Changes of Fluorescence Color in Novel Poly(azomethine) by the Acidity Variation

Myon Kil Choi, Hoi Lim Kim, Dong Hack Suh

Department of Chemical Engineering, Hanyang Univesity, Seongdong-Ku, Seoul 133–791, Korea

ABSTRACT: A novel polymer, poly(4,4'-oxydiphenylenemethylidynenitrilo-2,5-dihexyloxy-1,4-phenylenenitrilomethylidyne) (POPNM), with a azomethine structure, containing long alkoxy side chains, was synthesized by the polycondensation of 2,5-bis(hexyloxy)terephthalaldehyde with 4,4'-oxydianiline. It displayed acid-sensory properties as colorimetric and fluorescent transducers to the strong acid analytes because of the protonation of an imine group in the compound. To examine the sensitivity to the acid, the effect of absorption and fluorescence of the polymer was investigated by simply adding trifluoroacetic acid into a chloroform solution of the polymer, and as a result, the multiple colors of fluorescence were sharply changed. Increasing the amount of the acid, the maximum absorption bands of fluorescence spectra were bathochromically shifted from 470 to 570 nm and, then, treating the pyridine as a base, they were recovered. A polymer film containing both the polymer and a photoacid generator (PAG) was prepared by semi-interpenetrating network polymerization method. When the polymer film was exposed to UV in the presence of PAG through a photomask, well-resolved fluorescent image patterns were readily obtained. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 1228–1233, 2006

Key words: fluorescence; Schiff base; poly(azomethine); multicolor

INTRODUCTION

Fluorescence of organic molecules is a characteristic that has been observed, studied, and used in many applications, such as organic light emitting diodes, flat-panel displays, and chemical sensors, for several decades.

Chemical sensors using the fluorescence of organic materials, including polymers, are capable of continuously recording chemical species, and thus have found various applications in areas such as chemical industry, biotechnology, and medicine.[1–3]

For the application of chemical sensors, many conjugated aromatic poly(azomethine) have been synthesized[4] since 1923, and their electronic and photonic properties have also been investigated.

As known of conjugated polymers, poly(azomethine)s were also insoluble generally. For solving the problem of solubility, several soluble conjugated poly(azomethine)s, containing different aromatic hydrocarbon moieties in the backbone and various side-group substituents, have been prepared by the condensation of aromatic dialdehydes with aromatic or aliphatic diamines or both.[5–7]

Their photochromism and proton transfer reaction cycle of the internally H-bonded Schiff bases are phenomena that have been observed, studied, and practically used in many applications for several decades.[8] But to our knowledge, especially, the multicolor fluorescent changes of poly(azomethine)s for the pH variations have not been investigated.

In this work, we report the acid-sensory properties of a novel poly(azomethine) that was protonated by external H-donors, i.e., the strong acids.

EXPERIMENTAL

Materials

Unless otherwise indicated, chemical reagents were supplied by Aldrich, TCI, or Acros, and used without further purification. Spectroscopic-grade chloroform (Aldrich) and trifluoroacetic acid (TFAA, 99% Aldrich) were used for optical measurements. Chloroform, acetonitrile, diethylether, and methylenechloride (MC) were distilled over CaH_2. N,N-Dimethylformamide (DMF) was purified by distillation under reduced pressure, after drying over $MgSO_4$. All other chemicals were used as received, without further purification.

Synthesis

Synthesis of monomers

*1,4-bis(hexyloxy)benzene (**1**):* The mixture of 1,4-hydroquinone (11.01 g, 100 mmol) and sodium hydroxide

Correspondence to: D. H. Suh (dhsuh@hanyang.ac.kr).

(17.5 g, 420 mmol) in 150 mL of DMF was stirred for 30 min. To this solution, bromohexane (36.22 g, 220 mmol) was added, and the reaction mixture was refluxed for 2 days. After cooling the mixture to room temperature, the precipitate was filtered off. Recrystallization from isopropyl alcohol gave 23.7 g of 1,4-bis(hexyloxy)benzene (85% of yield) as a white solid, which was then filtered and dried under vacuum.

ppm in ^{1}H NMR(CDCl$_3$): 0.88 (6H), 1027 (8H),1.45 (4H), 1.78 (4H), 3.85 (4H), 6.82 (4H,aromatic).

