

Study on the Optical Properties of Sulfur-Containing Poly(methyl methacrylate)-Inorganic Hybrid

Shujuan Liu, Liying Tian, Zhen Zheng, Xinling Wang

School of Chemistry and Chemical Technology, State Key Laboratory of Metal Matrix Composites (Shanghai Jiao Tong University), Shanghai Jiao Tong University, Shanghai 200240, People's Republic of China

Received 14 November 2008; accepted 9 February 2009

DOI 10.1002/app.30220

Published online 8 May 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: High refractive index homogeneous hybrid materials were successfully prepared. The polymer matrix was the copolymer of methyl methacrylate, sulfur-containing monomer 2,2'-mercaptoethylsulfide dimethacrylate (MESDMA), and nanotitania was prepared by *in situ* solgel process of titanium n-butoxide. The transmission electron microscope (TEM) study suggested that the hybrid was homogeneous without inorganic agglomerate, and the inorganic particles were 4–7 nm. The refractive index was ~ 1.75 when the inorganic content of the hybrid film reached to 70 wt %, and the transmittance maintained

up to 85%. The sulfur-containing monomer was used to improve the refractive index, also, it was a crosslinking reagent, which improved the film-forming ability of the hybrid. After copolymerized with MESDMA, the film-forming ability of the hybrid was better than the one without MESDMA. Even if the inorganic content exceeded 75 wt %, the films kept integrity. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 3498–3503, 2009

Key words: hybrid materials; PMMA; sulfur-containing monomer; refractive index

INTRODUCTION

Since optical plastics are lightweight, fragmentation resistant, they have been developed rapidly in recent years for application as lenses of glasses, cameras, etc.

In general, there are two preferable methods to increase the refractive index of polymers. One is to prepare the sulfur-containing homopolymers and copolymers, and the other is to fabricate organic-inorganic hybrid materials containing high refractive index inorganic nanoparticles.^{1–4} For example, many patents have reported the sulfur-containing resin, but the refractive index was always between 1.50 and 1.65. Yang, B. et al.⁵ prepared ZnS/polythiourethane nanocomposites via immobilization of thiophenol/mercaptoethanol-capped ZnS nanoparticles into a thermoplastic polyurethane matrix, which had high refractive index and optical transparency. But the synthesis route was complicated. Chen, W.C. et al.⁶ prepared high-refractive-index trialkoxysilane-capped poly(methyl methacrylate) (PMMA)-titania hybrid optical thin films. But the films were easy to crack when the content of titania exceeded 50 wt %.

In this article, for the preparation of high refractive index hybrid, we tried to find a monomer to increase the refractive index, at the same time, which could

improve the film-forming ability of the hybrid with high inorganic content. So sulfur-containing monomer 2,2'-mercaptoethylsulfide dimethacrylate (MESDMA) was used to copolymerize with methyl methacrylate (MMA). The hybrid materials were characterized by Fourier Transform Infrared Spectroscopy (FTIR), TEM, Thermogravimetric Analysis (TGA), ellipsometer, etc.

EXPERIMENTAL

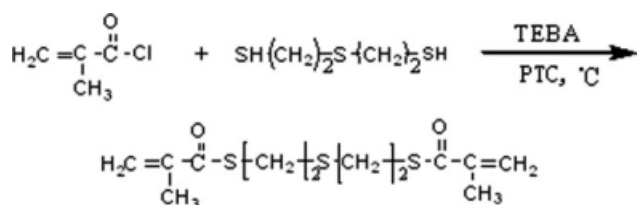
Materials

MMA, titanium n-butoxide ($\text{Ti}(\text{n-OBu})_4$), and azobis-isobutyronitrile (AIBN) were purchased from Sinopharm Chemical Reagent (China). MMA was purified by vacuum distillation, and then kept with 4A molecule sieve. Others were directly used as received. 3-(trimethoxysilyl) propyl methacrylate (MSMA) was purchased from Nanjing Shuguang Chemical (China). Methacryl chloride (MC) was obtained from Shanghai Saiya Chemical (China), and purified by vacuum distillation before used. 2,2-mercaptoethyl sulfide (MES) was obtained from Tokyo Kasei Kogyo (Japan) and directly used.

