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TiO₂ nanoparticles with an average diameter of less than 10 nm were prepared via a non-hydrolytic sol–gel route in a TiCl₄–diisopropyl ether–CH₂Cl₂ system. After modification with *n*-octylphosphonic acid (OPA) to increase their organophilic character, the TiO₂ nanoparticles were used for preparation of TiO₂/epoxy hybrid films. Characterization by FT-IR, solid-state ¹³C cross-polarization/magic angle spinning (CP/MAS) and ³¹P MAS NMR techniques showed the preservation of the *n*-octyl groups and the presence of Ti–O–P bonds on the surface of TiO₂ nanoparticles. Hybrid films with various TiO₂ contents were prepared via a wet process and casting using CH₂Cl₂ as a solvent. The resulting films were highly transparent. The refractive indices of TiO₂/epoxy hybrid films at 633 nm increased monotonously from 1.51 for the pure polymer to 1.66 for the hybrid containing 62.4 mass% of TiO₂ nanoparticles. Copyright © 2013 John Wiley & Sons, Ltd.

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Introduction

In recent years, the need for optical materials with high refractive indices and transparency has increased in the fields of antireflective coatings, lenses and waveguides.[1,2] To increase refractive indices of polymers, inorganic fillers with high refractive indices have been introduced into polymer matrices.[2,3] TiO₂, which exhibits a high refractive index [*n* = 2.5 (anatase) or 2.7 (rutile)], is particularly suitable as an inorganic filler for this purpose.[4–6] The greatest obstacle when preparing polymer hybrids is the optical scattering of inorganic fillers, resulting in opacity. To achieve preparation of highly transparent hybrids, at least two requirements must be met: the use of small particles with diameters below one-tenth the wavelength of visible light (<40 nm) and the achievement of high dispersibility of the fillers with high refractive indices in the polymer matrices in order to avoid any aggregation of nanoparticles (NPs) and Rayleigh scattering.[7]

Since epoxy resins have excellent optical transparency, thermal stability and mechanical properties, they are widely used in coating compounds, adhesive agents and encapsulation materials. It is particularly suitable for encapsulation of light-emitting diodes (LEDs). In this case, however, a high refractive index is required, because light extraction efficiency is increased by use of material with a high refractive index. Epoxy-based hybrid materials with inorganic fillers exhibiting high refractive indices have therefore been prepared.[5,8]

Several non-hydrolytic sol–gel routes have been developed, and in particular a route involving reactions of metal chloride or alkoxide with various oxygen donors other than water, such as ether, is a versatile route to various metal oxides.[9,10] Recently, organophilic TiO₂ NPs have thus been prepared via the non-hydrolytic sol–gel route using diisopropyl ether (ⁱPr₂O) as an oxygen donor.[11] In this method, the presence of Ti–Cl and/or Ti–OR groups on the surfaces of the NPs is sufficient to allow their partial solubility in an organic

solvent, and the negligible rate of condensation between these functions at room temperature prevents aggregation of the NPs in an aprotic solvent.[11] This unique surface chemistry makes the NPs highly reactive and, moreover, facilitates surface modification with various nucleophiles. It can thus allow easy adjustment of the organophilicity or hydrophilicity of the NPs. Such surface modification of metal oxide NPs is common, and it allows their stabilization by avoiding agglomeration and improving their compatibility with the organic phase.[12,13] In fact, for purposes of preparation, NPs are modified with phosphorus coupling agents[11,14,15] and carboxylic acids[5] prior to their incorporation into the polymer matrix. The choice of coupling agent is generally related to the stability of the bonds linking the inorganic NPs and the coupling agent. In the case of TiO₂ NPs, the formation of Ti–O–P bonds via treatment with organophosphonic acids is now recognized as a highly efficient means of surface modification.[16–18]

Non-hydrolytic sol–gel routes have been utilized for the preparation of polymer–metal oxide hybrids. Two strategies have been employed to prepare hybrids via non-hydrolytic sol–gel routes. In one strategy, metal oxides precursors and polymers

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were mixed and the precursors were converted into metal oxides via non-hydrolytic sol–gel routes.[19–22] The other strategy was the use of metal oxide NPs prepared via the non-hydrolytic sol–gel routes as fillers – the strategy utilized in the present study.[23–25] It should be noted that none of these studies aimed at preparing high-refractive-index materials.