2,5-Bis(bromomethyl)-1,4-bis(hexyloxy)benzene (2): a suspension of the compound **1** (11.78 g, 42.3 mmol), paraformaldehyde (17.5 g, 580 mmol), and nabr (21.8 g, 210 mmol) in 125 ml glacial acetic acid was heated to a temperature of 60°c. a 1 : 1 mixture of concentrated sulfuric acid and glacial acetic acid (50 ml) was added dropwise, and the reaction mixture was stirred for 5 h at 70°c. after cooling the mixture to below 0°c, the precipitate was filtered off, washed with water, and dissolved in chloroform. the solution was washed with water, dried over na$_2$so$_4$, and the solvent was removed completely followed by recrystallization from *n*-hexane, yielding 16.3 g of 2,5-bis(bromomethyl)-1,4-bis(hexyloxy)-benzene (83.2% of yield) as a white solid.

FTIR: 689.7 (C—Br). ppm in ^{1}H NMR(CDCl$_3$): 0.88 (6H), 1.28 (8H), 1.49 (4H), 1.81 (4H), 3.98 (4H), 4.52 (4H, CH2Br), 6.85 (2H, aromatic).

2,5-Bis(acetylmethyl)-1,4-bis(hexyloxy)benzene (3): a solution of the compound **2** (14.49 g, 31.2 mmol), sodium acetate (10.233 g, 124.8 mmol), and tetra-*n*-butylammonium bromide (1.5 g) in a mixture of acetonitrile (300 ml) and chloroform (150 ml) was heated by refluxing for 24 h. the resulting mixture was poured in water and extracted with chloroform. after removing the solvent, recrystallization from *n*-hexane gave white needle crystals as product (12.6 g, 95.5% of yield).

FTIR: 1717(C=O). ppm in ^{1}H NMR(CDCl$_3$): 0.88 (6H), 1.27 (8H), 1.44 (4H), 1.76 (4H), 3.94 (4H), 5.14 (4H, CH$_2$OAc), 6.88 (2H, aromatic).

2,5-Bis(hydroxymethyl)-1,4-bis(hexyloxy)benzene (4): to a suspension of the compound **3** (10.14 g, 24 mmol) in isobutyl alcohol (120 ml) and ethanol (50 ml) was added a solution of naoh (15 g, 360 mmol) in water (20 ml). the mixture was refluxed for 40 h and acidified with dilute hcl solution. the solution was evaporated to remove alcohol, and the solid was precipitated from cold acetone twice, and a white powder was formed (7.8 g, 96% of yield). ft-ir: 3304 (—oh).

ppm in ^{1}H NMR(CDCl$_3$): 0.89 (6H), 1.28 (8H), 1.44 (4H), 1.78 (4H), 3.97 (4H), 4.67 (4H, CH$_2$OH), 6.92 (2H, aromatic).

2,5-Bis(hexyloxy)benzene-1,4-dialdehyde (5): a suspension of the compound **4** (7.18 g, 21.2 mmol) and pyridinium chlorochromate (18.279 g, 84.8 mmol) in mc (600 ml) was stirred at room temperature for 5 h under nitrogen atmosphere. the reaction mixture was then directly transferred onto the top of a short column of silica gel. the highly fluorescent product was then washed off from the column with chloroform. thus, the compound **5** was obtained in 85.9% of yield (6.09 g).

FTIR: 1680(C=O). ppm in ^{1}H NMR(CDCl$_3$): 0.88 (6H), 1.28 (8H), 1.45 (4H), 1.84 (4H), 4.08 (4H), 7.43 (2H, aromatic), 10.52 (2H, aldehyde).

