Swelling-Induced Emission Enhancement in Substituted Acetylene Polymer Film with Large Fractional Free Volume: Fluorescence Response to Organic Solvent Stimuli

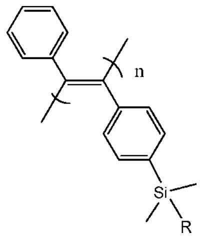
Giseop Kwak,*,† Wang-Eun Lee,† Heejun Jeong,†
Toshikazu Sakaguchi,‡ and Michiya Fujiki§

Department of Polymer Science, Kyungpook National University, 1370 Sankyuk-dong, Buk-ku, Daegu 702-701, Korea; Department of Materials Science and Engineering, Graduate School of Engineering, University of Fukui, Bunkyo, Fukui 910-8507, Japan; and Graduate School of Materials Science, Nara Institute of Science and Technology, 8916-5 Takayama, Ikoma, Nara 630-0101, Japan

Received November 7, 2008
Revised Manuscript Received December 8, 2008

Recently, many researches concerning the syntheses, physical properties, functions, and applications of disubstituted acetylene polymers have been done.[1] In 1991, Masuda et al. synthesized poly[1-phenyl-2-(*p*-trimethylsilyl)phenylacetylene] (PTMSDPA in Chart 1).[2] The PTMSDPA possesses several unique qualities including (a) an ultrahigh molecular weight, (b) excellent mechanical property, (c) chemical and thermal stability, (d) good solubility in organic solvents, and (e) film-forming ability. Especially, because PTMSDPA has an extremely large fractional free volume (FFV) of 0.26 in film, it has attracted much attention as a highly gas- and vapor-permeable membrane in practical use.[3] For instance, the oxygen permeability coefficient (P_{O_2}) of PTMSDPA is as large as 1100 barrers. As an another important feature of PTMSDPA, it should be noted that this polymer emits an intense fluorescence in a visible region because of the effective exciton confinement within the main chain due to the steric hindrance and/or intramolecular electron interactions of bulky aromatic substituents such as phenyl rings.[4] As functions and applications related to the intense fluorescence, we have recently reported new potential applications of PTMSDPA as a useful material for thermosensor,[5] electrospun optic nanofiber,[6] highly polarized fluorescent film,[7] and fluorescence image patterning.[8] PTMSDPA is a basically amorphous, semiflexible polymer with an extremely high molecular weight. Thus, it easily provides a very tough and flexible free-standing membrane as well as a thin film on various substrates, and also its film is highly transparent in visible regions. In this study, we thought that a combination of the fluorescence property of PTMSDPA and its high gas and vapor permeability would serve as the basis for a unique and practical application of PTMSDPA film to the optical detection of various organic solvent chemicals. That is, when some solvents diffuse into such a fluorescent polymer film with large FFV as PTMSDPA, the chemicals should stimulate entangled polymer chains to affect the interchain distances and solid-state electronic structures.

Chart 1. Chemical Structures of PTMSDPA (R = Methyl) and PODDMSDPA (R = Octadecyl)[a]



[a] Their syntheses were already reported in previous papers.[1,25] The polymers used in this study have high weight-average molecular weights (M_w) of 5.23 × 10^6 and 4.18 × 10^6 g/mol, respectively, and polydispersity indices (PDI = M_w/M_n) of 3.2 and 2.5, respectively.

