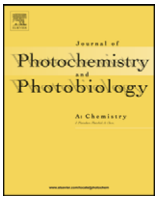
Journal of Photochemistry and Photobiology A: Chemistry 203 (2009) 161–165

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem



Photochromic properties of cationic oxazolylfulgimides in hydroxylic media

Yoshiumi Kohno*, Yuuki Tamura, Ryoka Matsushima

Materials Science and Chemical Engineering, Graduate School of Engineering, Shizuoka University, Johoku 3-5-1, Hamamatsu 432-8561, Japan

ARTICLE INFO

Article history:
Received 22 September 2008
Received in revised form
22 December 2008
Accepted 13 January 2009
Available online 30 January 2009

Keywords:
Cationic oxazolylfulgimides
Photochromic properties
Hydroxylic media
Solid films

ABSTRACT

Water-soluble cationic oxazolylfulgimides have been prepared to examine their photochromic properties in neutral aqueous solution and hydroxylic solid films. Introduction of the electron-withdrawing cationic substituents led to large shifts of the electronic transitions and significant changes in the photochromic response rates. In bare films of solid poly(vinyl alcohol) and κ-carrageenan gel exposed to the air, high photochemical reversibilities were found. Though extensive photochemical and thermal degradations occurred in bare Nafion film, they were substantially depressed by sealing the surface with PVA film.

1. Introduction

Recently, remarkable improvements in the synthetic methods and photochromic properties of fulgide derivatives have been reported. Thus, excellent thermal and photochemical properties have been achieved with novel dicyanomethylene derivatives [1,2] and indolyl derivatives [3–6], while rapid and high-yield, microwave-assisted synthesis of fulgimides has been developed [7]. Application of photochromic compounds to photoswitchable energy transfer [8,9] and photoswithcable assemblies in biological systems [10,11] has attracted particular attention.

In the present study, water-soluble cationic monomers of oxazolylfulgimides **3**–**5** (Scheme 1) were prepared to examine the influencies of cationic substituents and medium properties on the photochromic functions, as a preliminary study for the photochromic copolymers in aqueous or hydroxylic media. Many oxazolylfulgides and their derivatives are fairly resistant to both thermal and photochemical degradations presumably due to the higher oxidation potentials of the oxazole ring [12], while fulgimides are more resistant to solvolytic degradations in hydroxylic media [5,13]. However, little has been studied on the photochromic properties of fulgide derivatives in aqueous or hydroxylic media which might find wider applications in biological systems and ecomaterials.

2. Experimental details

2.1. Reagents and materials

Commercial reagents and solvents were of purest grade (Wako) unless otherwise noted. Solution of 5 wt.% Nafion® perfluorinated ion-exchange resin containing 45% water was purchased (Aldrich). Chromatographic separation was carried out on a silica gel column of Wakogel-1400 (Wako).

2.1.1. Fulgimide *1*

To a 70 mL solution of tetrahedrofuran (THF) containing 0.5 g (1.4 mmol) of an oxazolylfulgide (**FG**, Scheme 1) [14], ammonia gas was introduced at −78 °C, and stirred for 2 h. After removal of the solvent, 40 mL toluene, 30 mL methanol, and 3 mL hexane solution of trimethyldiazomethane were added, and the mixture was stirred for 1 h at room temperature. After removal of the solvent, the residual oil was solved in 80 mL THF and cooled on an ice bath to add 0.13 g of sodium hydride, then wormed to room temperature and stirred for 2 h. The mixture was extracted with ethyl acetate, and the organic layer was washed with water and dried over anhydrous sodium sulfate. Condensation gave yellow crystalline powder of **1** (a mixture of *E* and *Z* forms) in 63 mg (0.17 mmol). The filtrate was further condensed and passed through a column of silica gel with ethyl acetate, giving additional crystalline powder of **1** in 49 mg. The ^{1}H NMR data (Table 1) were consistent with the proposed structure.