Synthesis of polymer

In a 30-mL three-necked flask containing *m*-cresol (5 mL) was added 4,4′-oxydianiline (ODA, 1.00 mmol) and compound **5** (1.00 mmol), while a slow stream of nitrogen was maintained. The mixture was magnetically stirred at room temperature for 1 day. The solution was poured into methanol while stirring, and then the precipitate was collected by filtration, followed by thorough washing with methanol, and dried. The polymer was obtained as a yellow powder (0.4 g, 80% of yield). FTIR: 1625(C=N).

ppm in ^{1}H NMR(CDCl$_3$): 0.88 (6H), 1.28 (8H), 1.45 (4H), 1.84 (4H), 4.13 (4H), 6.67–7.42 (8H), 7.78 (2H), 8.94 (2H).

Preparation of semi-interpenetrating network polymer[9]

We used the semi-interpenetrating network (IPN) polymerization method to prepare a solid film. The crosslinkable compound forms the network, and the linear polymer is physically entrapped inside the network. Poly(ethylene glycol) dimethacrylate (PEG-DMA, Aldrich; M_n = 550 g/mol) is used as a crosslinking agent. Thin films of PEGDMA (88 wt %) mixed with poly(4,4′-oxydiphenylenemethylidynenitrilo-2,5-dihexyloxy-1,4-phenylene-nitrilo-methylidyne (POPNM, 1 wt %), benzoylperoxide, and triphenylsulfonium triflate (10 wt%), as a photoacid generator (PAG), were spin-casted from chloroform solution onto a glass plate. Then, the polymer film was cured in a vacuum oven, with a setting temperature of 80°C for 1 day.

RESULTS AND DISCUSSION

POPNM, being prepared by conventional organic methods (Scheme 1), displayed acid-sensory properties as colorimetric and fluorescent transducers to the strong acid analytes.

To examine acid sensitivity, it was determined that simply adding TFAA to 10 mL of chloroform solution $(1 \times 10^{-4} M)$ has an effect on the fluorescence of the polymer solution. Its fluorescence was changed by strong acids, such as hydrogen chloride (pK_a = −6.1), methansulfonic acid (pK_a = −1.9), and TFAA (pK_a = 0.5). However, POPNM does not respond to relatively weak acids (approximately positive pK_a), such
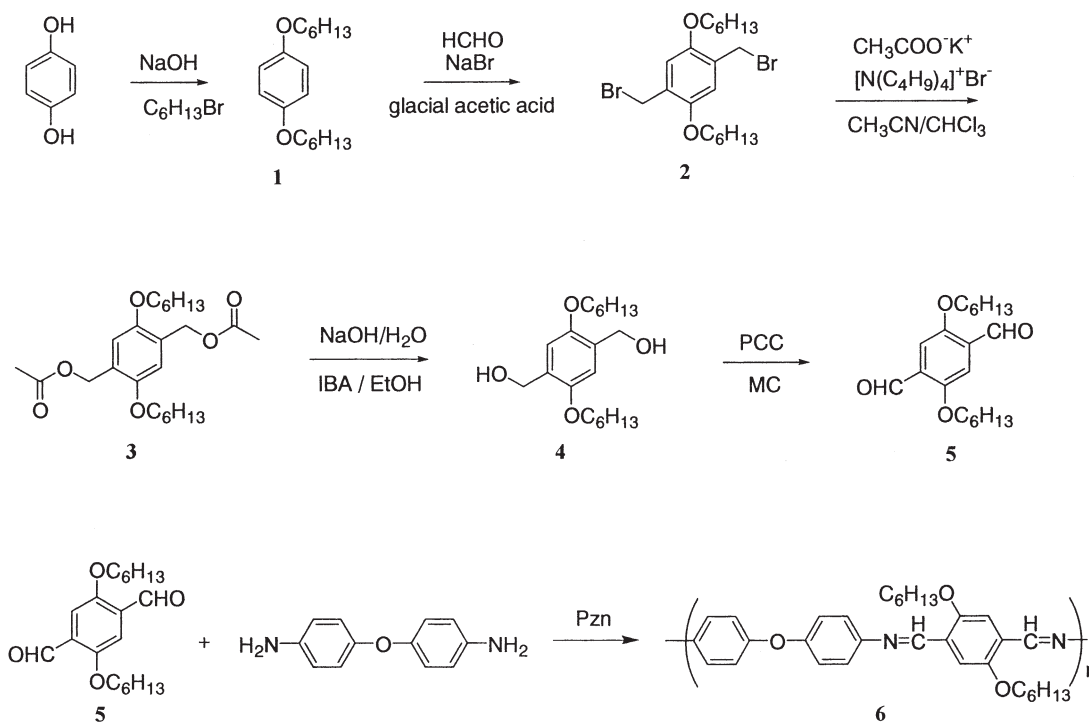
Scheme 1 The synthetic route to aldehyde monomer and a polymer.