PTMSDPA obtained with the group 5 transition metal catalysts has usually a high molecular weight more than 1 × 10^6 g/mol in a high yield.[1] Thus, theoretically, a fully extended polymer chain would be approximately more than 1000 nm in length (3961 × 2.545 Å) as estimated from the polymerization degree (n) of about 3961 and the alternative double−single bonds (repeat unit) length of 2.545 Å.[9] Also, the polymer chains are semiflexible as estimated from the viscosity index ($\alpha = 0.80$ in THF at 40 °C).[7a] Thus, the extremely long, semiflexible polymer chains of PTMSDPA should be more complicatedly entangled with one another than shorter, rigid-rod-like polymer chains of other conjugated polymers, e.g., polyfluorenes,[10] polythiophenes,[11] polyphenylenes,[12] poly(phenylenevinylene)s,[13] and poly(phennyleneethynlene)s,[14] with relatively low molecular weights in a range of 10^3−10^5 g/mol. Such a chain entanglement naturally results in a physical cross-link in a solid state. In addition, PTMSDPA is π-rich due to the π-conjugated main chain and aromatic side chain. Although an intermolecular π−π interaction is a weak intermolecular force, it can be partially multiplied at point of contact of randomly entangled polymer chains. From a viewpoint of solid-state electronic transition energy, the multiplied intermolecular interaction together with the chain entanglement will provide effective energy trapping sites mainly around cross-linking points.[15] This may result in a somewhat different appearance in fluorescence between the film and the ideal solution because the polymer chains are highly entangled in a solid but are isolated and untangled in an ideal solution. Actually as shown in Figure 1a, the fluorescence band of PTMSDPA[16] in a solid film significantly shifted to a longer wavelength (fluorescence maximum wavelength, $\lambda_{\mathrm{em,max}} = 539$ nm) by ~31 nm as compared to that of the solution (508 nm). As shown in the photographs in Figure 1b, the fluorescence in solution is intense and greenish-yellow while the film emits a relatively weak light, as recognized by the naked eye, and the emission color is no more greenish in film. This leads to the idea that randomly entangled chains around cross-linking points favor either intermolecular π−π interaction or main-chain planarization in order to more easily form energy-trapping sites with lower electronic transition energies. On the other hand, this phenomenon was not observed in a PTMSDPA derivative polymer, poly(1-phenyl-2-*p*-{dimethyl-*n*-octadecylsilylphenyl}acetylene) (PODDMSDPA in Chart 1), with a long alkyl side chain of octadecyl group. The fluorescence band of PODDMSDPA in a solid film little shifted to red as compared to that in an ideal solution as shown in Figure 1. According to our previous study, PODDMSDPA film has a lamellar layer structure with a long distance spacing of about 22 Å, and its FFV is quite low as 0.16 (density, $d = 0.96$ g/cm^3) relative to 0.26 ($d = 0.91$ g/cm^3) of PTMSDPA, indicating a highly dense, ordered, molecular packing structure in film.[7a] That is, such highly packed chains within the lamellar layers

---

* To whom correspondence should be addressed: Tel +82-53-950-7558; fax +82-53-950-6623; e-mail gkwak@knu.ac.kr.
† Kyungpook National University.
‡ University of Fukui.
§ Nara Institute of Science and Technology.