Synthesis of 2,2'-MESDMA

The route was shown in Scheme 1.⁷ 0.065 mol 2,2-MES, 50 mL dichloromethane, 6.60 mmol triethylbenzyl-ammonium and cooled potassium hydroxide (0.1 g/mL) were put into a three necked flask with a

Correspondence to: Z. Zheng (zzheng@sjtu.edu.cn).



Scheme 1 The synthesis route of sulfur-containing monomer MESDMA.

mechanical stirrer, a thermometer and a dropping funnel. After 20 min, the solution, 0.078 mol MC in 20 mL dichloromethane, was dropped into the flask with vigorous stirring at about 0°C for 4 h. The under layer was separated out and washed with deionized water until neutral. The solution was dried with anhydrous calcium chloride, filtered, and distilled to remove the solvent. Finally, colorless and transparent 2,2'-MESDMA liquid was synthesized.

Synthesis of the titania-nanohybrid material

The monomers, initiator AIBN and solvent tetrahydrofuran (THF) were charged into a flask with a magnetic stirring under nitrogen atmosphere. In this study, the mol ratio of the monomers, namely, MMA, MESDMA to MSMA was 3/3/1, and the weight percent of AIBN/monomers was 0.5 wt %. The polymerization was processed at 60°C for 2 h. Then $\text{Ti}(\text{n-OBu})_4$ in the mixture solvent of THF and n-butanol was dropped with rigorous stirring to avoid heterogeneous. The concentration of $\text{Ti}(\text{n-OBu})_4$ was 0.18 g/mL. The large amount of n-butanol in system could decrease the hydrolysis rate of $\text{Ti}(\text{n-OBu})_4$ to avoid the phase separation resulted from the different hydrolysis rate between $-\text{Si}(\text{OCH}_3)_3$ and $\text{Ti}(\text{n-OBu})_4$. After 15 min, deionized water and hydrochloric acid in THF were slowly added to adjust the pH value to 1–2 to promote hydrolysis. The mol ratio of deionized water to $\text{Ti}(\text{n-OBu})_4$ was 1.5. The reaction was continually kept for 4 h at 60°C. A transparent pale yellow solution was obtained, which was spin-coated on quartz plates or casted onto polytetrafluoroethylene (PTFE) dishes, dried, and stored in a vacuum oven. At last, the films were annealed at 60°C for 2 h, 100°C for 1 h, and 150°C for 2 h for characterization.

Characterization

The FTIR spectra were obtained by a Perkin-Elmer 1000 FTIR spectrometer with a resolution of 2 cm^{-1} . The dilute solution was cast onto potassium bromide disc and annealed for measurement.

An atom force microscope was also adopted to observe the surface of the hybrid films with tapping mode of Multimode Nanoscope IIIa (Digital Instrument) (Veeco Instruments Inc., USA).

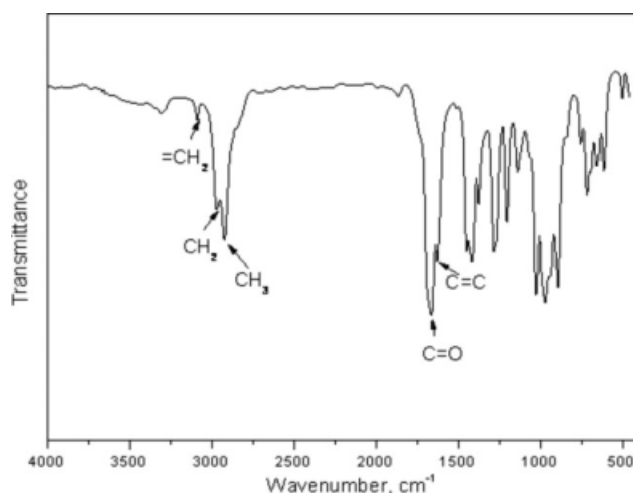


Figure 1 FTIR spectrum of sulfur-containing monomer MESDMA.