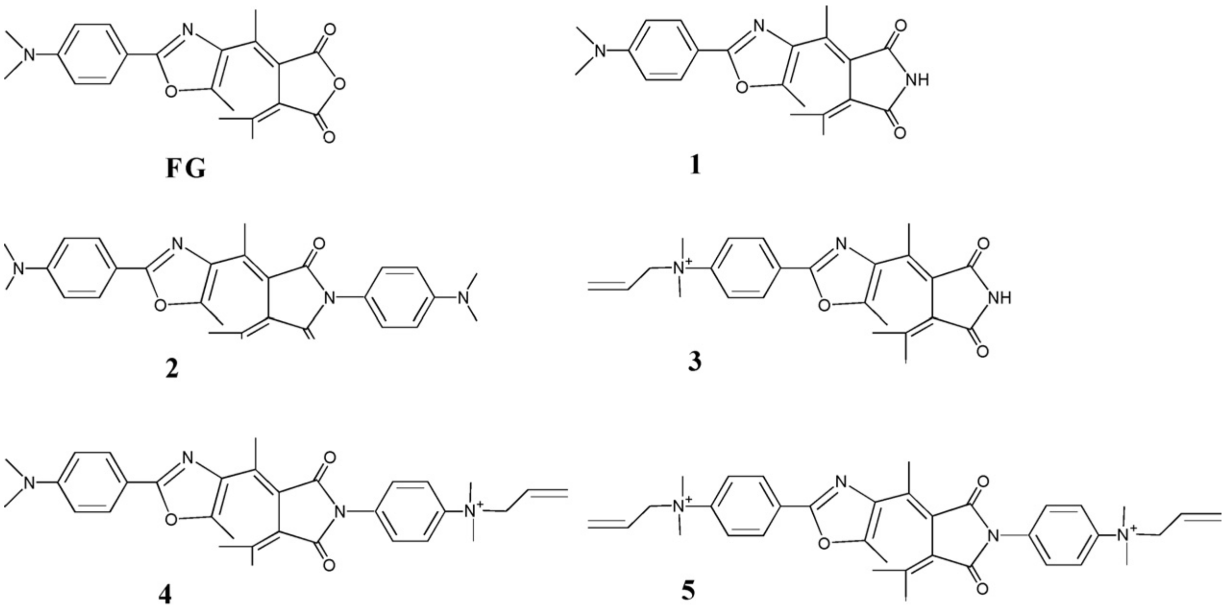
2.1.2. Fulgimide *2*

To a refluxing 100 mL THF solution containing 0.5 g of oxazolylfulgide (**FG**), 30 mL THF solution containing 1.0 g of *N*,*N*-

---

* Corresponding author. Tel.: +81 53 478 1623; fax: +81 53 478 1623.
E-mail address: tykouno@ipc.shizuoka.ac.jp (Y. Kohno).

1010-6030/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2009.01.013



Scheme 1. Oxazolylfulgide and fulgimides.

dimethyl-*p*-phenylenediamine was dropped over 1.5 h, and further refluxed for 2 h. After post-treatments as mentioned above, the mixture was passed through a column of silica gel with ethyl acetate, giving pink powder of fulgimide **2** (a mixture of *E* and *Z* forms) in 0.12 g (0.24 mmol, 17%). The ^{1}H NMR data (Table 1) were consistent with the proposed structure.

2.1.3. *Fulgimide **3***

A mixture of 0.50 g of fulgimide **1** and 1.0 g of allyl bromide was stirred in 60 mL methanol solution at room temperature. After addition of 10 mL of water, the mixture was further stirred for 2 days. After post-treatments as mentioned above, a bromide salt of allylated fulgimide **3** (a mixture of *E* and *Z* forms) was isolated by column chromatography in 5.8% yield (39 mg). The ^{1}H NMR data (Table 1) were consistent with the proposed structure, e.g., the chemical shift at 5.58–5.51 (3H, m) has been assigned to the vinyl protons of the allyl group.

2.1.4. *Fulgimides **4** and **5***

A mixture of 0.30 g of fulgimide **2** and 1.0 g of allyl bromide was stirred in 50 mL methanol solution at room temperature. After addition of 10 mL of water, the mixture was further stirred for 2 days. After post-treatments as mentioned above, bromide salts of fulgimides **4** and **5** were separated by column chromatography: **4** in 3.2% yield (12 mg), **5** in 2.2% (9.9 mg). The ^{1}H NMR data (Table 1) were consistent with the proposed structures.

Table 1
^{1}H NMR data of fulgimides.