In this study, we report on the preparation of TiO_2/epoxy hybrid films with high refractive indices according to the general procedure described in Scheme 1. In this process, TiO_2 NPs were synthesized via a non-hydrolytic sol–gel route using diisopropyl ether as an oxygen donor and modified with *n*-octylphosphonic acid to produce highly organophilic TiO_2 NPs. *n*-Octylphosphonic acid (OPA)-modified TiO_2 NPs and the optical properties of hybrid films were investigated in detail.

Experimental

Materials

All manipulations before the surface modification were carried out under an inert atmosphere using standard Schlenk techniques and a glove box filled with nitrogen.[26] A surface modification reagent, *n*-octylphosphonic acid (OPA; Daihachi Chemical Ind. Co., Ltd.) was purified by recrystallization from *n*-hexane. HNO_3 (69–70 mass%; Kanto Chemical Co., Inc.), H_2SO_4 (>96 mass%, Kanto Chemical Co., Inc.) and HF (49.5%, Kanto Chemical Co., Inc.) were also used without further purification. Dichloromethane (CH_2Cl_2, 99.5%; Wako Pure Chemical Ind., Ltd.) was purified by distillation over CaH_2. The 1.8 mass% colloidal solution of TiO_2 NPs was synthesized by heating a mixture of distilled diisopropyl ether (1.86 ml), titanium tetrachloride as 1 mol l^{-1} CH_2Cl_2 solution (6.47 ml) and CH_2Cl_2 (11.6 ml) at 80°C for 30 h in an autoclave.[11] An epoxy resin, (3,4-epoxycyclohexane)methyl-3′,4′-epoxycyclohexyl carboxylate (Daicel Corp.) and a mixture of 4-methylhexahydrophthalic anhydride and hexahydrophthalic anhydride (w/w = 70/30; New Japan Chemical Co., Ltd.) as a curing agent were used without further purification.

Surface modification experiments

OPA (0.388 g; 2.00 mmol) was dissolved in CH_2Cl_2 (24.8 ml) to prepare a 0.05 mol L^{-1} OPA solution. This solution was then added dropwise to the TiO_2 dispersion in CH_2Cl_2 (8.00 ml, 1.30 mmol) while stirring. The mixture was stirred for 24 h at room temperature under a nitrogen atmosphere. The OPA-modified TiO_2 (OPA–TiO_2) was collected as a powder by evaporating CH_2Cl_2. The powder is then washed with 20 ml dried acetone and centrifuged three times, and finally dried *in vacuo* (room temperature, 5 h) for characterization.
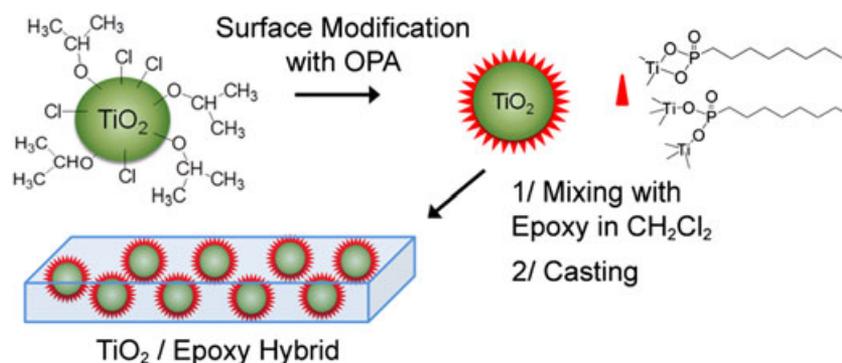
Preparation of TiO_2/epoxy hybrids

A stoichiometric mixture of the epoxy resin and the curing agent (w/w = 134:163) in CH_2Cl_2 was prepared with varying amounts of OPA–TiO_2. The polymer concentrations of these solutions were adjusted to 1 mass%. After stirring the polymer solution for 30 min, 150 µl of the solution was cast on a glass substrate and the resulting film on the substrate was heated at 80°C for 1 day in air to cure the epoxy resin.