The thermal stability of the materials was investigated by a Perkin Elmer 7 Series thermal analysis system from 20 to 800°C at a heating rate of 20°C/min under N_2 flow.

The refractive index of the thin films was measured by Ellipsometer (W-VASE32TM, J. A. Woolam, USA): the accuracy of the spectra is 0.5 nm. The diameter of the optical spot is 1 mm. The refractive index of the films was measured in the wavelength range of 390–800 nm.

RESULTS AND DISCUSSION

The sulfur-containing monomer 2,2'-MESDMA was characterized by FTIR and $^1\text{H-NMR}$. The spectra were shown in Figures 1 and 2, respectively. The result indicated that the monomer was successfully synthesized.

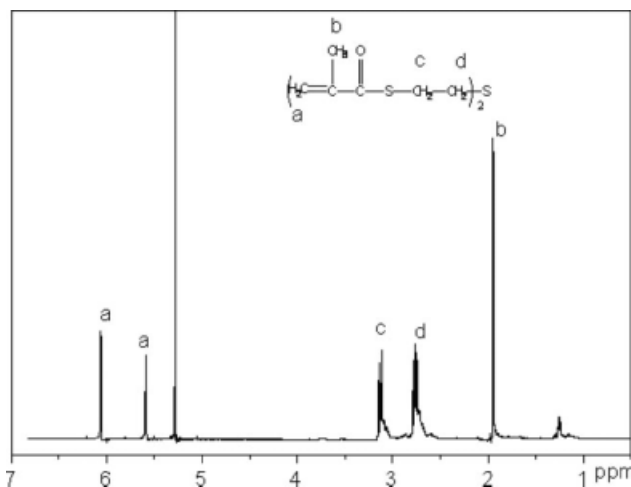
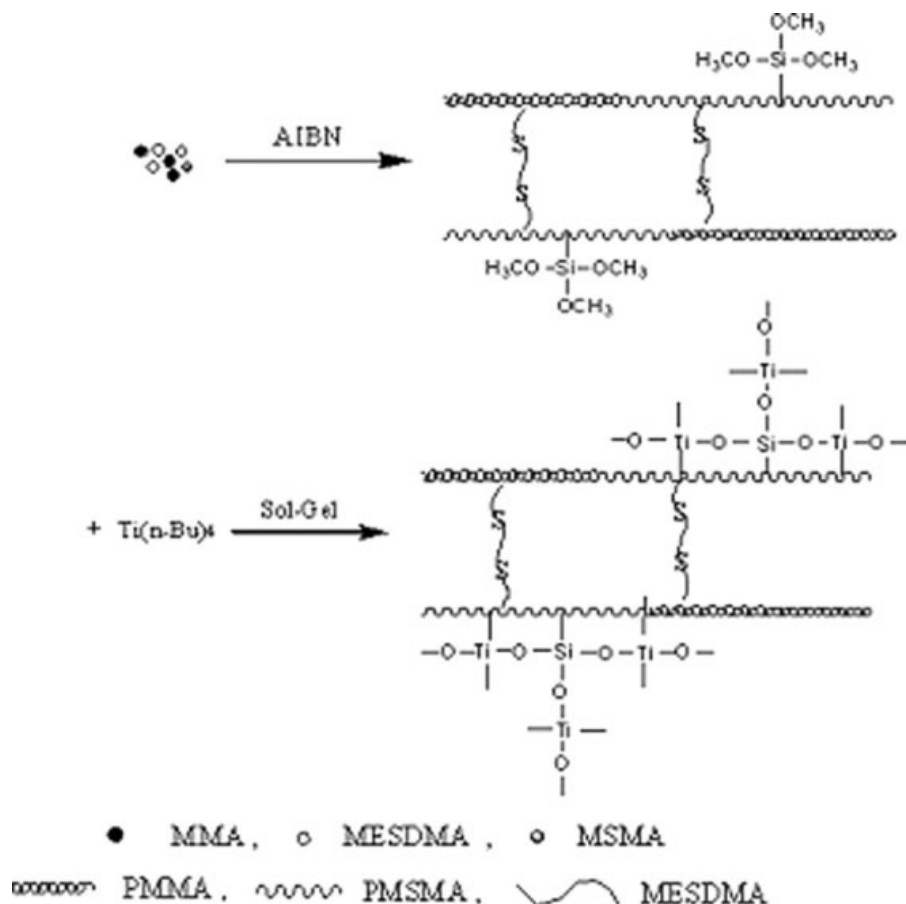


