, 2112. (c) Jeong, H.; Lee, W.-E.; Kwak, G. *Macromolecules* **2010**, *43*, 1152. (d) Lee, W.-E.; Kim, J.-W.; Oh, C.-J.; Sakaguchi, T.; Fujiki, M.; Kwak, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 1406. (e) Park, H.; Jeong, H.; Lee, W.-E.; Yoon, K.-B.; Oh, C.-J.; Kwak, G. *Macromol. Rapid Commun.* **2011**, *32*, 360. (f) Lee, W.-E.; Lee, C.-L.; Sakaguchi, T.; Fujiki, M.; Kwak, G. *Macromolecules* **2011**, *44*, 432.

(5) (a) Yagci, Y.; Jockusch, S.; Turro, N. *Macromolecules* **2010**, *43*, 6245. (b) del Campo, A.; Arzt, E. *Chem. Rev.* **2008**, *108*, 911.

(6) (a) Kim, J.-M.; Chang, T.-E.; Kang, J.-H.; Han, D.-K.; Ahn, K.-D. *Adv. Mater.* **1999**, *11*, 1499. (b) Kim, J.-M.; Chang, T.-E.; Kang, J.-H.; Park, K. H.; Han, D.-K.; Ahn, K.-D. *Angew. Chem., Int. Ed.* **2000**, *39*, 1780. (c) Lee, C.-W.; Yuan, Z.; Ahn, K.-D.; Lee, S.-H. *Chem. Mater.* **2002**, *14*, 4572. (d) Coenjarts, C.; Garcia, O.; Lluger, L.; Palfreymann, J.; Vinette, A. L.; Scaiano, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 620. (e) Doh, J.; Irvine, D. J. *J. Am. Chem. Soc.* **2004**, *126*, 9170. (f) Chae, K. H.; Kim, Y. H. *Adv. Funct. Mater.* **2007**, *17*, 3470. (g) Hu, W.; Lu, N.; Zhang, H.; Wang, Y.; Kehagias, N.; Reboud, V.; Sotomayor, T.; Clivia, M.; Hao, J.; Li, W.; Fuchs, H.; Chi, L. *Adv. Mater.* **2007**, *19*, 2119. (h) Kim, J.-M. *Macromol. Rapid Commun.* **2007**, *28*, 1191–1212. (i) Gao, L.; Lu, N.; Hao, J.; Hu, W.; Shi, G.; Wang, Y.; Chi, L. *Langmuir* **2009**, *25*, 3894.

(7) (a) Kwak, G.; Fujiki, M.; Sakaguchi, T.; Masuda, T. *Macromolecules* **2006**, *39*, 319. (b) Lee, W.-E.; Park, H.; Kwak, G. *Chem. Commun.* **2011**, *47*, 659–661.

(8) (a) Yan, M.; Rothberg, L. J.; Paradimitrakopoulos, F.; Galvin, M. E.; Miller, T. M. *Phys. Rev. Lett.* **1994**, *73*, 10194. (b) Scott, J. C.; Kaufman, J. H.; Brock, P. J.; Dipietro, R.; Salem, J.; Goitia, J. A. *J. Appl. Phys.* **1996**, *79*, 2745. (c) Abdou, M. S. A.; Orfino, F. P.; Son, Y.; Holdcroft, S. *J. Am. Chem. Soc.* **1997**, *119*, 4518. (d) De Jong, M. J. M.; Vissenberg, M. C. J. M. *Philips J. Res.* **1998**, *51*, 495. (e) Kaminorz, Y.; Smela, E.; Inganas, O.; Brehmer, L. *Adv. Mater.* **1998**, *10*, 765. (f) Yu, J.; Hu, D. H.; Barbara, P. F. *Science* **2000**, *289*, 1327. (g) Park, S.-J.; Gesquiere, A. J.; Yu, J.; Barbara, P. F. *J. Am. Chem. Soc.* **2004**, *126*, 4116. (h) Gesquiere, A. J.; Park, S.-J.; Barbara, P. F. *Eur. Polym. J.* **2004**, *40*, 1013. (i) Golovnin, I. V.; Bakulin, A. A.; Zapunidy, S. A.; Nechvolodova, E. M.; Paraschuk, D. Y. *Appl. Phys. Lett.* **2008**, *92*, 243311. (j) Wang, Y.-H.; Peng, Y.-J.; Mo, Y.-Q.; Yang, Y.-Q.; Zheng, X.-X. *Appl. Phys. Lett.* **2008**, *93*, 231902.