Fulgimide[a]	^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm)
1	1.95 (3H, s), 2.26 (3H, s), 2.32 (3H, s), 2.43 (3H, s), 3.03 (6H, s), 6.70–6.73 (2H, d), 7.34 (1H, s), 7.85–7.88 (2H, d)
2	2.00 (3H, s), 2.30 (3H, s). 2.34 (3H, s), 2.48 (3H, s), 3.02 (6H, s), 6.69–6.70 (2H, d), 6.71–6.73 (2H, d), 7.09–7.12 (2H, d), 7.83–7.87 (2H, d)
3	2.00 (3H, s), 2.24 (3H, s), 2.37 (3H, s), 2.44 (3H, s), 3.67 (6H, s) 4.55–4.57 (2H, d), 5.58–5.51 (3H, m), 7.98–8.01 (2H, d), 8.22–8.25 (2H, d)
4	2.10 (3H, s), 2.34 (3H, s), 2.41 (3H, s), 2.50 (3H, s), 3.64 (6H, s), 3.68 (6H, s), 4.55–4.58 (2H, m), 5.57–5.74 (3H, m), 7.99–8.30 (4H, m)
5	2.10 (3H, s), 2.34 (3H, s), 2.41 (3H, s), 2.50 (3H, s), 3.64 (6H, s), 3.68 (6H, s), 4.52–4.58 (4H), 5.55–5.68 (6H, m), 7.63–7.66 (2H, d), 7.93–7.96 (2H, d), 8.00–8.03 (2H, d), 8.23–8.26 (2H, d)

[a] As a mixture of cyclizable *E* form and non-cyclizable *Z* form.

2.2. *Apparatus and procedures*

The ^{1}H NMR spectra were recorded on a 300 MHz FT-NMR system (AL-300, JEOL), while UV and visible absorption spectra were recorded on a Hitachi U-3000 spectrophotometer. For photochromic reactions, a 400-W high-pressure mercury lamp (Riko Kagaku) was used as UV and visible light source. For isolation of the UV beams of 313–366 nm, UV-36D filter (Toshiba) was used, while L-40 or L−48 filter was used for isolation of the visible beams of 436−545 nm.

Fulgimide-doped films were prepared as follows: Solution of 5 wt.% Nafion® was spin-coated on a polyester sheet and dried at 80 °C. The film was then immersed in aqueous 10% sodium carbonate solution for 1 h, rinsed with deionized water, and dried. The neutralized Nafion-Na^+ film was immersed in aqueous solution of cationic fulgimide for 24 h to allow cation exchange reaction, rinsed with deionized water, and air-dried. For preparation of the Nafion film protected from air oxidation, the surface of the film was further covered with poly(vinyl alcohol) (PVA: $n = 1500-1800$) by spin-coating, and air-dried for 24 h at room temperature. Fulgimide-doped κ-carrageenan film was prepared from aqueous mixuture solution of fulgimide and carrageenan, by pasting on a pyrex glass (Micro Slide Glass, Iwaki) and air-dried for more than 24 h. Fulgimide-doped PVA film was prepared from aqueous mixture solution of cationic fulgimide and PVA, by pasting on a pyrex glass (Micro Slide Glass, Iwaki) and air-dried for more than 24 h. Before use in the photochromic experiments, all the fulgimide-doped films were alternatively irradiated with UV and visible light beams twice in order to convert the *Z*-isomers substantially into cyclizable *E*-isomers.

3. Results and discussion

3.1. *Absorption spectra*

Fig. 1 compares the absorption spectra of the colored forms of fulgimides **1***C*–**5***C* in methanol solution. The band of **3***C* (461 nm,

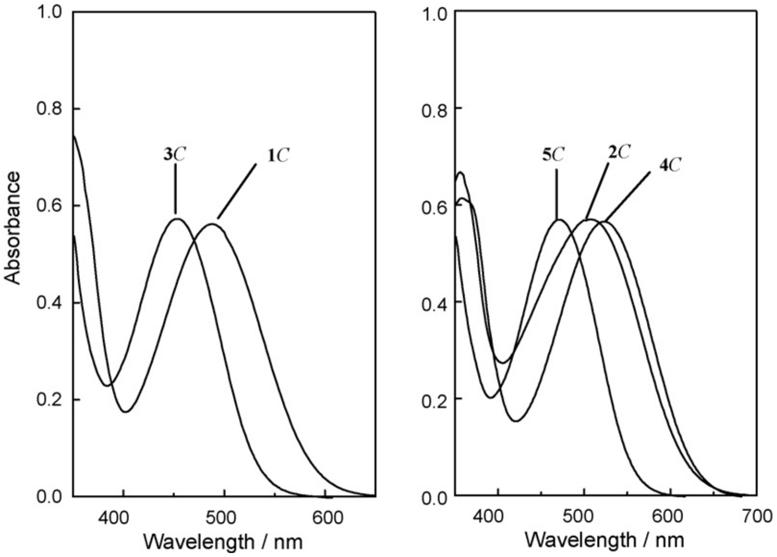


Fig. 1. Absorption spectra of the colored forms of fulgimides in methanol solution.

