902 *Macromolecules* **2009**, *42*, 902−904

Combinatorially Responsive, Polarity-Indicative, Charge Transfer Dye-Based Polymer Gels for Odor Visualization in VOC Sensor Array

Hyeryun Kim and Giseop Kwak*

Department of Polymer Science, Kyungpook National University, 1370 Sankyuk-dong, Buk-ku, Daegu 702-701, Korea

Received November 21, 2008
Revised Manuscript Received January 13, 2009

Recently, volatile organic compound (VOC) detection techniques have been in high demand for many applications such as environment monitoring and homeland security.[1] Up to date, metal oxide semiconductors,[2] conjugated polymer conductors,[3] and conductive particle−polymer hybrids[4] are well-known as promising VOC-sensing materials. These materials are all highly responsive to various VOCs, and some of them are now used in commercial chemical sensors. High selectivity, e.g., discriminating between polar and nonpolar VOCs, still remains a challenging issue for further intelligent sensor operations. Thus, research focused on a specific material that has good selectivity as well as high sensitivity to the substances that are to be detected has been highly encouraged. Some array-based devices with excellent VOC-sensing performances, which detect and differentiate between chemically diverse analytes, have been developed.[5] Also, very recently, Lambeth et al. demonstrated that extended chemical selectivity can be achieved by molecular structure modification of the conjugated polymers of polythiophene derivatives.[6]

Meanwhile, charge transfer dyes (CTDs) such as 4-(dicyanomethylene)-2-methyl-6-(*p*-(dimethylamino)styryl)-4*H*-pyran (DCM) and its derivatives have been intensively developed for applications using as photo (PL)- and electroluminescent (EL) materials in the fields of dye lasers,[7] sensors,[8] dye-sensitized solar cells,[9] and organic light-emitting devices (OLED).[10] The most apparent feature of their photophysical properties is an intrinsic intramolecular charge transfer (ICT) character.[11] Their excited energy levels are highly dependent on media (solvent or polymer matrix[12]) polarity. In general, their fluorescence (FL) bands thus significantly shift to longer wavelengths with an indirect, nonradiative process in a polar external environment, whereas the CTDs surrounded by nonpolar media emit shorter wavelength FL lights in a direct, radiative process. A solvatochromism such as this can be subjected to extended chemical selectivity for the differentiation of the organic solvents in a VOC-sensing performance. Thus, CTD may be one of the promising candidates for a new VOC-sensing basic material.

However, organic-based materials may dissolve in VOC over a long period, after being exposed several times, which may cause serious problems in terms of durability and chemical resistance in an actual sensor operation. As a simple synthetic strategy to solve this problem, one can design highly durable gel materials with three-dimensional network structures.

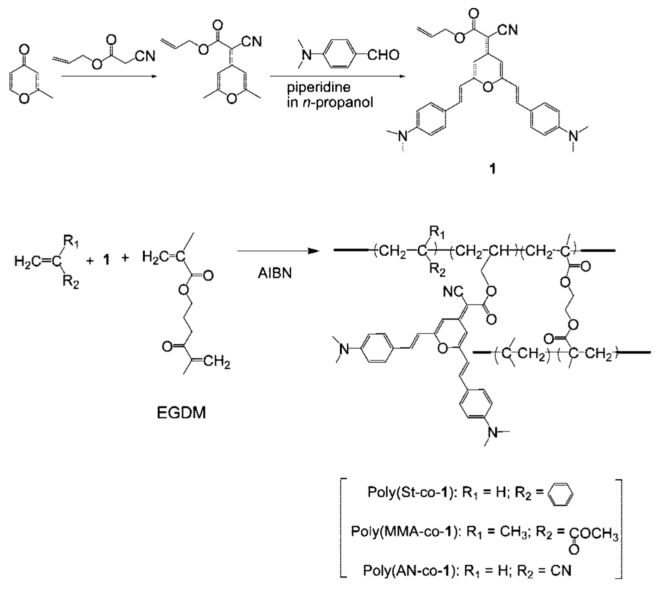
On the basis of this idea, polarity-indicative CTD-based polymer gels were prepared as a new type of VOC-sensing material. The combination of three different types of chemically selective gels with different media polarity greatly enhanced the discrimination of VOCs.