10.1021/ma802506x CCC: $40.75

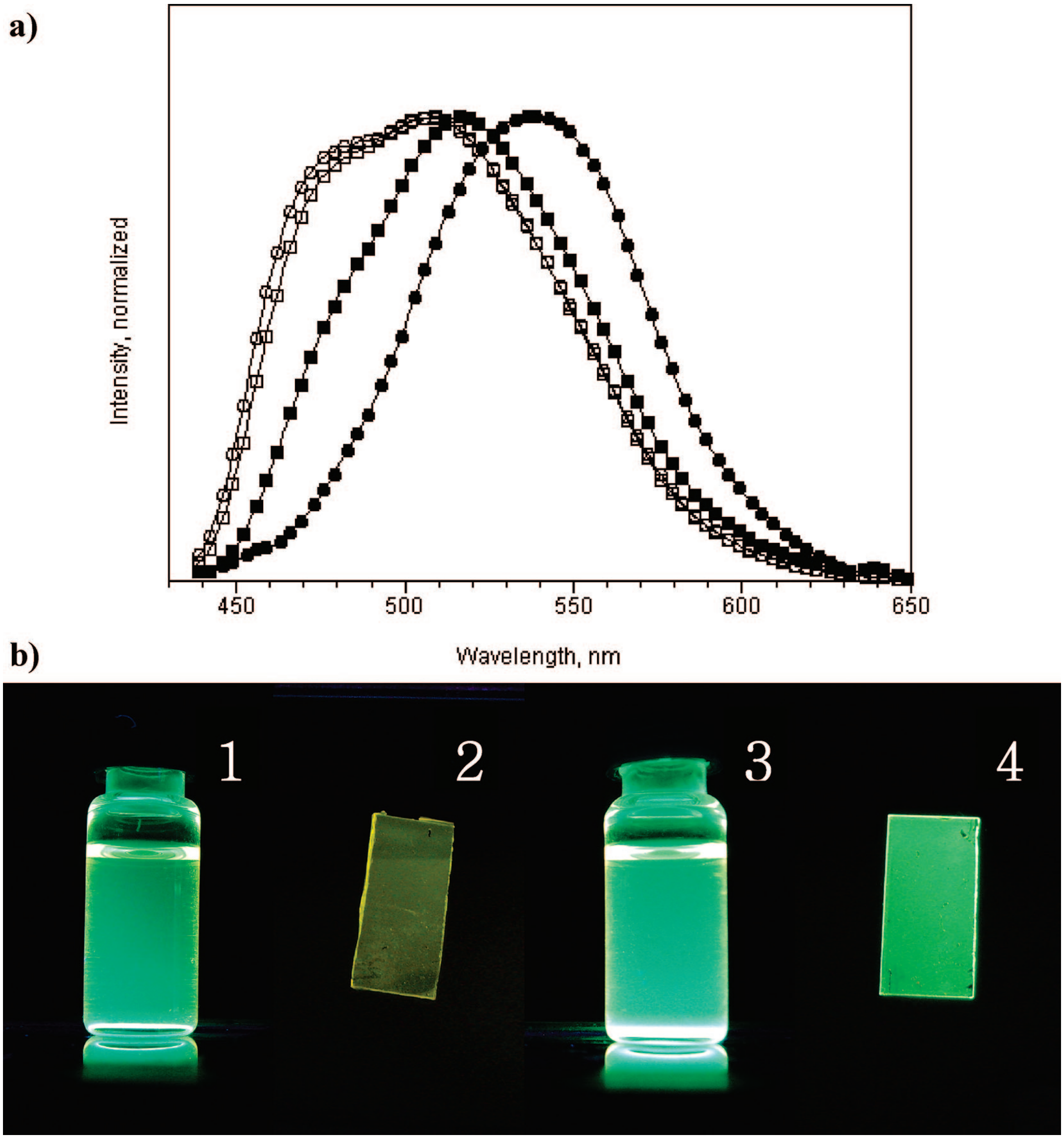


Figure 1. (a) Fluorescence spectra (excited at 420 nm, ○: PTMSDPA in solution; □: PODDMSDPA in solution; ●: PTMSDPA in film; ■: PODDMSDPA in film) and (b) photographs (excited at >420 nm, **1**: PTMSDPA in solution; **2**: PTMSDPA in film; **3**: PODDMSDPA in solution; **4**: PODDMSDPA in film) of PTMSDPA and PODDMSDPA in solutions (concentration $<1.0 \times 10^{-7}$ M in cyclohexane) and cast films (thickness $\approx 10\ \mu$m).

with a long interchain distance would not be entangled not to easily form energy-trapping sites in a solid film. This can also be explained by the idea that the long alkyl side chains of octadecyl groups, attached to rid-rod-like main chain (PODDMSDPA: $\alpha = 1.03$ in THF at 40 °C), behave like a solvent even in a solid film to keep constant interchain distance to prevent interchain $\pi-\pi$ interaction. As will be mentioned later, such intrinsic physical properties as large FFV and chain entanglement in PTMSDPA film affect swelling degree of the film when organic solvent chemicals diffuse to the film, and its fluorescence sensitively responds to the chemicals stimuli.

Owing to the intrinsic conjugation cooperativity, conjugated polymers can promptly respond to minor changes in a molecular electronic structure.[17] This is one of the great advantages of conjugated polymers when using as chemosensor materials. Also, if such conjugated polymers prove thermally, chemically, and mechanically stable like PTMSDPA, the sensory materials would be more appealing for practical applications. Porosity, related to FFV, in a polymer film has been thought as a very important factor in the field of chemosensory materials for the detection of nitroaromatic explosive TNT (2,4,6-trinitrotoluene).[18] Swager et al. have induced high porosity in solid films of fluorescent conjugated polymers based on poly(*p*-phenyleneethynlene)s[18a,b,d,e] and poly(*p*-phenylenevinylene)s[18c] by introducing an extremely bulky, rigid three-dimensional pentiptycence scaffold to the films. This facilitated rapid analyte diffusion in the polymer film to achieve quicker and larger amplitude responses to TNT. That is, the fluorescence significantly decreased upon exposure to the highly electron-deficient TNT vapor molecules. Such a highly porous polymer film as PTMSDPA may afford sufficiently large spaces for chemicals diffusing into the polymer film, leading to a quick fluorescence response to analytes. Actually, Schanze et al. have nicely conducted an explosive-sensing performance using PTMSDPA thin films with nanosized thickness.[19] Here is one question of concern: Is PTMSDPA also responsive to common organic solvents and the response mechanism the same as the explosive-response mechanism?