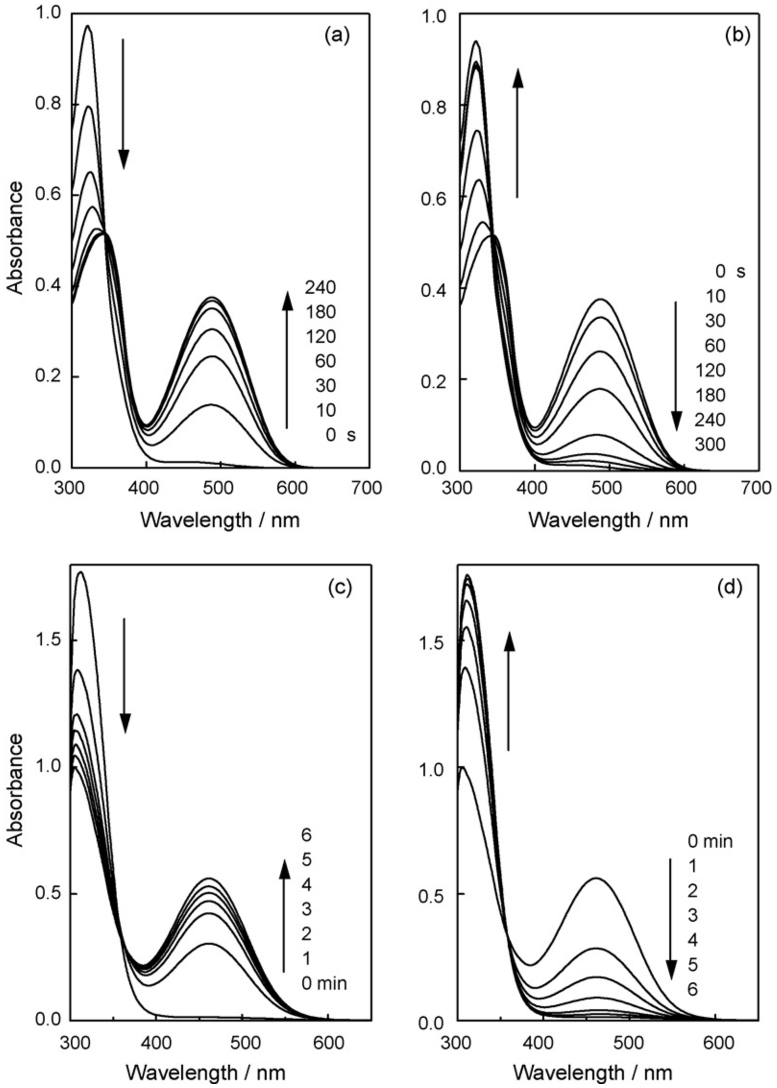


Fig. 2. Photochromic reactions of **1** in ethyl acetate and **3** in water, on irradiation with 313–365 nm for coloration, and with 436–545 nm for decoloration. Coloration (a) and decoloration (b) of **1** in ethyl acetate, coloration (c) and decoloration (d) of **3** in water. Initial concentrations of **1** and **3** were 0.50 μM.

Table 2
Absorption maxima and photochromic responses of fulgimides in methanol.

Fulgimide	*E* form	*C* form at PSS[a]		Response time[b] (s)	
	λ_{max} (nm)	λ_{max} (nm)	A_{PSS}	τ_C	τ_E
1	323	490	0.58	11	80
2	321	508	0.58	11	660
3	310	461	0.56	45	60
4	329	520	0.56	53	1060
5	310	479	0.59	30	53

[a] A_{PSS} refers to the absorbance attained at the photostationary state of coloration (PSS).

[b] τ_C and τ_E refer to the halftimes of coloration and decoloration, respectively.

yellow color) revealed a blue shift by ca. 30 nm from that of **1***C* (490 nm, red color), reflecting the change from the electron-donating N atom to the electron-withdrawing N$^+$ atom. By ZINDO calculations with PM5-optimized structures [15], the first band of **1***C* (with calcd. λ_{max} around 437 nm) has been assigned to intramolecular electron-transfer transition (IETT) from the *p*-dimethylaminophenyl group on the oxazole ring (HOMO-1) to the imide moiety (LUMO), while the band of **3***C* to IETT within succinimide moiety (from HOMO to LUMO + 2) implying a substantially reduced electron-transfer nature. Similarly, fulgimide **5***C* (orange) revealed significant blue shift from **2***C* (red). Contrary, **4***C* (magenta color) revealed a slight red shift from **2***C*, implying enhanced IETT by the electron-withdrawing N$^+$ atom on the imide phenyl group. The band shifts of the *E* forms were almost comparable to those of the *C* forms: a blue shift by the change from **1***E* to **3***E*, or **2***E* to **5***E*, while a red shift by the change from **2***E* to **4***E* (Table 2).