as acetic acid (pK_a = 4.76), because of very weak basic properties of the imine group of POPNM. As shown in Figure 1, the gradual changes of the UV–visible absorption spectra, upon the addition of TFAA to a chloroform solution of POPNM ($1 \times 10^{-4}M$), was examined at room temperature. The absorption spectra at 480 nm increase with increasing the concentration of acid. Dependence on the fluorescence spectrum of chloroform solution of POPNM ($1 \times 10^{-4}M$) by the concentration of acid was examined. Relative to the UV–visible absorption spectrum, the transductive effect of the protonation on the fluorescence spectrum is very large. Increasing the amount of TFAA, the fluorescence maximum at 470 nm, corresponding to blue color, is largely shifted. As the proton-induced change is saturated, the fluorescence spectrum shows the maximum band at 570 nm, corresponding to the yellow color.

Multicolor of fluorescent change of the polymer according to the pH is due to the degree of interaction and the concentration of the charge transfer complex between the acid and the nitrogen of the Schiff base in the polymer.

Figures 2 and 3 show that UV–visible absorption and fluorescence spectra gradually change upon the addition of pyridine to TFAA ($5 \times 10^{-2}M$) and POPNM ($1 \times 10^{-4}M$) solutions of chloroform at room temperature. By increasing the amount of pyridine, absorption and fluorescence spectra are hypsochromically shifted because of the deprotonation of POPNM. As a result, the fluorescence color of the acidic

POPNM solution is yellow in a pristine state, but it turns to blue at a concentration of $1 \times 10^{-4}M$. This efficient regeneration of the fluorescence color is due to the weak basicity of an imine group. Also, Figure 4 shows that they were recovered by treating various solvents. These solvents act as a base on an imine group of the polymer. At this time, the recovered level is dependent on the pK_a value of the solvent. The pK_a values of protonated solvents are as follows: pyridine (5.5), diethyl ether (-3.5), acetic acid (-6), ethyl acetate (-6.5), acetonitrile (-10), and so on.

Figure 5 shows the optical acid sensitivity of POPNM, which provides the potential for a film optical sensor. A polymer thin film containing the polymer and a PAG was prepared by the semi-IPN polymerization method.[8] In the chemical amplification (CA) system, the photoirradiation generates a strong acid from a PAG, which catalytically protonates an imine group of POPNM. The semi-IPN polymer film changes from nonfluorescent to blue fluorescent color, with the increase of irradiation. As a result, when the polymer film was exposed to UV light (254 nm, 500 mJ/cm²) in the presence of PAG through a photomask (300-mesh TEM grid), well-resolved fluorescent image patterns were readily obtained as shown in Figure 6.