We investigated the variation in the fluorescence spectra of PTMSDPA film upon exposure to some volatile organic

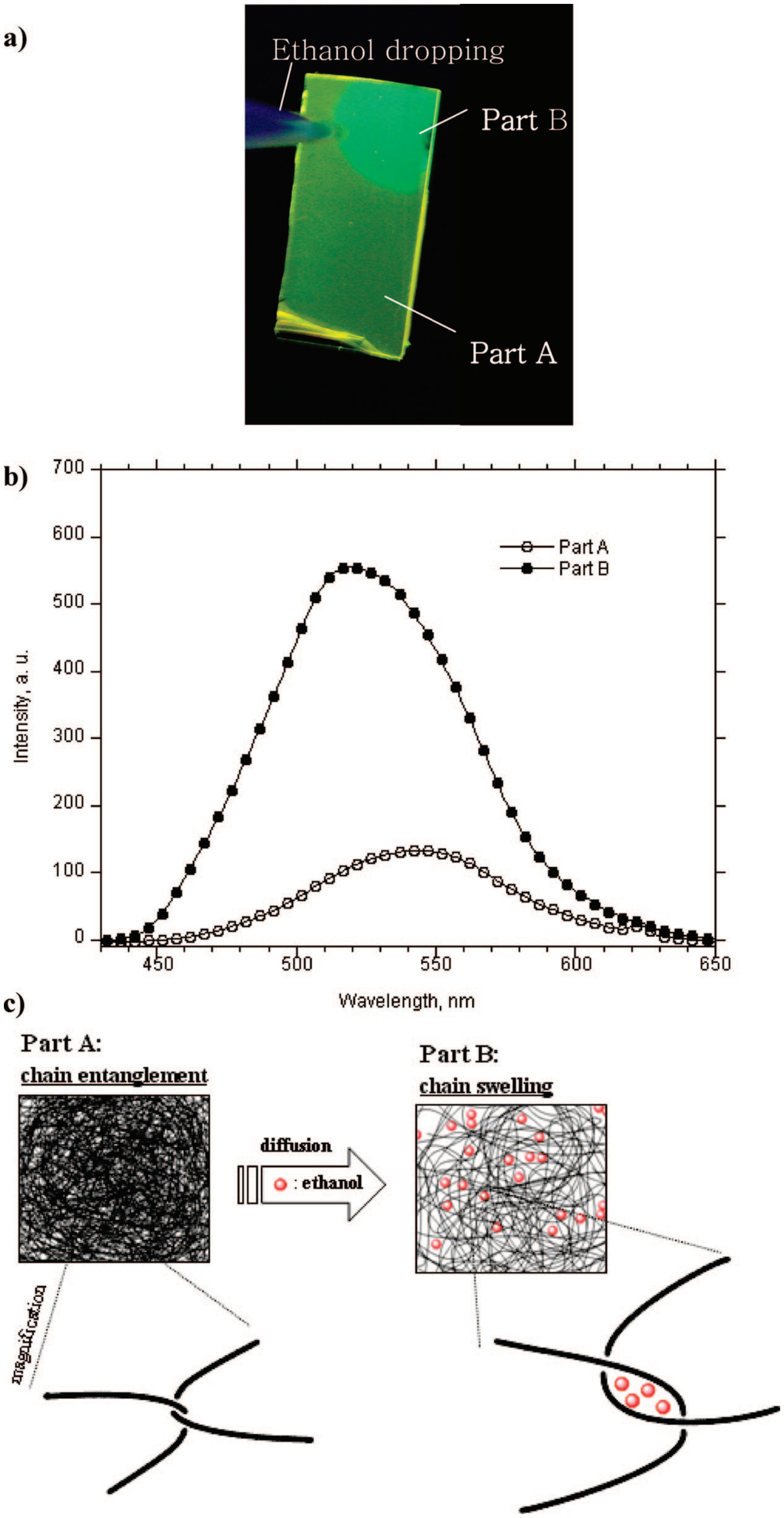


Figure 2. (a) Photograph and (b) fluorescence spectra of PTMSDPA film before and after ethanol contact and (c) schematic representation of change in fluorescence of PTMSDPA film.

compounds (VOCs). When the cast film was contacted to alcohols such as methanol, ethanol, and isopropanol, the film was slightly swollen and became more flexible, while the film never did so when contacted to water.[20] At the same time, the fluorescence immediately responded to the alcohols stimuli and significantly increased. This contrasted sharply to the fluorescence quenching phenomenon in respect to the explosive chemicals. For example, Figure 2a,b shows the actual photograph and fluorescence spectra of the PTMSDPA film before (part A in Figure 2a) and after (part B in Figure 2a) coming in contact with ethanol. (As for methanol and isopropanol, see Figures S1 and S2 in the Supporting Information.) As soon as the ethanol comes in contact with the polymer film, the fluorescence intensity immediately increased about 4.3 times, and simultaneously, the fluorescence band shifted to a shorter wavelength by 25 nm. These changes in emission along with ethanol contact can be explained as follows: (i) Before coming in contact with ethanol, the polymer chains in the solid film are highly entangled and physically cross-linked to provide some fluorescence quenching sites mainly around cross-linking points, leading to a relatively weak fluorescence. (ii) And then when contacted with ethanol, ethanol molecules rapidly diffuse into the polymer film composed of three-dimensionally cross-linked polymer chains through many microvoids and then swell out the polymer chains by a hydrophilic−hydrophobic repulsion, in order to let the chains be free from entanglement. (iii) Finally, intermolecular $\pi-\pi$ interaction is considerably reduced leading to enhanced emission in a shorter wavelength. This is correspondent to the fact that, as mentioned above, the fluorescence was stronger and the emission band shifted to blue in a solution as compared to the film. In other words, this indicates that the oscillator strength and irradiative $\pi^*-\pi$ transition energy of PTMSDPA in a swollen film become close to those of the solution due to the chain relaxation from entanglement. A schematic explanation is also shown in Figure 2c.