3.2. Relative photochemical responses

On irradiation with UV light, a photostationary state of coloration (PSS) was attained and the absorbance of the colored form (A_{PSS}) was obtained in 3 min for **1** (0.50 μM) in ethyl acetate, while in over 6 min for **3** (0.50 μM) in water (Fig. 2). A_{PSS} is defined as the absorbance value at the λ_{max} of the colored form at the photostationary state (PSS) attained on prolonged UV irradiation. Based on the decreased absorbances of the *E* forms around 310–320 nm, the completion of the photochemical coloration, i.e. mole fraction of the colored form was estimated to be around 0.6–0.7 at the PSS. As rough measures for relative photochromic rates, halftime of coloration (τ_C: UV-irradiation time needed to attain 50% of A_{PSS}) and halftime of decoloration (τ_E: irradiation time of visible light for 50% reduction of A_{PSS}) were estimated. In methanol solution, τ_C of **3** was 4-fold longer than that of **1**, while τ_E of **3** was slightly shorter than that of **1** (Table 2). Derivative **4** revealed a 5-fold longer τ_C and a slightly shorter τ_E whereas derivative **5** revealed a 3-fold longer τ_C but a 10-fold shorter τ_E, as compared to those of **2**. No reasonal correlation was found between the coloration rate and the distance of the terminal carbon atoms pertinent to the 6-π electrocyclic reaction. The 2pz-coefficients of LUMO of the terminal atoms were substantially reduced in the cationic derivatives **3***E*–**5***E* as compared to those in **1***E* and **2***E*, causing slower rates of photochemical cyclization (longer τ_C) of **3***E*–**5***E*.

3.3. Photochromic properties and thermal stabilities in solid hydroxylic films

Photochromic properties of the cationic fulgimides **3**–**5** have been examined in solid hydroxylic films of Nafion, κ-carrageenan, and PVA, as well as in aqueous solution (Table 3). The photochromic response times in the solid films were almost comparable to those in aqueous solution. Fulgimide-doped films of PVA and κ-carrageenan, both exposed to the air, revealed high fatigue resistances after 20 cycles of photochemical coloration and decoloration. Contrary, bare Nafion films (without PVA sealing) revealed extensive degradations while the films sealed with PVA revealed high resistances. It is implied that the bare Nafion films allow permeation and transpotation of molecular oxygen to cause oxidative degradations which can be substantially depressed by sealing with PVA film. Nafion membranes are known to permeate and transport oxygen gas, and have been widely used as electrolyte membranes of fuel cells [16,17].

Thermal stabilities of the cationic fulgimides were tried to examine in the films of PVA, Nafion, and carrageenan. However, upon heating at 80 °C the colored form **3***C* decomposed into **1***C* in PVA film while carrageenan film peeled off from the glass plate. Eventually, thermal stabilities could be measured only in Nafion film. Upon heating at 80 °C for 10 days, **3***C*–**5***C* in the bare Nafion films revealed extensive degradations but the films sealed with PVA revealed good stabilities (Table 4). The vinyl groups might play some roles in the

Table 3
Photochromic properties of cationic fulgimides in aqueous hydroxylic media.

Fulgimide	Medium[a]	Colored form at PSS[b]		Response time[c] (s)		Photoreversibility[d]
		λ_{max} (nm)	A_{PSS}	τ_C	τ_E	A_{20}/A_0
3	Water	456	0.56	60	55	–
	Nafion	459	0.16	6	55	0.44
	Nafion/PVA	459	0.16	–	–	0.92
	κ-Carageenan	461	0.28	65	65	0.91
	PVA	460	0.14	55	70	0.91
4	Water	514	0.56	30	1500	–
	Nafion	525	0.16	55	590	0.49
	Nafion/PVA	525	0.16	–	–	0.90
	κ-Carageenan	528	0.25	60	640	0.92
	PVA	528	0.20	50	640	0.86
5	Water	470	0.59	45	55	–
	Nafion	485	0.15	6	50	0.61
	Nafion/PVA	485	0.15	–	–	0.89
	κ-Carageenan	482	0.30	60	65	0.99
	PVA	482	0.18	45	60	0.92

[a] Nafion/PVA: The surface of fulgimide-doped Nafion film was further covered with PVA film to keep air-tight. Surfaces of other solid films were exposed to the air during photoreactions.