Figure 2 $^1\text{H-NMR}$ spectrum of sulfur-containing monomer MESDMA.



Scheme 2 Schematic illustration of the formation of the hybrid materials.

The hybrid material was a kind of titania-polymer connected network as shown in Scheme 2. The hybrid material containing both of sulfide and nanotitania was synthesized to improve the refractive index of polymer matrix. Although the $(\text{Ti}(\text{n-OBu})_4)$ content was > 90 wt %, the shape of the hybrid films did not get destroyed. This was because MESDMA was used not only as a sulfur-containing monomer to improve the optical property of the matrix, but also as a cross linking reagent to increase the dimensional stabilities of the hybrid materials.

Five transparent reacted solutions, with different weight percent of $(\text{Ti}(\text{n-OBu})_4)$ varied from 50 to 100 wt % were cast onto KBr plate and annealed for FTIR measurement. The characteristic absorptions of the hybrid films were shown in Figure 3. The $(\text{Ti}(\text{n-OBu})_4)$ content (wt %) was calculated as following equation.

$$C_i = m_1 / (m_1 + m_2) \times 100\% \quad (1)$$

wherein C_i represents the weight percent of $(\text{Ti}(\text{n-OBu})_4)$, m_1 represents the mass of $(\text{Ti}(\text{n-OBu})_4)$, and m_2 represents the total mass of monomers.

A broad absorption in the range of $3400\text{--}3500$ cm^{-1} was assigned to the hydroxyl groups of

Ti-OH and Si-OH . The broad absorption band between $900\text{--}400$ cm^{-1} was supposed to the characteristic absorption of Ti-O-Ti .⁸ The presence of Ti-OH was because the curing temperature was not high enough for the synthesis of pure titania

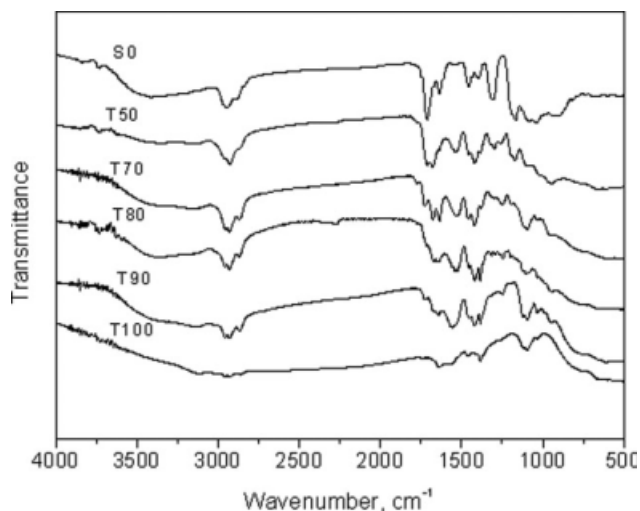


Figure 3 FTIR spectra of hybrid materials with different $\text{Ti}(\text{n-OBu})_4$ contents.