The swelling-induced emission enhancement (SIEE) was also observed when the PTMSDPA film was contacted to poor solvents such as hydrocarbons of *n*-hexane (bp 69 °C, d 0.66 g/mL), *n*-decane (bp 174 °C, d 0.73 g/mL), and paraffin oil (see Figures S3−S5 in the Supporting Information). The I/I_0 ratio, where I_0 and I are intensities at fluorescence maximum wavelength before and after coming in contact with *n*-hexane, respectively, was estimated to be 3.4. Although hexane is a larger molecule relative to alcohols tested previously, it is a basically hydrophobic and a poor solvent to PTMSDPA but has still an affinity to PTMSDPA and, thus, readily diffuses into the PTMSDPA bulk solid film through the microvoids within the polymer film.[21] The poor solvent, *n*-hexane, presumably makes the highly entangled polymer chains temporarily free at a swollen state, like in the case of alcohols, leading to lessening the $\pi-\pi$ interaction and then eventually to enhancing a fluorescence. Also, other larger size molecules of hydrocarbons such as *n*-decane and paraffin oil showed the same phenomenon. It should be also noted that the I/I_0 ratios for *n*-decane and paraffin oil were estimated to be 4.4 and 7.6, respectively. The larger the molecular size of the diffused molecules, the higher the I/I_0 ratio. This indicates a possibility of molecular size recognition using the PTMSDPA film. On the other hand, when the PTMSDPA film was exposed to smaller molecules relative to *n*-hexane, e.g., gaseous hydrocarbons of propane (bp −42 °C) and butane (bp 0 °C), fluorescence did not change. This is due to the fact that the gas molecules rapidly diffuse into the film, and the molecular sizes are too small to swell out polymer chains. Noticeably, the solvent-triggered SIEE was completely reversed to the initial state after natural evaporation of the solvents (see Figure S6 in the Supporting Information). On the other hand, the PODDMSDPA with ordered packing structure and small FFV did not exhibit significant SIEE against any alcohols tested here (Figures S7 and S8 in the Supporting Information). A poly(phenylenevinylene) (PPV) derivative was also tested for SIEE. The fluorescence band of the PPV derivative in the film never changed against such common organic solvents as alcohols and hydrocarbons (Figures S9 and S10 in the Supporting Information).[22]

It may be reasonable to think that swelling is the process changing from solid to solution. Namely, a solution state can be regarded as the complete swollen-out state of the polymer chains which were restrained by interchain interaction in chain entanglement. Thus, the comparison of the time-resolved emission decay in a solution with that in film may help us to further comprehensively understand the dynamic fluorescence property of a swollen film. Table 1 summarizes the fluorescence lifetimes of PTMSDPA and PODDMSDPA in films and solutions. The photoemission decay of PTMSDPA in a solution ($c = 1.0 \times 10^{-6}$ mol/L in cyclohexane) obeyed monoexponential decay, while two-exponential was required to adequately fit the observed decay dynamics in the film. The emission of PTMSDPA in a film is characterized by a shorter dominant fluorescence lifetime (τ_1) rather than a longer one (τ_2), whereas the emission in solution comes exclusively from the longer-lived excited species. The shorter-lived emission excited species in PTMSDPA film was presumably formed due to a rapid energy transfer into the energy trapping sites. Thus, when the polymer chains in film are sufficiently swollen out by solvent molecules, the generation of shorter-lived excited species may be restrained along with a degree of swelling. This comparison of the dynamic fluorescence property of PTMSDPA in a solution with that in film strongly supports the idea of SIEE in PTMSDPA film with a large FFV. In contrast to PTMSDPA, the emission of PODDMSDPA is characterized by a longer dominant fluorescence lifetime (τ_2) either in film or in solution, indicating no generation of shorter-lived emission excited species even in film. As discussed previously, this can be explained by the idea that the long alkyl side chain of octadecyl group in PODDMSDPA behaves like a solvent even in a solid film to keep the interchain distance at a constant to prevent interchain interaction.

