Preparation of Low Refractive Index Fluorinated Materials for Antireflection Coatings

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ABSTRACT: Novel low refractive index fluorinated polymers were prepared from perfluoroalkylsilane and polyethoxysiloxane by a sol-gel technique for antireflection applications. Perfluoroalkylsilane having low refractive index fluoroalkyl groups incorporate polyethoxysiloxane by condensation of their siloxane groups to improve the adhesion and hardness of the fluorinated polymers. Syntheses and characteristics of the fluorinated polymers were investigated by the studies of FTIR, GPC, UV–vis, ellipsometry, and mechanical tests. The experimental results reveal that the refractive index and hardness of the coating using the optimal fluorinated polymer were about 1.39 and 3H, respectively, which meet the requirements in practical applications. It was also found that the fluorinated polymer made from polyethoxysiloxane had a better hardness than that made from tetraethyl orthosilicate. J Appl Polym Sci 118: 1615–1619, 2010

Key words: antireflection; low refractive index; fluorinated polymer

INTRODUCTION

For glass and most plastics, about 4–5% of incident light is reflected from the surface. To eliminate disturbance of the external light and increase light transmission to enhance the clarity of display images and the performance of optical components, antireflection (AR) coatings are usually applied to optical lenses, solar cells, displays, thermochromic windows, eye glasses, camera lenses, and so on.[1–3] Destructive interference in the light reflected from the interfaces between layers having different refractive indices is the main AR mechanism for most practical applications. If the surface would like to achieve zero reflection, the refractive index of the AR coating, for the case of a single-layer AR coating, must be equal to the square root of the refractive index of the substrate. Because the refractive indices of glass and most plastics are ~ 1.5, the required refractive index of the coating must be ~ 1.22. This refractive index is so low that no known bulk materials can meet the criterion. Therefore, a large number of approaches have been reported, including surface-relief structures made by phase separation,[3,4] selective dissolution,[5,6] or lithography techniques,[7] and homogenous porous coatings prepared by sol-gel processes[8–10] or nanoparticle multilayers.[11–13] In particular, the self-assembled single-layer deposition of nanoparticles has shown excellent AR performance.[14–18] Although these techniques can create very low refractive index coatings, the mechanical properties of the coatings are generally poor unless the coatings are calcined at very high temperatures or improved by hydrothermal treatment.[19] This results in a significant limitation of their practical application because of the poor heat resistance of the substrates and the complex processes involved.

For the practical AR application in flat displays, the AR products include two categories: low-grade AR and high-grade AR. The reflectance of an AR coating below 1.5% is considered as low-grade AR and below 0.5% is high-grade AR.[20] Low refractive index coatings in the range of refractive indices of 1.38–1.39 are sufficient to meet the low-grade AR requirements in the case of a single-layer AR structure and the high-grade AR requirements in the case of a multilayer AR structure utilizing high-refractive index materials. In particular, the pencil hardness is a crucial property in practical applications because of the displays suffering external forces easily. 3H is the usual criterion for pencil hardness to prevent AR coatings from damage. Therefore, manufacturing low refractive index coatings having the both

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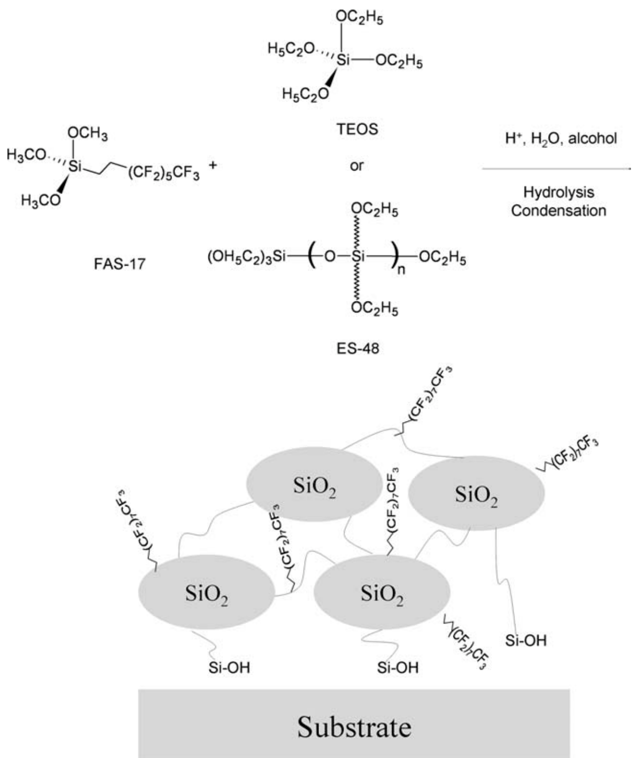

Scheme 1 Preparation of the low refractive index fluorinated polymers by hydrolysis and condensation reactions.

properties of low refractive index and hardness is more important than only pursuing the lower refractive index coatings.