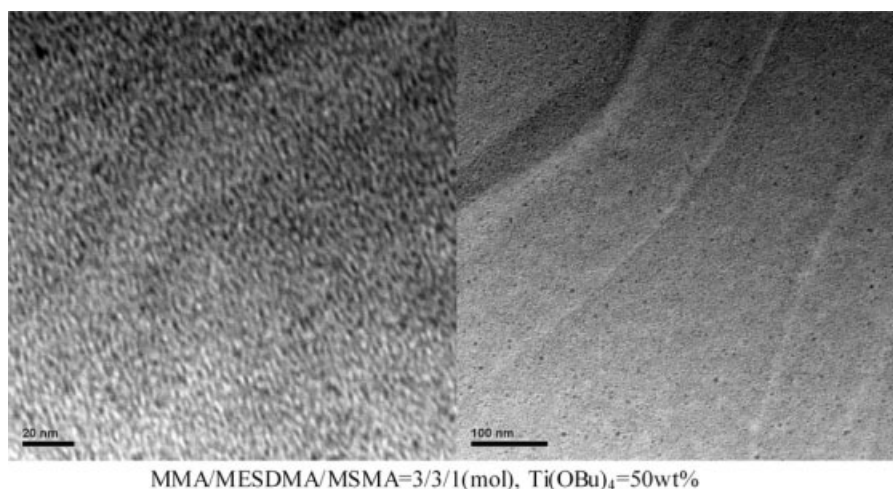


Figure 4 TEM photographs of PMMA/PMESDMA/TiO₂ hybrid film.

materials, namely the condensation of (Ti(n-OBu)₄) was not complete. Meanwhile, the hydrochloric acid promoted the rate of hydrolysis reaction more than that of polycondensation reaction, so more linear Ti-OH structure rather than crosslinked -Ti-O-Ti- structure formed, the latter often caused the high viscosity of the reacted solution and the three-dimensional inorganic network structure with more compact domains. The stretching vibration absorption was at 1635 cm⁻¹ may be owing to titania, because this absorption was observed in T100 and its intensity increased with increase of titania content. The absorption of Ti-O-Si group was observed at 946 cm⁻¹, which were the interaction between the organic phase and the inorganic one. The absorption at 1530 cm⁻¹ was assigned to -COS- in MESDMA. The absorption at 1730 cm⁻¹ was the stretching vibration of -C=O in MMA. The FTIR spectra suggested that the polymer-titania connect network was formed.

TEM was used to characterize the morphology of the hybrid films. The TEM photographs of the hybrid films with 50 wt % (Ti(n-OBu)₄) content were shown in Figure 4. The titania nanoparticles of ~ 4–7 nm were uniformly dispersed in the continuous polymer matrix. There were no large inorganic domains, so the transmittances of the films were high in the visible region. The homogeneity of the hybrid was not affected by the crosslinking reagent MESDMA.

The surface of the films was characterized by AFM. The AFM images of the hybrid film were shown in Figure 5. On the surface of the hybrid film, there were no obvious cracks or agglomerations. The surface of the film was mainly composed of organic component, and inorganic particles could not be found on the surface because the movement of trialkoxysilane toward the surface would

lead to less titania on the surface of the film compared with the bulk of the film.⁹ TEM photographs and AFM images indicated the hybrid films were homogeneous and suitable for the optical application.

The thermal properties of the prepared hybrid films were tested. TGA curves were shown in Figure 6. There was no obvious weight loss after 500°C. For sample a, the residue at 800°C mainly consisted of silica, and for other curves, the residue mainly consisted of titania and silica, which increased with increase of titania content. This indicated that (Ti(n-OBu)₄) incorporated into the network of the polymer matrix successfully through *in situ* sol-gel process. The first stage of weight loss was at ~ 350°C and exhibited very broad, which should be attributed to the scission of side groups on the polymer chains as well as the random decomposition of main chains. The second stage was at ~ 450°C, which might be ascribed to the decomposition and dehydroxylation of the groups bonded to Si and Ti.¹⁰

The optical properties of the hybrid films are important for application, especially the optical transparency. Small particles with diameters below one tenth of the visible light, typically smaller than 25 nm, can avoid Rayleigh scattering to fabricate transparent high refractive hybrid film. In Figure 7, the transmittances of the films were >85% in the visible region. The thickness of the films was 1–2 μm. This confirmed that the inorganic particles were smaller than 25 nm and dispersed in the matrix uniformly. The crosslinked structure of the polymer did not hinder the dispersity of the inorganic particles. This result was consistent with the TEM photographs and AFM images. Figure 7 shows that the transmittance of the film was still high when the inorganic content increased in the visible region.