Table 1. Fluorescence Lifetimes of PTMSDPA and PODDMSDPA in Films and Cyclohexane Solutions[a]

	in film			in cyclohexane		
polymer	τ_1 (f_1)	τ_2 (f_2)	χ^2	τ_1 (f_1)	τ_2 (f_2)	χ^2
PTMSDPA	0.17 (0.78)	0.73 (0.22)	1.68	−	0.71 (1.00)	1.34
PODDMSDPA	0.05 (<0.01)	1.43 (>0.99)	1.91	−	1.11 (1.00)	0.99

[a] Monitor wavelength is 550 nm, τ_1 and τ_2 are lifetimes (ns), f_1 and f_2 are fractional intensities, and χ^2 is the reduced chi-square.

In summary, PTMSDPA film showed a significant emission enhancement when contacted to various organic solvent compounds such as alcohols and hydrocarbon liquids. This SIEE phenomenon was ascribed to the large FFV in the film. The SIEE mechanism proposed in this study for PTMSDPA film is conceptually very similar to swelling-induced conductivity changes of conducting polymers,[23] such as polythiophene and polypyrrole derivatives, and conductive particle−polymer hybrids.[24] From a viewpoint of sensor application, therefore, this SIEE phenomenon may be very useful for optical detection of various VOCs in a fluorescence-enhancing (turn-on) mode unlike the TNT detection in a fluorescence turn-off mode. Controls of pore size and FFV in fluorescent conjugated polymer film may be achieved by a delicate molecular design, which can make it possible to recognize the molecular sizes of analytes. Thus, the sensor application of PTMSDPA derivative films may extend to optical detection of either gaseous, small-sized molecules or large-sized supramolecules or virus molecular clusters by controlling the pore size in film.

Acknowledgment. This paper is dedicated to Professor Toshio Masuda on the occasion of his retirement from Kyoto University and to recognize his outstanding contributions in polymer chemistry and engineering. This work was supported by the Korea Science and Engineering Foundation (KOSEF) grants funded by the Korea government (MEST) (R01-2008-000-10069-0, R11-2008-105-03002-0). This research was also supported by Kyungpook National University Research Fund, 2007. G.K. is acknowledged in part for a grant from the Korean Government (MOEHRD, Basic Research

Promotion Fund) (KRF-2008-521-D00113). The authors thank NOF Co., Ltd., Japan, for the donation of PTMSDPA.

Supporting Information Available: Experimental methods; fluorescence spectra of PTMSDPA film before and after coming in contact with methanol, isopropanol, *n*-hexane, *n*-decane, and paraffin oil (Figures S1−S5); variation in fluorescence spectra of PTMSDPA film after contacting to ethanol and subsequently natural evaporation (Figure S6); fluorescence spectra of PODDMSDPA film before and after coming in contact with ethanol and isopropanol (Figures S7 and S8); chemical structure of PPV derivative (Figure S9); fluorescence spectra of the PPV derivative film before and after coming in contact with ethanol (Figure S10). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) See related essay and review papers: (a) Tang, B. Z. *Macromol. Chem. Phys.* **2008**, *209*, 1303–1307. (b) Lam, J. W.; Tang, B. Z. *Acc. Chem. Res.* **2005**, *38*, 745–754. (c) Lam, J. W. Y.; Tang, B. Z. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 2607–2629. (d) Nagai, K.; Masuda, T.; Nakagawa, T.; Freeman, B. D.; Pinnau, I. *Prog. Polym. Sci.* **2001**, *26*, 721–798. (e) Choi, S. K.; Gal, Y. S.; Jin, S. H.; Kim, H. K. *Chem. Rev.* **2000**, *100*, 1645–1682.

(2) (a) Tsuchihara, K.; Masuda, T.; Higashimura, T. *J. Am. Chem. Soc.* **1991**, *113*, 8548–8549. (b) Tsuchihara, K.; Masuda, T.; Higashimura, T. *Macromolecules* **1992**, *25*, 5816–5820.