Fluorinated polymers are one of the lowest refractive index materials known and have been widely applied in optical waveguides,[21,22] low-k materials,[23] aerogels,[24] and AR coatings.[25] However, the main drawbacks of the fluorinated polymers are poor adhesion and softness. Miyatake et al.[26] prepared low refractive index hybrid materials composed of tetramethyl orthosilicate (TMOS) and tridecafluorooctyltrimethoxysilane (FAS-13). The coatings have good mechanical properties, but the refractive indices are high. In this study, we prepared a low refractive index coating from perfluoroalkylsilane and polyethoxysiloxane by condensation of their siloxane groups (Scheme 1). Perfluoroalkylsilanes have low refractive index fluoroalkyl groups and siloxane groups, which can be incorporated into organic or inorganic materials. Polyethoxysiloxane was used to improve the adhesion and hardness of the AR coatings. The effect of the ratio of perfluoroalkylsilane to polyethoxysiloxane on the physical properties and the optical performance of the AR coatings were investigated.

EXPERIMENTAL

Materials

Tetraethyl orthosilicate (TEOS, MW: 208, Aldrich), heptadecafluorodecyltrimethoxysilane (FAS-17, MW: 568.1, KHL Interchem), polyethoxydisiloxane (ES-48, Colcoat), and hydrochloric acid (36% aqueous solution, Katayama Chemical) were used as received. Ethanol (99.9%, J.T. Baker) and ethylene glycol monopropyl ether (EGMPE, 99.4%, Aldrich) were used as solvents for the synthesis and coating process. Concentrated sulfuric acid (95%, Fluka) and hydrogen peroxide (30%, Aldrich) were used for Piranha solution. Deionized water (DI water, >18 MΩ cm) was used in the experiments.

Preparation of AR coatings

A total of 4.5 g of 0.1*N* hydrochloric acid as a catalyst and 30 g of ethanol were first mixed in the reaction vessel and placed in an oil bath. Then, ES-48 or TEOS was added to the vessel. After the solution was heated to 83°C, FAS-17 was slowly added to the vessel. The pH value of the mixed solution was about 2. The required amounts of ES-48, TEOS, and FAS-17 for the various fluorinated polymers were summarized in Table I. The solution was stirred at a constant rate of 450 rpm for 6 h. A few samples of the solution were drawn out at different reaction times for Fourier-transform infrared (FTIR) spectrometry and gel permeation chromatography (GPC) analyses to evaluate variations of the reaction.

Glass substrates were immersed in Piranha Solution (H_2SO_4/H_2O_2, 7/3, v/v) for 30 min and then washed with DI water. The washed glass was

TABLE I
Composition and Properties of the Synthesized Fluorinated Polymers

Code	Compositions of reactants (g)			Reaction time (h)	Minimum reflectance (%)	Pencil hardness	Adhesion	Refractive index[a]
	FAS-17	ES-48	TEOS					
FE14	3	12		6	1.83	4H	5B	1.405
FE23	6	9		6	1.44	3H	5B	1.384
FE23-1	6	9		3	–	2H	–	–
FE11	7.5	7.5		6	1.35	1H	5B	1.371
FT23	6		14.9	6	1.45	1-2H	5B	1.386

[a] Reflective indices of the fluorinated polymers at 633.67 nm.