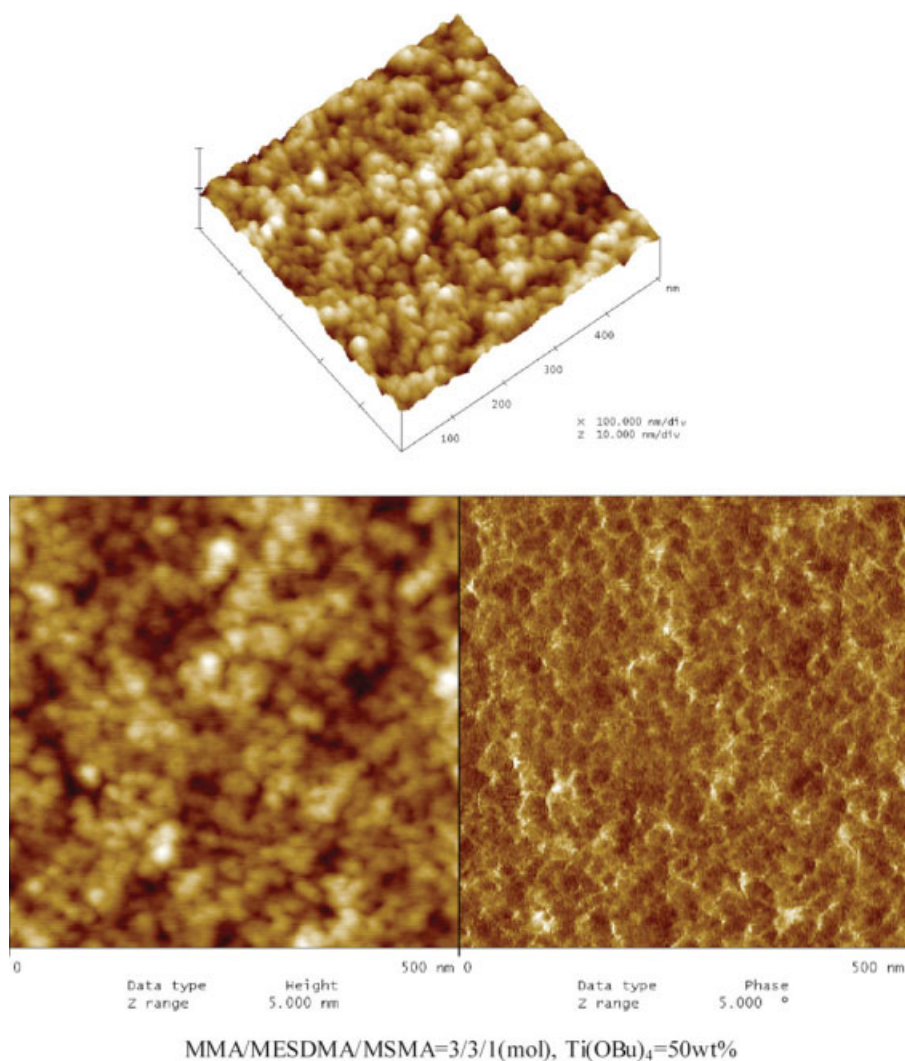


Figure 5 AFM images of the PMMA/PMSDMA/ TiO_2 hybrid film. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The UV-Vis absorbance spectra indicated the character of the films in the UV region. The absorbance of the films with different $(\text{Ti}(\text{n-O}i\text{Bu})_4)$ contents are

shown in Figure 8. The absorbance of the studied films were almost zero in the wavelength range of 350–500 nm, which suggested their excellent optical