[b] A_{PSS} refers to the maximal absorbance at λ_{max} of the colored forms attained at PSS on UV irradiation.

[c] τ_C refers to the UV irradiation time needed to attain 50% A_{PSS} and τ_E refers to the irradiation time of visible light needed for 50% reduction of A_{PSS}.

[d] A_0 and A_{20} refer to the absorbances at λ_{max} of the colored forms, before and after repeated 20-cycles of coloration and decoloration.

Table 4
Thermal stability of the colored forms in Nafion film[a].

Fulgimide	λ^{C}_{max}(nm)	Thermal stability A_{10}/A_0	
		Exposed to air	Sealed with PVA
3C	459	0.54	0.92
4C	525	0.81	0.89
5C	485	0.64	0.92

[a] A_0 and A_{10} refer to the absorbances at λ^{C}_{max} before and after heating at 80 °C in the dark for 10 days, respectively.

degradation reactions since the vinyl groups are sensitive to photochemical and/or thermal radical processes.

4. Conclusion

Photochromic properties of water-soluble cationic fulgimides have been studied in hydroxylic solution and solid media. Introduction of the N^+ atom caused significant changes in the electronic spectra and photochromic reaction rates. In bare films of PVA and carrageenan, good fatigue resistances were found upon repeated photochromic cycles. Though photochemical and thermal degradations occurred extensively in bare Nafion film, such degradations were substantially depressed by coating with PVA film to keep air-tight. Thus, the majority of the photochromic functions of the fulgide derivatives obtained so far mainly in organic media would be utilized in aqueous or hydroxylic media. For plactical application, however, the photochemical stability of the PVA-sealed films would be insufficient and much more improvement would be needed while the thermal stability are fairly good as such.

References

[1] H.G. Heller, D.S. Hughes, M.B. Hursthouse, K.V.S. Koh, J. Chem. Soc., Chem. Commun. (1994) 2713.
[2] H.G. Heller, D.S. Huges, M.R. Hursthouse, N.G. Rowles, J. Chem. Soc., Chem. Commun. (2000) 1397.
[3] Y. Yokoyama, K. Takahashi, Chem. Lett. (1996) 639.
[4] C.J. Thomas, M.A. Wolak, R.R. Birge, W.J. Lees, J. Org. Chem. 66 (2001) 1914.
[5] M.A. Wolak, C.J. Thomas, N.B. Gillespie, R.B. Birge, W.J. Lees, J. Org. Chem. 68 (2003) 319.
[6] N.I. Islamova, X. Chen, S.P. Garcia, G. Guez, Y. Silva, W.J. Lees, J. Photochem. Photobiol. A 195 (2008) 228.
[7] W.-W.W. Lee, L.-M. Gan, T.-P. Loh, J. Photochem. Photobiol. A 185 (2007) 106.
[8] J. Walz, K. Ulrich, H. Port, H.C. Wolf, J.M. Endtner, f. Effenberger, Chem. Phys. Lett. 213 (1993) 321.
[9] H. Port, A. Hartschuh, M. Mennrich, H.C. Wolf, J.M. Endtner, F. Effenberger, Mol. Cryst. Liq. Cryst. 344 (2000) 145.
[10] I. Willner, B. Willner, Mol. Cryst. Liq. Cryst. 344 (2000) 15.
[11] I. Willner, B. Willner, in: B.L. Ferings (Ed.), Molecular Switches, Wiley-VCH, Weinheim, Germany, 2001, pp. 165–218.
[12] R. Matsushima, H. Morikane, Y. Kohno, Chem. Lett. 32 (2003) 302.
[13] R. Matsushima, H. Sakaguchi, J. Photochem. Photobiol. A 108 (1997) 239.
[14] A. Tomoda, A. Kaneko, H. Tsuboi, R. Matsushima, Bull. Chem. Soc. Jpn. 65 (1992) 1262.
[15] J.J.P. Stewart, MOPAC 2002 in Windows Cache 5. 04 softwares, Fujitsu Limited, 2002.
[16] X. Zhang, P. Shi, Electrochem. Commun 8 (2006) 1615.
[17] J. Choi, K.M. Lee, R. Wycisk, P.N. Pintauro, P.T. Mather, Macromolecules 41 (2008) 4569.