Instrumentation

FT-IR spectra were recorded on a JASCO FT-IR-460 Plus spectrometer using the KBr disk technique. Solid-state ^{13}C and ^{31}P NMR spectroscopy was performed with a JEOL ECX-400 spectrometer at 160.26 and 99.55 MHz, respectively. Solid-state ^{13}C NMR spectra were obtained with cross-polarization (CP) and magic angle spinning (MAS) techniques (pulse delay, 5 s; contact time, 1.5 s; spinning rate, 8 kHz), while ^{31}P NMR spectra were obtained with a MAS technique only (pulse delay 20 s; spinning rate 8 kHz). TG was performed with a Rigaku TG8120 Thermoplus EVO thermo balance from 50 to 800°C at a heating rate of 10°C min^{-1} under a nitrogen flow. Thermogravimetry–mass spectrometry (TG-MS) was performed with a RigakunThermo Mass Photo, TG-DTA-PIMS 410/S from 50 to 600°C at a heating rate of 10°C min^{-1} under an He flow. X-ray diffraction (XRD) patterns were obtained with a Rigaku RINT-2500 diffractometer (Ni-filtered Cu-Kα radiation). Transmission electron microscopy (TEM) images were obtained with a JEOL JEM-1011 operating at 100 kV. TEM samples were prepared by evaporating dilute solutions of TiO_2 NPs in CH_2Cl_2 on a carbon-coated copper mesh TEM grid. Ion chromatography (IC) was performed with a TOSOH IC-2001 instrument after stirring the sample in ultrapure water for 30 min. Inductively coupled plasma (ICP) emission spectrometry was performed with a VISTA-MPX CCD simultaneous ICP-OES instrument after dissolving the samples in a mixture of HNO_3 (5 ml, 69–70 mass%), H_2SO_4 (5 ml, >96 mass%) and HF (10 ml, 46–48 mass%) at 200°C for 2 h.

The transmittance spectra of hybrid films were recorded with a JASCO V-630 UV–visible spectrometer in the range 300–800 nm. The refractive indices of hybrid films were determined by ellipsometric measurements using an Otsuka Electronics FE-3000 instrument.

Scheme 1. Overview of preparation of TiO_2/epoxy hybrid film via a non-hydrolytic sol–gel route.

Results and Discussion

### Preparation of TiO_2 NPs and their Surface Modification with *n*-Octylphosphonic Acids

According to Scheme 1, the preparation of TiO_2/epoxy hybrids started with the preparation of the specific TiO_2 NPs via the non-hydrolytic sol–gel route. As this preparation has already been reported,[11] the NPs consisted mainly of amorphous TiO_2 with Ti–Cl and Ti–O^{i}Pr groups remaining on the surface. The second step is chemical modification of their surface conducted to enhance their organophilicity from the perspective of mixing with the epoxy resin.

The grafting of OPA moieties onto the surface of the TiO_2 NPs is obvious from a comparison of the FT-IR spectra of OPA–TiO_2, TiO_2 NPs and pure OPA (supporting information, Fig. S1). Absorption bands due to *n*-octyl groups are present at 2960–2850 cm^{-1} (C–H stretching bands) and 1464 cm^{-1} (CH$_2$ bending band),[27] in addition to, or as replacements for, the absorption bands due to the O–^{i}Pr groups remaining from the original TiO_2 NPs. The P–OH stretching band at 937 cm^{-1} disappears, moreover, and a broad P–O stretching band is observed between 950 and 1200 cm^{-1} after the surface modification reaction.[15] A broad band between 400 and 950 cm^{-1}, characteristic of the Ti–O stretching modes, is also present in the spectra of TiO_2 NPs and OPA–TiO_2.[28]

The grafting of OPA moieties is also evidenced by the data collected from the solid-state ^{13}C CP/MAS NMR spectrum of OPA–TiO_2 (Fig. 1). It shows signals at 15, 24, 31 and 33 ppm, assignable to *n*-octyl groups in similar compounds.[29]