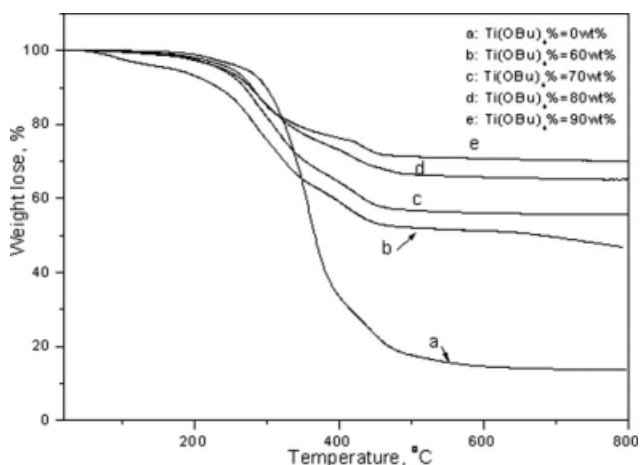


Figure 6 TGA curves of the hybrid materials.

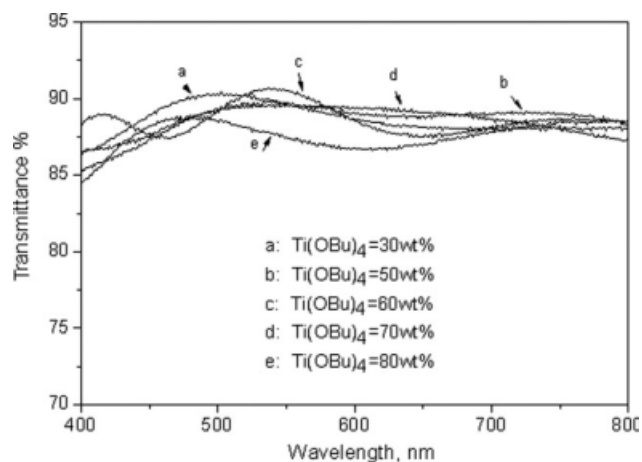


Figure 7 UV-Vis spectra of the hybrid films with different inorganic contents.

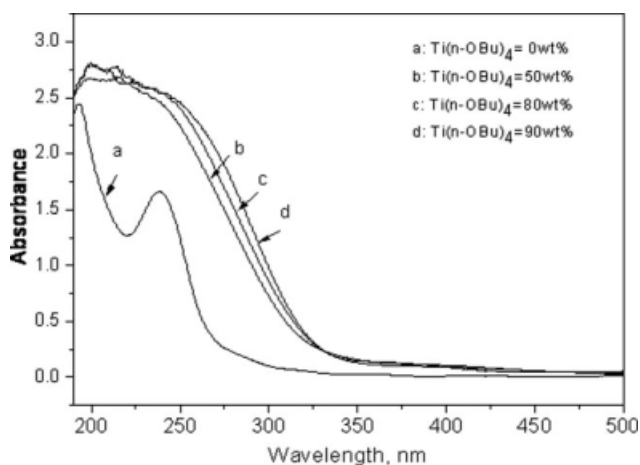


Figure 8 The absorbance of the hybrid films.

transparency. This was consistent with the results got from the UV-Vis transmittance spectra. The increase of absorption in the wavelength range of 190–350 nm was caused by electronic transitions of the Ti—O—Ti chains. Meanwhile, the maximum absorption has a slight red shift with increase of titania content, it is possible because the size of titania increased a little with its content, but the particles were still nanoscaled.¹¹ The absorbance of the hybrid films in the UV region suggested that the hybrid films could improve the UV shielding property of the polymer without decreasing the transparency.