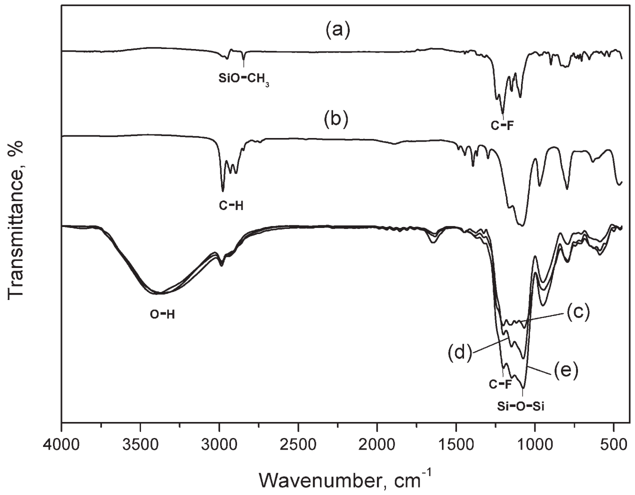

Figure 1 FTIR spectra of FAS-17 (a), ES-48 (b), and FE23 synthesized with reaction times of 2 h (c), 3 h (d), and 6 h (e).

dipped in a solution consisting of 12 g of the as-prepared low refractive index sol, 35 g of ethanol, and 8.33 g of EGMPE for 3 min, and subsequently raised from the dipping bath at a rate of 50 mm/min. The coated substrate was placed in an oven at 60°C for 5 min and then at 100°C for 1 day to postcure the low refractive index coating.

Measurements

The samples extracted during the various stages of polymerization were characterized in terms of their compositions and molecular weights. The compositions of the low refractive index sols were examined by FTIR spectra using a FTIR spectrophotometer (Spectrum One, PerkinElmer). Liquid samples were prepared by dropping appropriate amounts of the low refractive index sols onto a KBr disc and subsequently evaporating the solvent at 40°C for 10 min. Molecular weights of the low refractive index fluorinated polymers with different reaction times were determined by GPC using a Jasco apparatus equipped with a Jasco RI-930 detector, a Jasco PU980 pump, and a Phenogel 500 Å column (eluent: THF; flow rate: 1.0 mL/min). The GPC chromatogram was calibrated against standard polystyrene samples. Reflection spectra for the AR coatings were performed by using a UV–vis spectrophotometer (U4100, Hitachi) at an incident angle of 5°. An ellipsometer (SpecEL-2000-VIS, Mikropack) was used to measure the refractive index of the AR coatings. Pencil hardness of the AR coatings were determined by a motorized pencil hardness test (JL-3086-1, Fu-Chien Enterprise) complying with ASTM specification D3363 for a 500 g load. The adhesion test was in compliance with ASTM specification D3359.

RESULTS AND DISCUSSION

Figure 1 depicts the FTIR spectra of FAS-17, ES-48, and FE23 synthesized with different reaction times. The spectrum of FAS-17 exhibits absorption peaks at 1200 cm^{-1} for C—F and 2841 cm^{-1} for C—H from SiO—CH_3. A strong absorption band at 2800–3000 cm^{-1} for C—H is observed in the spectrum of ES-48. No broad absorption band near 3400 cm^{-1} for O—H is found in either FAS-17 or ES-48 spectrum. The above information reveals that FAS-18 and ES-48 were not hydrolyzed before reaction. The strong absorption band at around 1070–1080 cm^{-1} for Si—O—Si appears in the spectrum of ES-48 and that of the synthesized fluorinated polymer. The absorption intensity ratios of Si—O—Si/O—H and Si—O—Si/C—F for the synthesized fluorinated polymer increased with increasing reaction time due to the condensation reaction of Si—OH groups. Comparing reaction times of 3 and 6 h, the intensity ratio of Si—O—Si/O—H increased moderately. This suggests that the reaction was still proceeding after 3 h. Comparing FE23-1 (3 h) and FE23 (6 h), the hardness increases with increasing reaction time as shown in Table I. This can be because the molecular weight still increases from 3 to 6 h to enhance the hardness. Figure 2 shows the GPC chromatograms of ES-48 and FE23 synthesized with reaction times of 3 and 6 h. The average molecular weight of ES-48 measured by GPC was 1600 with a very broad molecular weight distribution. After the reaction was carried out for 3 h, the refractive indices of the synthesized fluorinated polymer became bimodal: the higher molecular weight polymer had a refractive index higher than 1.407 (the refractive index of THF) and the lower molecular weight polymer had a refractive index lower than 1.407. This indicates that the lower molecular weight polymer consists of the higher