Pyran-based dye monomer, **1**, indicates an unusual photophysical property related to the charge transfer character as mentioned above.[13] Its chemical structure is shown in Scheme 1. The allyl group within **1** was designated for the covalent-bonding incorporation of **1** into polymer chain. The typical procedure used for the fabrication of the polymer gels is schematically presented in Scheme 1. Copolymerization of **1** with various vinyl monomers such as styrene (St), methyl methacrylate (MMA), and acrylonitrile (AN) in the presence of a small amount of the cross-linker of ethylene glycol dimethylacylate (EGDM) produced the target polymer gels of P(St-*co*-**1**), P(MMA-*co*-**1**), and P(AN-*co*-**1**), respectively, in relatively high yields. So as to completely remove unreacted **1** from the gels, Soxhlet extraction with water, methanol, and acetone was conducted several times in turn.

The VOC analytes tested in this study are divided into several types of organic solvents as follows: aliphatic hydrocarbon (1,4-dioxane), aromatic hydrocarbons (BTX: benzene, toluene, xylene; styrene), ester (ethyl acetate), weak acid (acetic acid), ether (THF), chlorinated hydrocarbons (chloroform, methylene chloride, dichloroethane), amine (pyridine), ketones (MEK, acetone), nitrile compounds (acrylonitrile, acetonitrile), and aprotic polar solvents (DMF, DMSO).

Figure 1 shows the swelling ratio (*Q*) of the present polymer gels in these solvents with different dielectric constants. Although the *Q* values vary depending on the degree of cross-linking of the polymer, a tendency to be dependent on a polymer matrix polarity is clearly seen in the *Q* values. For instance, P(St-*co*-**1**) gel swelled appropriately in nonpolar hydrocarbons in a *Q* range of approximately 4−6, whereas P(AN-*co*-**1**) gel never swelled in the same solvents. On the other hand, the latter gel swelled in polar solvents, such as nitrile compounds and aprotic polar solvents, in a *Q* range of about 1−4, while the former gel did not swell except for in DMF. Especially, only P(AN-*co*-**1**) gel swelled in a polar DMSO. P(MMA-*co*-**1**) gel

Scheme 1. Syntheses and Chemical Structures of 1 and Polymer Gels of P(St-*co*-1), P(MMA-*co*-1), and P(AN-*co*-1)



---

* Corresponding author: Tel +82-53-950-7558; Fax +82-53-950-6623; e-mail gkwak@knu.ac.kr.

10.1021/ma802593b CCC: $40.75

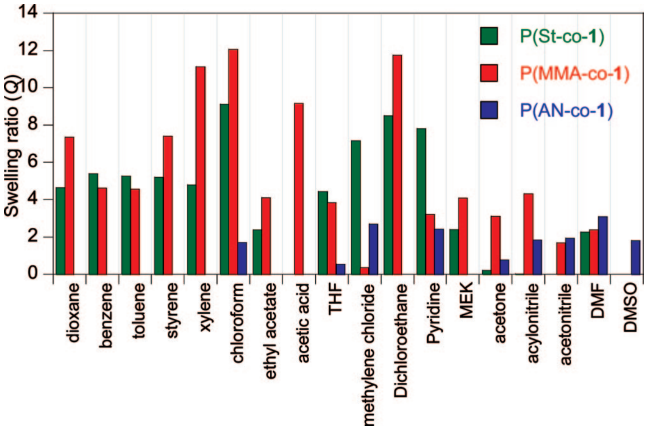


Figure 1. Swelling ratios (*Q*) of P(St-*co*-**1**), P(MMA-*co*-**1**), and P(AN-*co*-**1**) gels in various solvents.

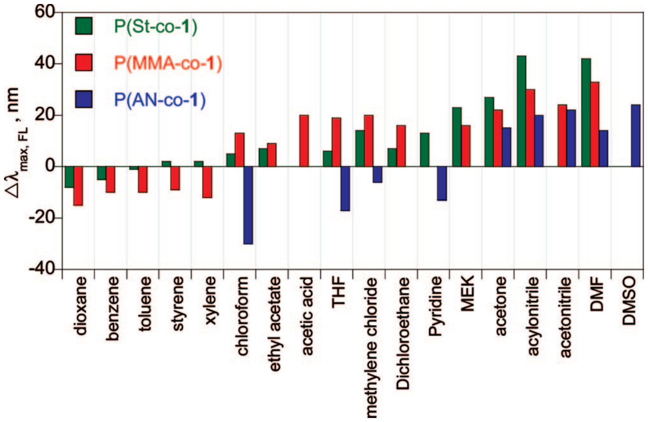


Figure 2. Variations of fluorescence wavelength ($\Delta\lambda_{max,FL}$) in P(St-*co*-**1**), P(MMA-*co*-**1**), and P(AN-*co*-**1**) gels upon exposure to various solvents (excited at 455, 470, and 475 nm, respectively).

swelled in all solvents other than DMSO in a wide *Q* range of 1−12. As expected from the dielectric constant (ε) order of PSt (2.5) < PMMA (3.3) < PAN (5.5),[14] the significant difference in *Q* values of the present polymer gels may come from the difference in molecular electronic affinity between the gel and solvent. In this way, the *Q* value significantly varies according to the gel types. Thus, the *Q* value should be considered in any practical application using the gels as VOC sensor materials.