The solid-state ^{31}P MAS NMR spectrum of OPA–TiO_2 (Fig. 2) presents two overlapped signals centered at 21 and 27 ppm, and these signals exhibit upfield shifts with respect to the signal of pure OPA (38.0 ppm by liquid-state ^{31}P NMR). This spectrum indicates that OPA moieties are linked to the TiO_2 surface by Ti–O–P bonds, most likely a result of the condensation of P–OH groups with surface Ti–Cl and Ti–O^{i}Pr groups. The presence of two contributions and their broadness indicates that different situations are dependent on the number of P–O–Ti bonds and the angles in the structure of this bonding.[30]

The molar ratios of Ti and Cl in TiO_2 NPs and OPA–TiO_2 were measured by ion chromatography (IC) and inductively coupled plasma (ICP). The amount of Cl per Ti in OPA–TiO_2 was 0.32, which was smaller than the value of 0.68 in TiO_2 indicating that
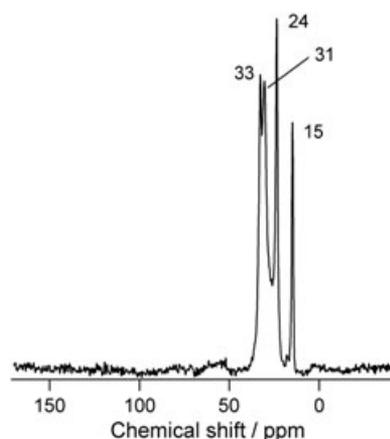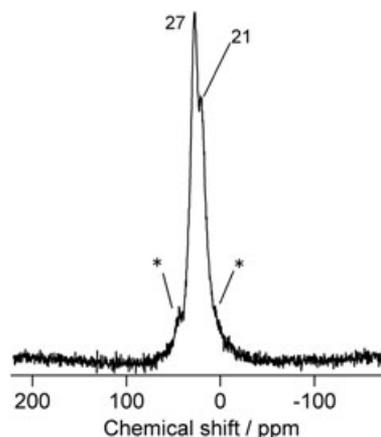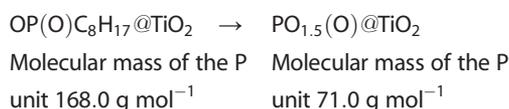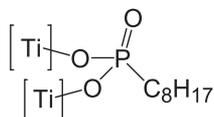

Figure 2. ^{31}P MAS NMR spectrum of NP OPA–TiO_2. Spinning sidebands are marked with asterisks.

the amount of Cl decreased after the surface modification reaction involving surface Ti–Cl groups. It is obvious that Cl groups partially remained after the reaction, however, possibly due to the presence of inaccessible Ti–Cl groups. It should be noted that remaining Ti–Cl groups may catalyze epoxy ring opening reaction.[31]
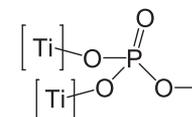
Figure 3 shows the TG curve of OPA–TiO_2. A first mass loss up to 200°C (10.4 mass%) is assumed to result from the elimination of residual organic groups adsorbed on the surface of the TiO_2 NPs, but it could also result from the final condensation between the Ti–Cl and P–OH or Ti–O^{i}Pr groups, as reported previously.[9] Above 400°C, the mass loss of 22.2% is attributable only to the thermal decomposition of organic moieties (C$_8$H$_{17}$).[15,16,32] Some fragment ions such as 55 and 57 (*m/e*) derived from octyl group were also observed in TG mass spectrum of OPA–TiO_2 because of ionization/cleavage mechanism for the long-chain linear hydrocarbons.[32,33] In addition, as the bond dissociation energies of P–C bond (264 kJ mol^{-1}) and C–C bond (331 kJ mol^{-1}) are smaller than that of P–O bond (351 kJ mol^{-1}), the TG-MS results are in agreement with the degradation scheme.[32] The final remaining mass was 55.1 mass%. Assuming the complete condensation (situation A) at 400°C, the combustion of the material up to 1000°C should result in the loss of an *n*-octyl group, leading to conversion of the OPA moiety into a phosphate group (situation B). This corresponds to the loss of one C$_8$H$_{17}$ group (MM 113 g mol^{-1}) and the addition of 0.5 O (8.0 g mol^{-1}) atom per phosphorus, according to the following equations:

$$OP(O)C_8H_{17}@TiO_2 \quad \rightarrow \quad PO_{1.5}(O)@TiO_2$$

Molecular mass of the P unit 168.0 g mol^{-1}	Molecular mass of the P unit 71.0 g mol^{-1}