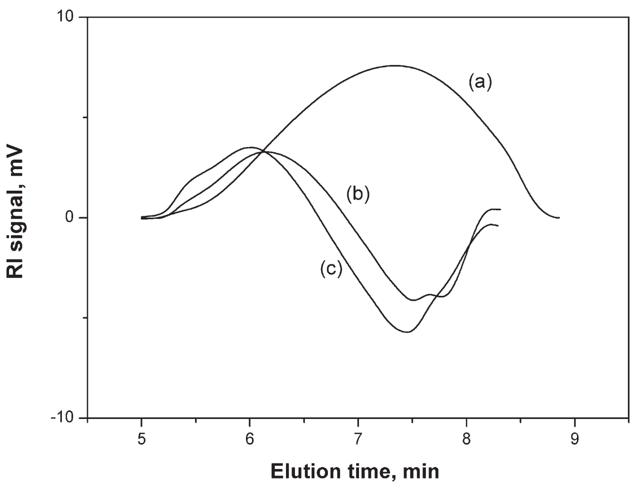

Figure 2 GPC chromatograms of ES-48 (a) and FE23 synthesized with reaction times of 3 h (b) and 6 h (c).

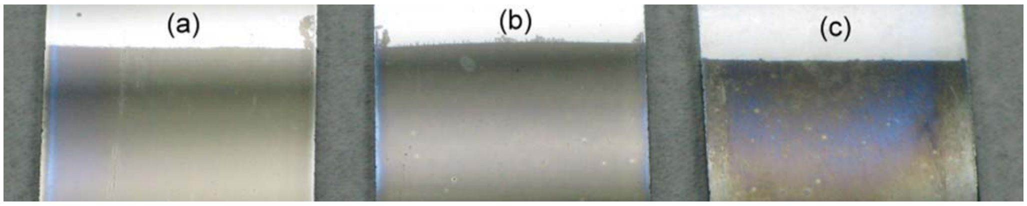

Figure 3 Photographs of the AR coatings prepared by FE14 (a), FE23 (b), and FE11 (c). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

amount of FAS-17 or self-condensation clustering of FAS-17. In accord with the results of the FTIR measurements, the molecular weight of the synthesized fluorinated polymer increased when the reaction time went from 3 to 6 h. The average molecular weight of FE23 was about 16,800.

The minimum reflectance and hardness of the fluorinated polymers prepared by various weight ratios of FAS-17 to ES-48 are shown in Table I. When the content of fluoroalkyl groups was increased in the hybrid fluorinated polymers (FE14 → FE23 → FE11), the reflectance was reduced from 1.83% to 1.44 to 1.35% but the pencil hardness became worse from 4H to 3H to 1H. This was a trade-off between reflectance and mechanical properties for the low refractive index fluorinated polymers. The photographs of the AR coatings for the cases of FE14, FE23, and FE11 are shown in Figure 3. Although no adhesion problems occur for all the synthesized polymers shown in Table I, the appearance of the coating for the case of FE11 became poor, and shrinkage and nonuniformity occurred because of the nature of fluoroalkyl compounds. Based on the results of minimum reflectance, hardness, and appearance, FAS-17/ES-48 at a 2 : 3 ratio (FE23) showed the optimal composition.

The refractive indices of the synthesized fluorinated polymers are shown in Table I. The results reveal that the refractive index is proportional to the minimum reflectance. Because the refractive index is dependent on the wavelength of the incident light, expression of an average value of the refractive index is highly desired in the practical AR application because of convenience to rank the materials. The average refractive index of the synthesized polymer can be estimated by the Fresnel coefficient of reflection for a single-layer model. For a single-layer coating of thickness d on a transparent substrate, the reflectance, R, is expressed as[27]

$$R = \frac{n_c^2(n_0 - n_s)^2\cos^2\phi + (n_s - n_c)^2\sin^2\phi}{n_c^2(n_0 + n_s)^2\cos^2\phi + (n_s + n_c)^2\sin^2\phi} \tag{1}$$

where n_c, n_0, and n_s are the refractive indices of the coating layer, air, and substrate, respectively, and

$$\phi = 2\pi\frac{n_c d}{\lambda}\cos\theta \tag{2}$$

where θ is the incident angle of light. The reflectance of FE23, the optimal composition, coated on glass is shown in Figure 4. The average refractive index of FE23 estimated from Figure 4 using eq. (1) was about 1.39. The value is close to the result measured at the wavelength of 633.67 nm shown in Table I. The reflectance and refractive index of FE23 can meet the requirements of practical applications.