This Schiff base is possessed of imine receptors for protons. The unshared electron pair on the nitrogen atom of an imine group is not a part of the π-conjugated system, and these electrons confer the weak base properties on imine groups.[10,11] Migchels and Huyskens reported that a Schiff base derivative dis-
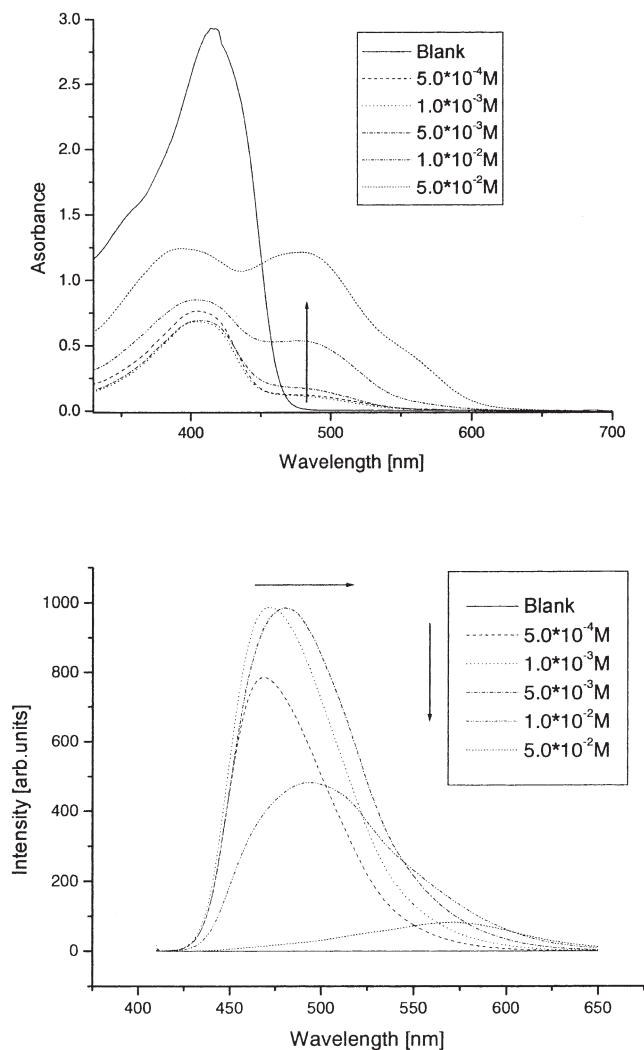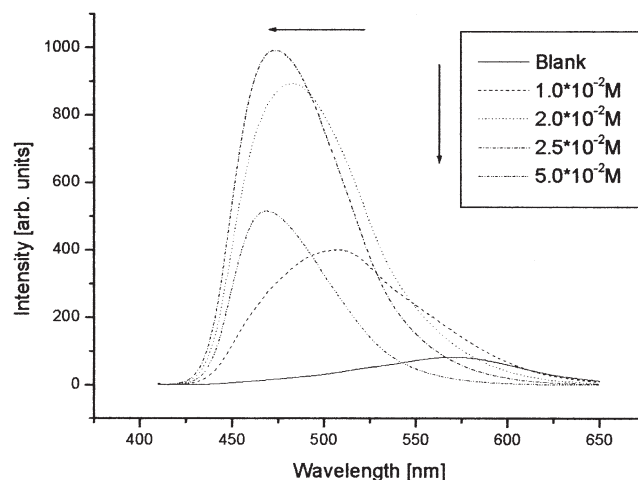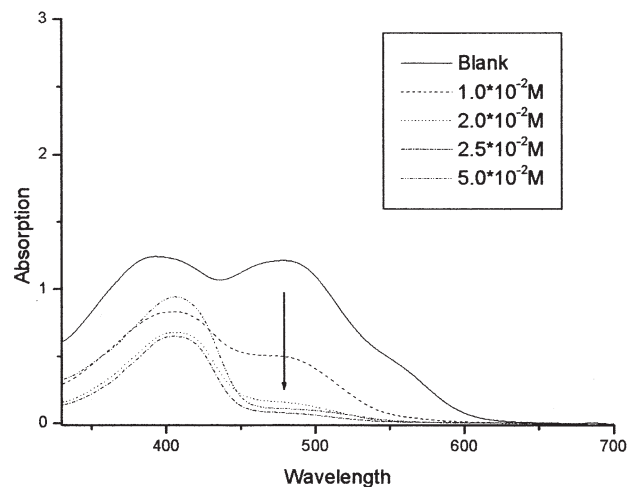
Figure 1 The change of the absorption/PL spectra (the excitation at 406 nm) at $1 \times 10^{-4}M$. Chloroform solution of POPNM upon the addition from 5.0×10^{-4} to $5.0 \times 10^{-2}M$.