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

(4) (a) Shukla, A. *Chem. Phys.* **2004**, *300*, 177–188. (b) Shukla, A.; Ghosh, H.; Mazumdar, S. *Synth. Met.* **2001**, *116*, 87–90. (c) Hidayat, R.; Fujii, A.; Ozaki, M.; Teraguchi, M.; Masuda, T.; Yoshino, K. *Synth. Met.* **2001**, *119*, 597–598. (d) Fujii, A.; Hidayat, R.; Sonoda, T.; Fujisawa, T.; Ozaki, M.; Vardeny, Z. V.; Teraguchi, M.; Masuda, T.; Yoshino, K. *Synth. Met.* **2001**, *116*, 95–99. (e) Gontia, I.; Frolov, S. V.; Liess, M.; Vardeny, Z. V.; Ehrenfreund, E.; Tada, K.; Kajii, H.; Hidayat, R.; Fujii, A.; Yoshino, K.; Teraguchi, M.; Masuda, T. *Synth. Met.* **2001**, *116*, 91–94. (f) Shukla, A.; Ghosh, H.; Mazumdar, S. *Synth. Met.* **2001**, *116*, 87–90. (g) Hidayat, R.; Tatsuhara, S.; Kim, D. W.; Ozaki, M.; Yoshino, K.; Teraguchi, M.; Masuda, T. *Phys. Rev. B* **2000**, *61*, 10167–10173. (h) Ghosh, H.; Shukla, A.; Mazumdar, S. *Phys. Rev. B* **2000**, *62*, 12763–12774. (i) Frolov, S. V.; Fujii, A.; Chinn, D.; Hirohata, M.; Hidayat, R.; Teraguchi, M.; Masuda, T. *Adv. Mater.* **1998**, *10*, 869–872.

(5) Kwak, G.; Fukao, S.; Fujiki, M.; Sakaguchi, T.; Masuda, T. *Chem. Mater.* **2006**, *18*, 2081–2085.

(6) Kwak, G.; Fukao, S.; Fujiki, M.; Sakaguchi, T.; Masuda, T. *Chem. Mater.* **2006**, *18*, 5537–5542.

(7) (a) Kwak, G. ; Minakuchi, M.; Sakaguchi, T.; Masuda, T.; Fujiki, M. *Macromolecules* **2008**, *41*, 2743–2746. (b) Kwak, G. ; Minakuchi, M.; Sakaguchi, T.; Masuda, T.; Fujiki, M. *Chem. Mater.* **2007**, *19*, 3654–3661.

(8) Kwak, G. ; Fujiki, M.; Sakaguchi, T.; Masuda, T. *Macromolecules* **2006**, *39*, 319–323.

(9) The polymerization degree (*n*) value was obtained by dividing polymer molecular weight ($M_{\mathrm{w,polymer}}$) by repeat unit molecular weight ($M_{\mathrm{w,repeat\ unit}} = 252.43$) on the supposition that $M_{\mathrm{w,polymer}}$ is 1.0×10^6. The repeat unit length was calculated by using Chem3D Ultra 8.0 (CambridgeSoft Co.)

(10) (a) Scherf, U.; List, E. J. W. *Adv. Mater.* **2002**, *14*, 477–487. (b) Grell, M.; Knoll, W.; Lupo, D.; Meisel, A.; Miteva, T.; Neher, D.; Nothofer, H.-G.; Scherf, U.; Yasuda, A. *Adv. Mater.* **1999**, *11*, 671–675.

(11) (a) Bjornholm, T.; Greve, D. R.; Reizel, N.; Hassenkam, T.; Kjaer, K.; Howes, P. B.; Larsen, N. B.; Bogelund, J.; Jayaraman, M.; Ewbank, P. C.; McCullough, R. D. *J. Am. Chem. Soc.* **1998**, *120*, 7643–7644. (b) Prosa, T. J.; Winokur, M. J.; McCullough, R. D. *Macromolecules* **1996**, *29*, 3654–3656. (c) McCullough, R. D.; Williams, S. P. *J. Am. Chem. Soc.* **1993**, *115*, 11608–11609.

(12) (a) Gin, D. L.; Conticello, V. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 10934–10947. (b) Stille, J. K.; Gilliams, Y. *Macromolecules* **1971**, *4*, 515–517.

(13) (a) Pasco, S. T.; Lahti, P. M.; Karasz, F. E. *Macromolecules* **1999**, *32*, 6933–6937. (b) Kretschmann, H.; Meier, H. *J. Prakt. Chem.* **1994**, *336*, 247–254, 255−259.

(14) (a) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605–1644. (b) Bunz, U. H. F. *Acc. Chem. Res.* **2001**, *34*, 998–1010. (c) Mitschke, U.; Bauerle, P. *J. Mater. Chem.* **2000**, *10*, 1471–1507. (d) McQuade, D. J.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2357–2574. (e) Swager, T. M. *Acc. Chem. Res.* **1998**, *31*, 201–207. (f) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402–428.

(15) Thomas, S. W., III; Joly, G. D.; Swager, T. M. *Chem. Rev.* **2007**, *107*, 1339–1386.