Figure 5 shows the results of a pencil hardness test for the AR coating. No scratch was found on the surface of FE23 when a 3H pencil was loaded for the test [Fig. 5(a)]. To do further study on the mechanism of coating hardness, we replaced ES-48 by TEOS to prepare fluorinated sols with the same silica content by the same process. The synthesized polymer (FT23) was also evaluated in a pencil hardness test. However, the result failed in a 3H test [Fig. 5(b)]. This indicates that the hardness of the AR coating is affected by the silica morphology. Because the average molecular weight of ES-48 is larger than that of TEOS, it could be that the higher molecular weight of the silica moiety enhances the mechanical properties including hardness. In addition, the reflectances of AR coatings prepared by FE23 and FT23 are shown in Figure 4.

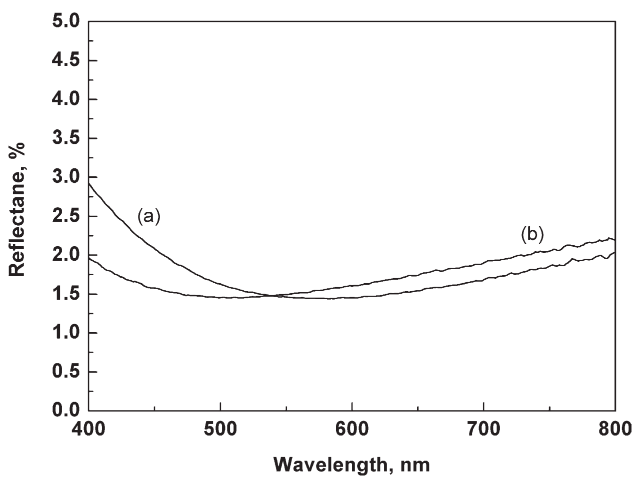

Figure 4 Reflection spectra of FE23 (a) and FT23 (b) coated on the glass substrates.

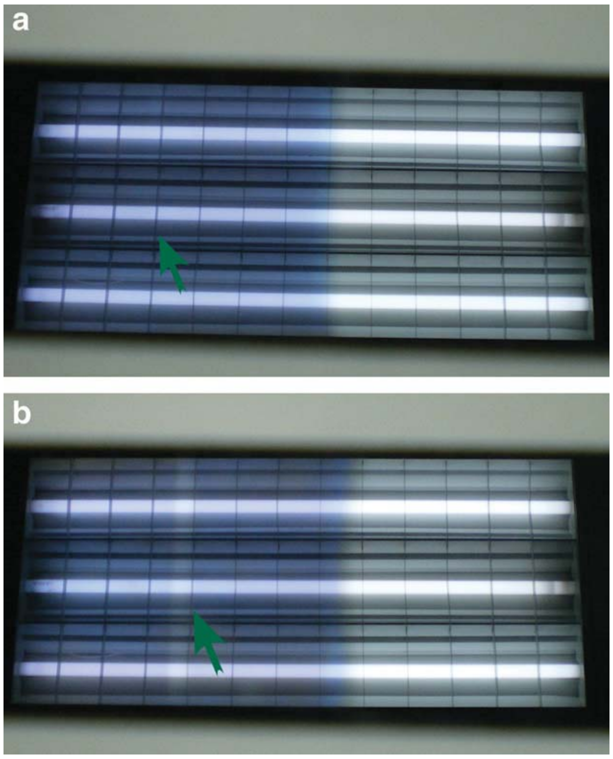

Figure 5 Resulting photographs of the AR coatings tested by a 3H pencil for the cases of FE23 (a) and FT23 (b). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Their minimal reflectances are almost the same. According to eq. (1), this reveals that their refractive indices are also the same. For a porous homogenous layer, the refractive index can be expressed as[28]

$$n_{eff}^2 = (1 - \rho)n_p^2 + \rho n_0^2 \quad (3)$$

where ρ is the porosity of the coating layer and n_p is the refractive index of the polymer. That the effective refractive indices of FE23 and FT23 are the same thus implies similar porosity. In other words, the poor hardness of FT23 is likely caused by the morphology of the silica moiety rather than by different porosity. The higher molecular weight of ethyl silicate should result in a better hardness. The similar result was found in the study of Miyatake et al.[26] To meet the mechanical requirements, they added some prepolymer condensated from TMOS to the fluorinated sols prepared by TMOS and FAS-13. Although the minimum reflectance rose from 1.9% to 2.0%, the antiscratch property was significantly improved.