imine linkage is not coplanar with the neighboring phenylene ring in Schiff base molecules.[7] This nonplanar molecular structure results from the conjugation between the imine nitrogen lone pair electrons and the π-electrons on the N-phenyl ring. The X-ray diffraction studies on benzylidene aniline show that it has a nonplanar conformation, in which the N-phenyl ring is twisted 55° from the CH=N plane, and the benzylidene ring is twisted 10° from the CH=N plane in the opposite direction. Such a nonplanar structure can be expected to be maintained in the polymers and cause a decrease in the efficiency of π-electron delocalization along the polymer backbone. It is notable, however, that the pristine polymers did not exhibit luminescence in solution and solid film, as reported elsewhere.[5,15] It has been reported in literature that the intramolecular hydrogen bonding prevents the nitro-

played very weak basic properties ($pK_{BH^+} = 6.0$–3.5), determined by involving phenol derivatives combined with stretching frequencies.[12] One of the most interesting properties of the materials containing this group is the large red shift that occurs in the optical absorption and photoluminescence, upon protonation of the nitrogen atom in an imine group. This shift is explained by the enhancement of the process of charge transfer from other adjacent groups, relatively electron rich to the imine moiety.[13,14]

An oxygen atom in the ODA contribute to increasing the basicity of the Schiff base nitrogen atom in the polymer, resulting in the stronger interaction to the acid and increasing the solubility of poly(azomethine)s.

Also, a consequence of the poor electron delocalization in the pristine polymer leads to the lack of coplanarity of the N-phenylene rings with the azomethine units. It has been documented in literature that the

Figure 2 The change of the absorption/PL spectra (the excitation at 406 nm) at 5×10^{-2} M. TFAA and the $1.0 \times 10^{-4}M$ polymer solution in chloroform upon the addition from 1.0×10^{-2} to $5.0 \times 10^{-2}M$ of pyridine.
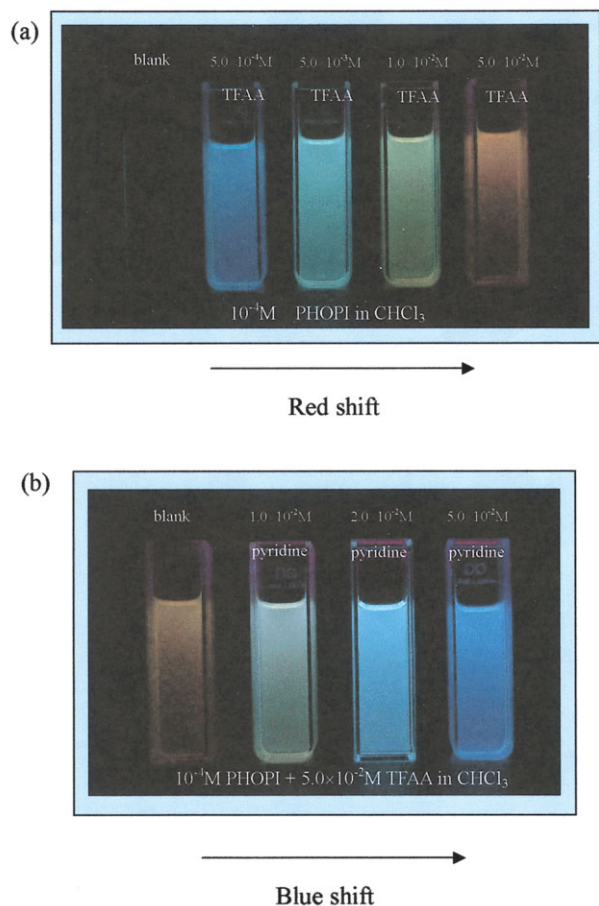
Figure 3 The changes of PL colors at the $1 \times 10^{-4}M$ polymer solution (a) and the $1.0 \times 10^{-4}M$ polymer solution with $5 \times 10^{-2}M$ TFAA (b).