Figure 2 shows the variation of maximum FL wavelengths ($\lambda_{max,FL}$) of the present polymer gels upon exposure to various solvents with different dielectric constants. As for P(St-*co*-**1**) gel, the $\lambda_{max,FL}$ shifted to shorter wavelengths when swollen in dioxane, benzene, and toluene, whereas $\lambda_{max,FL}$ shifted to longer wavelengths in solvents other than those. As for P(MMA-*co*-**1**) gel, red shifts were shown in chloroform and solvents with higher dielectric constants than that. In contrast to these two polymer gels, P(AN-*co*-**1**) gel showed shorter wavelength shifts in semipolar solvents such as chloroform, THF, methylene chloride, and pyridine, while the $\lambda_{max,FL}$ shifted to longer wavelengths in solvents that are more polar than pyridine.

Figure 3 plots the changes in FL wavelength ($\Delta\lambda_{max,FL}$) of P(St-*co*-**1**), P(MMA-*co*-**1**), and P(AN-*co*-**1**) gels as a function of dielectric constants of solvents. These three different types of polymer gel show different FL responses upon exposure to the organic solvents. P(St-*co*-**1**) and P(MMA-*co*-**1**) gels respond to nonpolar solvents lower than $\varepsilon = 2.38$ in the shorter wavelength shift mode, whereas P(AN-*co*-**1**) gel never responds to nonpolar solvents due to its nonswelling property. As for semipolar solvents in a ε range of 2.47−13.26, P(St-*co*-**1**) and P(MMA-*co*-**1**) gels are responsive in the longer wavelength shift mode, whereas P(AN-*co*-**1**) gel is active in the shorter wavelength shift mode. Also, if these three polymer gels respond to a certain organic solvent in the longer wavelength shift mode, the solvent may be a highly polar solvent of more than $\varepsilon = 18.56$, such as nitrile compounds and aprotic solvents. Thus, the algorithm for differentiating solvent chemicals by the FL emission spectroscopy, while simultaneously considering the swelling ratio, is suggested as shown in Figure S1 in the Supporting Information.

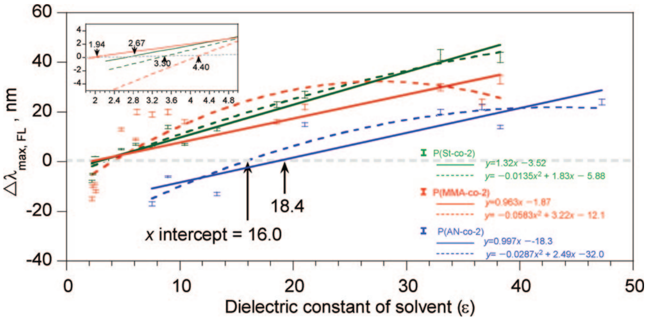


Figure 3. Plots of the changes in fluorescence wavelength ($\Delta\lambda_{max,FL}$) of P(St-*co*-**1**), P(MMA-*co*-**1**), and P(AN-*co*-**1**) gels as a function of dielectric constant.

For mathematical analysis, the functional equations between the dielectric constant (x) of solvent chemicals and $\Delta\lambda_{max,FL}(y)$ of the present polymer gels were obtained as shown in the inset of Figure 3. At first, the functional equations for P(St-*co*-**1**), P(MMA-*co*-**1**), and P(AN-*co*-**1**) gels were expressed as linear equations of $y = 1.32x - 3.52$, $y = 0.963x - 1.87$, and $y = 0.997x - 18.3$, respectively.[15] These three equations, if used in combination, may be very useful to more exactly estimate the polarity of unknown VOC analytes. Noticeably, the linear equation for P(St-*co*-**1**) gel quite accurately fits the observed $\Delta\lambda_{max,FL}$ values. Actually, when $y = 0$ for P(St-*co*-**1**) gel, the x intercept value is calculated to be 2.67, which is very close to the ε value (2.5) of PSt. This confirmed the accurate fitting of the linear equation for P(St-*co*-**1**). Also as for P(MMA-*co*-**1**) gel, a relatively accurate fitting of the linear equation is recognized from the fact that the x intercept value is 1.94 at $y = 0$, which is not so different from the ε value (3.3) of PMMA. However, when $y = 0$ for P(AN-*co*-**1**) gel, the x intercept values is calculated to be 18.4, which is far from the ε value (5.5) of PAN. The y intercept value of the linear equation for P(AN-*co*-**1**) gel is quite different from those for the other two polymer gels. Thus, for the more exact estimation of unknown analytes, adequately polarity-controlled copolymer gels, e.g., P(St-*co*-AN-*co*-**1**) and P(MMA-*co*-AN-*co*-**1**) with appropriate composition ratios, are needed in an y intercept range of −3.52 to −18.3. Also, the quadratic functional equations for P(St-*co*-**1**), P(MMA-*co*-**1**), and P(AN-*co*-**1**) gels are expressed as $y = -0.0135x^2 + 1.83x - 5.88$, $y = -0.0583x^2 + 3.22x - 12.1$, and $y = -0.0287x^2 + 2.49x - 32.0$, respectively. The x intercepts in these quadratic equations are 3.30, 4.40, and 16.0, respectively. As shown in Figure 3, the quadratic equation for P(AN-*co*-**1**) gel fits better than the linear one.