CONCLUSIONS

In this study, we used FAS-17 and ES-48 to prepare low refractive index fluorinated polymers for antireflection applications. When the ratio of FAS-17/ES-48 increased from 1/4 to 1/1, the reflectance was reduced from 1.83 to 1.35% but the pencil hardness became worse from 4H to 1H. The results revealed that the optimal ratio of FAS-17 to ES-48 was 2 : 3. The average refractive index, minimum reflectance, and hardness of the optimal fluorinated polymer were ∼ 1.39, 1.44%, and 3H, respectively, which can meet the requirements of practical applications. It was found that the fluorinated polymer made from ES-48 had better hardness than that made from TEOS.

References

1. Nakada, T.; Motoyama, K.; Gunji, K.; Wakabayashi, M.; Furusho, H.; Fukuro, H. U.S. Pat. 6,472,012 (2002).
2. Nomura, H.; Sasaki, T. U.S. Pat. 56,046,382 (1997).
3. Walheim, S.; Schaffer, E.; Mlynek, J.; Steiner, U. Science 1999, 283, 520.
4. Steiner, U.; Walheim, S.; Schaffer, E.; Eggert, S.; Mlynek, J. U.S. Pat. 6,605,229 (2003).
5. Ibn-Elhaj, M.; Schadt, M. Nature 2001, 410, 796.
6. Seiberle, H.; Schadt, M.; Ibn-Elhaj, M.; Benecke, C.; Schmitt, K. W.O. Pat. 01/29148 (2001).
7. Glaser, T.; Ihring, A.; Morgenroth, W.; Seifert, N.; Schroter, S.; Baier, V. Microsyst Technol 2005, 11, 86.
8. Hinze, P.; Dislich, H. J Non-Cryst Solids 1986, 82, 411.
9. Yoldas, B. E.; Partlow, D. P. Appl Opt 1984, 23, 1418.
10. Uhlmann, D. R.; Suratwala, T.; Davidson, K.; Boulton, J. M.; Teowee, G. J Non-Cryst Solids 1997, 218, 92.
11. Wu, Z.; Walish, J.; Note, A.; Zhai, L.; Cohen, R. E.; Rubner, M. F. Adv Mater 2006, 18, 2699.
12. Prevo, B. G.; Hwang, Y.; Velev, O. D. Chem Mater 2005, 17, 3642.
13. Krogman, K. C.; Druffel, T.; Sunkara, M. K. Nanotechnology 2005, 16, S338.
14. Hattori, H. Adv Mater 2001, 13, 51.
15. Liu, X.; He, H. J Colloid Interface Sci 2007, 314, 341.
16. Jiang, H.; Yu, K.; Wang, Y. Opt Lett 2007, 32, 575.
17. Liu, B. T.; Yeh, W. D. Colloids Surf A 2010, 356, 145.
18. Zhang, X. T.; Sato, O.; Taguchi, M.; Einaga, Y.; Murakami, T.; Fujishima, A. Chem Mater 2005, 17, 696.
19. Gemici, Z.; Shimomura, H.; Cohen, R. E.; Rubner, M. F. Langmuir 2008, 24, 2168.
20. http://www.sonycid.jp.
21. Liang, J.; Toussaere, E.; Hierele, R.; Levenson, R.; Zyss, J.; Ochs, A. V.; Rousseau, A.; Boutevin, B. Opt Mater 1998, 9, 230.
22. Bosc, D.; Rousseau, A.; Morand, A.; Benech, P.; Tedjini, S. Opt Mater 1999, 13, 205.
23. Jayasuriya, A. C.; Tasaka, S. J. Polymer 1995, 27, 122.
24. Zhou, B.; Shen, J.; Wu, Y.; Wu, G.; Ni, X. Mater Sci Eng C 2007, 27, 1291.
25. Kim, J. Y.; Han, Y. K.; Kim, E. R.; Suh, K. S. Curr Appl Phys 2002, 2, 123.
26. Miyatake, M.; Masuda, T.; Shigematsu, T.; Yoshioka, M. U.S. Pat. 6,773,121 (2004).
27. Macleod, H. A. Thin Film Optical Filters; Institute of Physics Pub.: Bristol and Philadelphia, 2001; Vol. 3.
28. Southwell, W. H. J Opt Soc Am A 1991, 8, 549.