gen lone pair electrons from conjugation with adjacent ring π-electrons, thus leading to a coplanar polymer backbone structure, and consequently more efficient
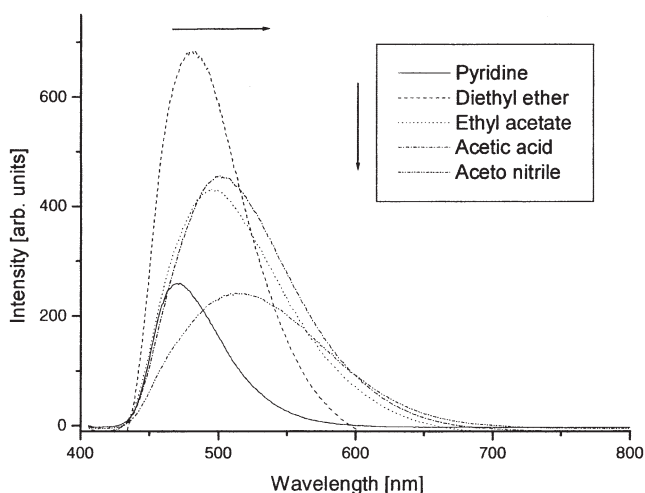
Figure 4 The change of the PL spectra (the excitation at 406 nm) at $5 \times 10^{-2}M$ TFAA and the $1.0 \times 10^{-4}M$ polymer solution in chloroform upon the addition of $5.0 \times 10^{-2}M$ bases.
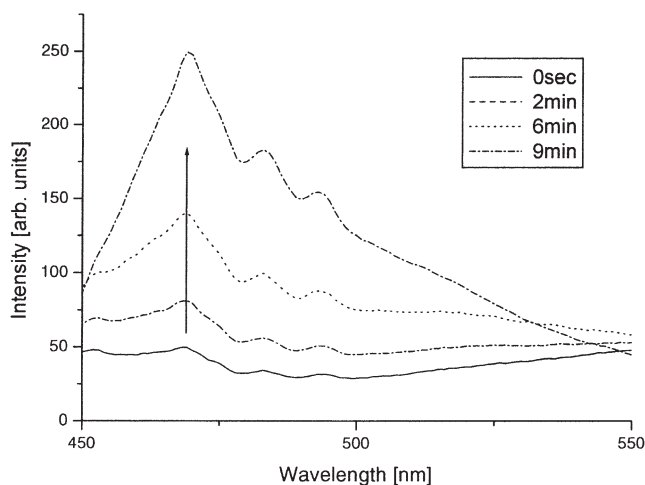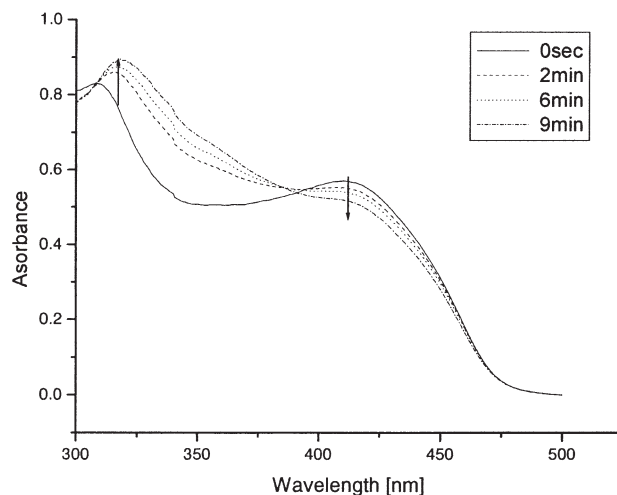

Figure 5 The change of the absorption/PL spectra *versus* UV irradiation time of a 0.3-μm semi-IPN film on a glass plate was exposed to UV light (254 nm, 500 mJ/cm^2).

π-electron delocalization. This knowledge on the role of the imine nitrogen lone pair electrons on the planarity, and consequently on the electronic structure of the poly(azomethine) suggests that, in addition to the intramolecular hydrogen bonding, other methods, such as complexation of the imine nitrogen, should be effective for backbone planarization of this kind of polymers.