The hybrid films have high refractive index due to the existence of sulfur-containing monomer and nanotitania component. The refractive index of the films prepared by MMA and MSMA at the mol ratio of 6/1 was only 1.48. After MESDMA was used as a monomer instead of part MMA, the refractive index of the polymer matrix increased to 1.58. Then nanotitania was *in situ* prepared in the polymer network, the refractive index of the film tended to rise with increase of (Ti(n-OBu)₄) content as expected. In Figure 9, when the weight percent of titania in the hybrid film was near 70 wt %, calculated from eq. (2), the refractive index of the hybrid film was near 1.75.

$$C = \left(\frac{m_1}{M_1} \times M_2 \right) / \left(\frac{m_1}{M_1} \times M_2 + m_3 \right) \times 100\% \quad (2)$$

where, *C* represents the weight percent of titania in the hybrid film, *m*₁ represents the mass of (Ti(n-OBu)₄), *M*₁ represents the molecular weight of (Ti(n-OBu)₄), *M*₂ represents the molecular weight of titania, and *m*₃ represents the total weight of the monomers.

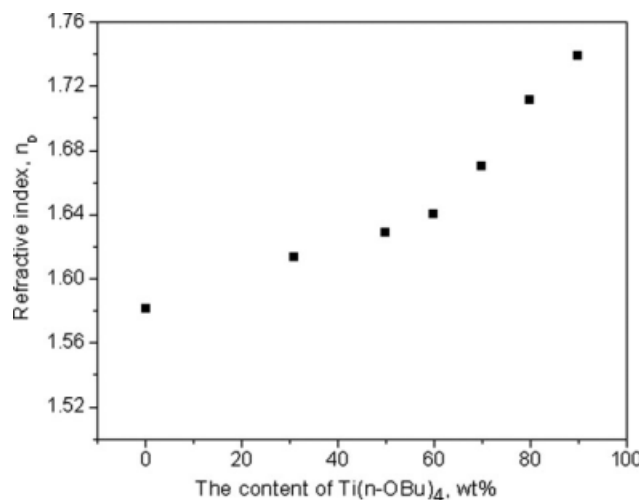


Figure 9 The effect of the content of Ti(n-OBu)₄ on the *n_b* of the hybrid films at 633 nm.

CONCLUSIONS

A kind of transparent hybrid films with a titania-polymer connective network structure was prepared via *in situ* sol-gel reaction of (Ti(n-OBu)₄). In the visible region, the hybrid films showed good optical transparency and high refractive index. The sulfur-containing crosslinking reagent MESDMA was copolymerized into the matrix to improve the refractive index and film-forming ability of the hybrid films. In this article, a feasible way to fabricate optical hybrid films was shown, may be it is a potential way to obtain high refractive index films and optical coatings.

The authors thank Soken Chemical and Engineering (Japan) for its sustainable support to our researches.

References

- Casari, W. *Macromol Rapid Commun* 2000, 21, 705.
- Papadimitrakopoulos, F.; Wisniecki, P.; Bhagwagar, D. E. *Chem Mater* 1997, 9, 2928.
- Yoshida, M.; Prasad, P. N. *Chem Mater* 1996, 8, 235.
- Jiang, H.; Kakkar, A. K. *Adv Mater* 1998, 10, 1093.
- Lü, C. L.; Cui, Z. C.; Wang, Y.; Li, Z.; Guan, C.; Yang, B.; Shen, J. C. *J Mater Chem* 2003, 13, 2189.
- Lee, L.-H.; Chen, W.-C. *Chem Mater* 2001, 13, 1137.
- Gao, C.; Yang, B. *J Appl Polym Sci* 2000, 75, 1474.
- Yuwono, A. H.; Liu, B.; Xue, J. *J Mater Chem* 2004, 14, 2978.
- Xiong, M.; Zhou, S. *Polymer* 2004, 45, 8127.
- Xiong, M.; You, B. *Polymer* 2004, 45, 2967.
- Chen, W.-C.; Lee, S.-J. *J Mater Chem* 1999, 9, 2999.