Figure 4 shows the actual FL colors of the three polymer gels when exposed to organic solvents. All are different from each other as recognized by the naked eye. The chemoselective responses of CTD-based polymer gels potentially permit the visual identification of a wide range of organic solvents. This also strongly suggests that the present polymer gels have use

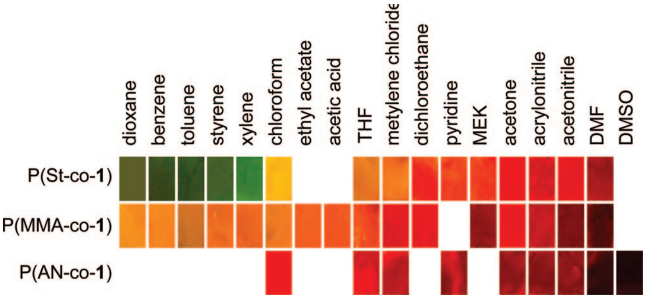


Figure 4. Photographs of fluorescence colors of P(St-*co*-**1**), P(MMA-*co*-**1**), and P(AN-*co*-**1**) gel films when exposed to organic solvents (excited at >450 nm).

as fluorescent materials for a litumus-type VOC sensor array for odor visualization. Now, it is expected that combination of such different types of polymer gels in an array will give combinatorial response information in a sensor operation. Also, studies on chemical sensitivities of the polymer gels for an actual sensor operation are now underway in the laboratory.

Acknowledgment. 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).

Supporting Information Available: Experimental section; flowchart of the algolithm for differentiating solvent chemicals by using P(St-*co*-**1**), P(MMA-*co*-**1**), and P(AN-*co*-**1**) gels (Figure S1). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Ampuero, S.; Bosset, J. O. *Sens. Actuators, B* **2003**, *94*, 1. (b) McDonagh, C.; Burke, C. S.; MacCraith, B. D. *Chem. Rev.* **2008**, *108*, 400.

(2) (a) Srivastava, A. K. *Sens. Actuators, B* **2003**, *96*, 24. (b) Tomchenko, A. A.; Harmer, G. P.; Marquis, B. T.; Allen, J. W. *Sens. Actuators, B* **2003**, *93*, 126. (c) Afridi, M. Y.; Suehle, J. S.; Zaghloul, M. E.; Berning, D. W.; Hefner, A. R.; Cavicchi, R. E.; Semancik, S.; Montgomery, C. B.; Taylor, C. J. *IEEE Sens. J.* **2002**, *2*, 644. (d) Pasini, P.; Powar, N.; Gutierrez-Osuma, R.; Daunert, S.; Roda, A. *Anal. Bioanal. Chem.* **2004**, *378*, 76.

(3) (a) Hamilton, S.; Hepher, M. J.; Sommerville, J. *Sens. Actuators, B* **2005**, *107*, 424. (b) Crone, B.; Dodabalapur, A.; Gelperin, A.; Torsi, L.; Katz, H. E.; Lovinger, A. J.; Bao, Z. *Appl. Phys. Lett.* **2001**, *78*, 2229. (c) Janata, J.; Josowicz, M. *Nat. Mater.* **2003**, *2*, 19. (d) Sakurai, Y.; Jung, H.-S.; Shimanouchi, T.; Inoguchi, T.; Morita, S.; Kuboi, R.; Natsukawa, K. *Sens. Actuators, B* **2002**, *83*, 270. (e) Torsi, L.; Tafuri, A.; Cioffi, N.; Gallazzi, M. C.; Sassella, A.; Sabbatini, L.; Zambonin, P. G. *Sens. Actuators, B* **2003**, *93*, 257.