CONCLUSION

A novel poly(azomethine), POPNM, that has two hexyl oxy-groups was synthesized by the six step reactions. The synthesized POPNM showed a good solubility due to long alkoxy side chains. Also, the polymer exhibited the reversible change from 470 to 570 nm of the absorption and the fluorescence spectra, upon the variation of acidity in the solution. Multi-
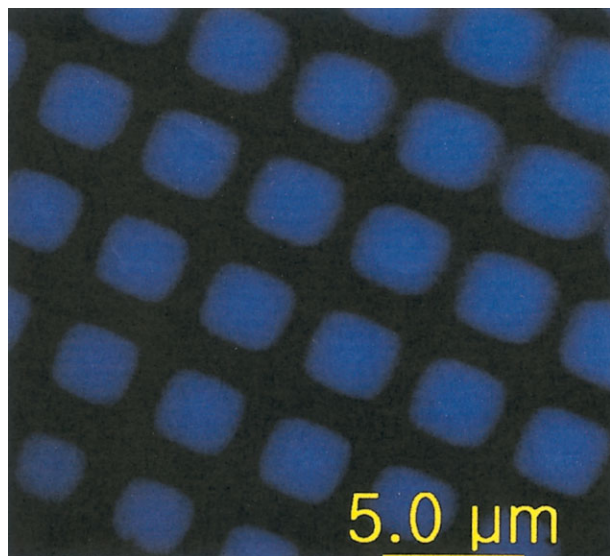
Figure 6 2D fluorescence patterned image generated from the semi-IPN film after the photolithographic treatment.

color of fluorescent changes can be explained by the protonation of the imine group in the polymer because of the degree of interaction and concentration of the charge transfer complex. We prepared a polymer thin film through the semi-IPN polymerization method. A patterned fluorescent image of the polymer film was developed by the photochemically generated acid.

A fluorescent sensor is very useful to determine the acid-selectivity of analytes used in a chemical sensor, because the current fluorescence microplate readers can measure signals from hundreds of samples in a matter of minutes. This kind of fluorescence color changes has potential applications in the reversible color-switching sensors.

References

1. Fluorescent Chemosensors for Ion and Molecular Recognition; Czamik, A. W., Ed.; American Chemical Society: Washington, DC, 1993. ACS Symposium Series, Vol. 538.
2. Zhou, Q.; Swager, T. M. J Am Chem Soc 1995, 117, 12593
3. Zhou, Q.; Swager, T. M. J Am Chem Soc 1995, 117, 7017.
4. Adams, R.; Bullock, J. E.; Wilson, W. C. J Am Chem Soc 1923, 45, 521.
5. Thomas, O.; Inganas, O.; Andersson, M. R. Macromolecules 1998, 31, 2676.
6. Park, S. B.; Kim, H.; Zin, W. C.; Jung, J. C. Macromolecules 1993, 26, 1627.
7. Yang, C. J.; Jenekhe, S. A. Macromolecules 1995, 28, 1180.
8. Gabowska, A.; Kownacki, K.; Karpuik, J.; Dobrin, S.; Kaczmarek, L. Chem Phys Lett 1997, 267, 132.
9. Oh, B.; Vissers, D.; Zhang, Z.; West, R.; Tsukamoto, H.; Amine, K. J Power Sources 2003, 442, 119.
10. Dean, J. A. Lange's Handbook of Chemistry, 13th ed.; McGraw-Hill: New York, 1985.
11. Joule, J. A.; Mills, K.; Smith, G. F. Heterocyclic Chemistry, 3rd ed.; Chapman & Hall: London, 1995.
12. Migchels, P.; Huyskens, T. Z. J Mol Struct 1991, 247, 173.
13. Liu, Y.; Liu, M. Thin Solid Films 2002, 415, 248.
14. Papkovsky, D. B.; Ponomarev, G. V.; Wolfbeis, O. S. J Photochem Photobiol A 1997, 104, 151.
15. Weaver, M. S.; Bradley, D. D. C. Synth Met 1996, 83, 61.