(16) PTMSDPA was donated from NOF Co., Ltd., Japan, and used as received. The polymer used in this study has a high weight-average molecular weights (M_w) of 5.2×10^6 g/mol and polydispersity index (PDI = $M_\mathrm{w}/M_\mathrm{n}$) of 3.2. Recently, this polymer became commercially available (for inquiry, contact NOF Co., Ltd., Japan: http://www.nof.co.jp/english/index.html).

(17) See review papers: (a) McQuade, D. J.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2357–2574. (b) Swager, T. M. *Acc. Chem. Res.* **1998**, *31*, 201–207. (e) Swager, T. M.; Marsella, M. J. *Adv. Mater.* **1994**, *6*, 595–597.

(18) (a) Thomas, S. W., III; Swager, T. M. *Adv. Mater.* **2006**, *18*, 1047–1050. (b) Zhao, D.; Swager, T. M. *Macromolecules* **2005**, *38*, 9377–9384. (c) Kim, Y.; Zhu, Z.; Swager, T. M. *J. Am. Chem. Soc.* **2004**, *126*, 452–453. (d) Yang, J.-S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 11864–11873. (e) Yang, J.-S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 5321–5322.

(19) Lui, Y.; Mill, R. C.; Boncella, J. M.; Schanze, K. S. *Langmuir* **2001**, *17*, 7452–7455.

(20) PTMSDPA is ethanol-permselective as high as $\alpha_{\mathrm{EtOH/H_2O}}$ of 6.86 in ethanol (EtOH)/water (H_2O) mixture pervaporation, although the ethanol is nonsolvent to PTMSDPA and its molecular size is larger than the water molecule and so seems to be quite difficult to permeate [refer to our previous paper: Sakaguchi, T.; Yumoto, K.; Kwak, G.; Yoshikwa, M.; Masuda, T. *Polym. Bull.* **2002**, *48*, 271]. The gas/vapor permeability of polymer is decided by two factors, namely, diffusion and solution. In the case of the alcohol permeability of PTMSDPA, the diffusion mechanism may be dominant rather than solution mechanism because PTMSDPA has a large FFV due to many molecular-scale voids (microvoids) and is basically hydrophobic due to the hydrocarbon-based molecular skeleton.

(21) PTMSDPA does not promptly dissolve in hexane but finally dissolves completely after long exposure to *n*-hexane for about 3 days.

(22) Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] was used in this study, which is commercially available from Sigma-Aldrich Co. Ltd. The chemical structure and fluorescence spectral data are shown as Figures S9 and S10, respectively, in the Supporting Information.

(23) (a) Li, B.; Sauve, G.; Iovu, M. C.; Jeffries-El, M.; Zhang, R.; Cooper, J.; Santhanam, S.; Schultz, L.; Revelli, J. C.; Kusne, A. G.; Kowalewski, T.; Snyder, J. L.; Weiss, L. E.; Fedder, G. K.; McCullough, R. D.; Lambeth, D. N. *Nano Lett.* **2006**, *6*, 1598–1602. (b) Hamilton, S.; Hepher, M. J.; Sommerville, J. *Sens. Actuators, B* **2005**, *107*, 424. (c) Janata, J.; Josowicz, M. *Nat. Mater.* **2003**, *2*, 19. (d) Torsi, L.; Tafuri, A.; Cioffi, N.; Gallazzi, M. C.; Sassella, A.; Sabbatini, L.; Zambonin, P. G. *Sens. Actuators, B* **2003**, *93*, 257. (e) Sakurai, Y.; Jung, H.-S.; Shimanouchi, T.; Inoguchi, T.; Morita, S.; Kuboi, R.; Natsukawa, K. *Sens. Actuators, B* **2002**, *83*, 270. (f) Crone, B.; Dodabalapur, A.; Gelperin, A.; Torsi, L.; Katz, H. E.; Lovinger, A. J.; Bao, Z. *Appl. Phys. Lett.* **2001**, *78*, 2229.

(24) (a) Snow, E. S.; Perkins, F. K.; Houser, E. J.; Badescu, S. C.; Reinecke, T. L. *Science* **2005**, *307*, 1942. (b) Ha, S.-C.; Kim, Y. S.; Yang, Y.; Kim, Y. J.; Cho, S.-M.; Yang, H.; Kim, Y. T. *Sens. Actuators, B* **2005**, *105*, 549. (c) Lonergan, M. C.; Severin, E. J.; Doleman, B. J.; Beaber, S. A.; Grubbs, R. H.; Lewis, N. S. *Chem. Mater.* **1996**, *8*, 2298.

(25) Sakaguchi, T.; Yumoto, K.; Shiotsuki, M.; Sanda, F.; Yoshikawa, M.; Masuda, T. *Macromolecules* **2005**, *38*, 2704–2709.

MA802506X