(4) (a) Lonergan, M. C.; Severin, E. J.; Doleman, B. J.; Beaber, S. A.; Grubbs, R. H.; Lewis, N. S. *Chem. Mater.* **1996**, *8*, 2298. (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) Snow, E. S.; Perkins, F. K.; Houser, E. J.; Badescu, S. C.; Reinecke, T. L. *Science* **2005**, *307*, 1942. (d) Itoh, T.; Wang, J.; Matsubara, I.; Shin, W.; Izu, N.; Nishibori, M.; Murayama, N. *Mater. Lett.* **2008**, *62*, 3021.

(5) (a) Dickinson, T. A.; White, J.; Kauer, J. S.; Walt, D. R. *Nature (London)* **1996**, *382*, 697. (b) Walt, D. R. *Acc. Chem. Res.* **1998**, *31*, 267. (c) Rakow, N. A.; Suslick, K. S. *Nature (London)* **2000**, *406*, 710. (d) Yoon, J.; Chae, S. K.; Kim, J.-M. *J. Am. Chem. Soc.* **2007**, *129*, 3038.

(6) (a) Li, B.; Sauvé, 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. (b) Li, B.; Santhanam, S.; Schultz, L.; Jeffries-EL, M.; Iovu, M. C.; Sauve, G.; Cooper, J.; Zhang, R.; Revelli, J. C.; Kusne, A. G.; Snyder, J. L.; Kowalewski, T.; Weiss, L. E.; McCullough, R. D.; Fedder, G. K.; Lambeth, D. N. *Sens. Actuators, B* **2007**, *123*, 651.

(7) (a) Webster, F. G.; McColgin, W. C. US Patent 3,852,683, Dec 3, 1974. (b) Hammond, P. R. *Opt. Commun.* **1979**, *29*, 331. (c) Antonov, V. S.; Hohla, K. L. *Appl. Phys.* **1983**, *B32*, 9. (d) Speiser, S.; Shakkour, N. *Appl. Phys.* **1985**, *B38*, 191. (e) Taylor, J. R. *Opt. Commun.* **1986**, *57*, 117.

(8) Suzuki, Y.; Yokoyama, K. *J. Am. Chem. Soc.* **2005**, *127*, 17799.

(9) (a) Batchelder, J. S.; Zewil, A. H.; Cole, T. *Appl. Opt.* **1981**, *20*, 3733. (b) Sansregret, J.; Drake, J. M.; Thomas, W. R. L.; Lesiecki, M. L. *Appl. Opt.* **1983**, *22*, 573.

(10) (a) Zhang, X. H.; Chen, B. J.; Lin, X. Q.; Wong, O. Y.; Lee, C. S.; Kwong, H. L.; Lee, S. T.; Wu, S. K. *Chem. Mater.* **2001**, *13*, 1565. (b) Bulovic, V.; Deshpande, R.; Thompson, M. E.; Forrest, S. R. *Chem. Phys. Lett.* **1999**, *308*, 317. (c) Tang, C. W.; VanSlyke, S. A.; Chen, C. H. *J. Appl. Phys.* **1989**, *65*, 3610.

(11) See the related review papers: (a) Burland, D. M.; Miller, R. D.; Walsh, C. A. *Chem. Rev.* **1994**, *94*, 31. (b) Kanis, D. R.; Marks, T. J.; Ratner, M. A. *Chem. Rev.* **1994**, *94*, 195. (c) Long, N. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 21. (d) Marks, T. J.; Ratner, M. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 155. (e) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515. (f) Mishra, A.; Behera, R. K.; Behera, P. K.; Mishra, B. K.; Behera, G. B. *Chem. Rev.* **2000**, *100*, 1973. (g) Grabowski, Z. R.; Rotkiewicz, K.; Rettig, W. *Chem. Rev.* **2003**, *103*, 3899.

(12) Kwak, G.; Okada, C.; Fujiki, M.; Takeda, H.; Nishida, T.; Shiosaki, T. *Jpn. J. Appl. Phys.* **2008**, *47*, 1753.

(13) Kwak, G.; Wang, S.; Choi, M.-S.; Kim, H.; Choi, K.-H.; Han, Y.-S.; Hur, Y.; Kim, S.-H. *Dyes Pigments* **2008**, *78*, 25.

(14) (a) Mark, J. E. *Polymer Data Handbook*; Oxford University Press: New York, 1999. (b) Lide, D. R. *Handbook of Organic Solvent*; CRC Press: Boca Raton, FL, 1994.

(15) The functional equations were obtained by using KaleidaGraph (Synergy Software).

MA802593B