Situation A

Situation B

The observed mass loss is 22.2%, which represents 0.227 mol *n*-octyl groups lost during the calcination of 100 g starting NPs.
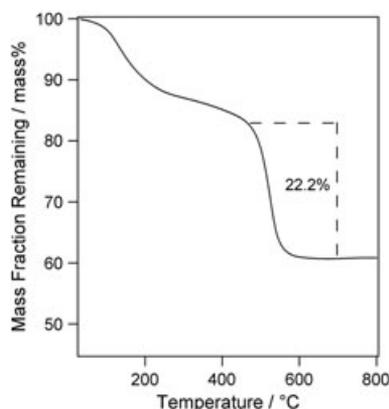

Figure 1. ^{13}C CP/MAS NMR spectrum of NP OPA–TiO_2.

Figure 3. TG curve of NP OPA–TiO₂.

Figure 4. UV–visible spectrum of the TiO₂/epoxy hybrid film with a TiO₂ content of 62.4 mass%.

Thus if we assume all the OPA moieties are in situation A, the amount of OPA moieties is calculated to be $0.227 \times 168.0 = 38.1$ g for 100 g starting NPs.

The mass loss above 400°C therefore permits calculation of the number of moles of *n*-octyl groups, i.e. the number of moles of OPA grafted onto the surface of the NPs in the present case. Accordingly, and assuming that the cross-section area of the –PO$(O^-)_2$ group is 0.24 nm^2,[27] it can be concluded that the OPA units cover a surface area of 330 m^2 g^{-1}. This value should be compared with the specific surface area estimated for TiO₂ NPs $5 < \varnothing < 10$ nm assuming a spherical shape and a density of TiO₂ NPs (2.9 g cm^{-3}): 210 m^2 g^{-1} for NPs $\varnothing = 10$ nm and 410 m^2 g^{-1} for NPs $\varnothing = 5$ nm. Since the surface of TiO₂ NPs is most likely rough (see the TEM analysis below), these estimates suggest that a large portion of the surface of TiO₂ NPs is covered by OPA moieties.

The TEM images of TiO₂ NPs and OPA–TiO₂ show the presence of roughly spherical NPs with diameters less than 10 nm (supporting information, Fig. S2). It is assumed that the reaction of TiO₂ NPs with OPA proceeds with good preservation of the morphology of the TiO₂ NPs.

The XRD patterns of TiO₂ NPs and OPA–TiO₂ exhibited no reflections corresponding to the crystalline TiO₂ forms, anatase, rutile and brookite, indicating that these NPs are essentially amorphous. In addition, dissolution of TiO₂ NPs could lead to the formation of crystalline titanium *n*-octylphosphonate, but no reflection due to this phase was detected by XRD.

Preparation of TiO₂/Epoxy Hybrid

Figure S3 shows photographs of the prepared TiO₂/epoxy hybrid films with various TiO₂ contents. These photographs reveal that all the films are transparent and colorless. This is an important point from the perspective of the preparation of films with excellent optical properties; it shows the excellent affinity of these TiO₂ NPs to the epoxy resin matrix.

The optical transparency of the hybrid films on quartz glass plates is characterized by UV–visible spectroscopy. Figure 4 shows the UV–visible spectrum of the hybrid film with the highest TiO₂ content (62.4 mass%). It is observed that transmittance of the hybrid film is above 94% at visible wavelengths (400–800 nm), suggesting that TiO₂ NPs are uniformly dispersed in the epoxy resin matrices.[7]

The refractive indices at $\lambda = 633$ nm are plotted against the TiO₂ content, as shown in Figure 5. The refractive index increases
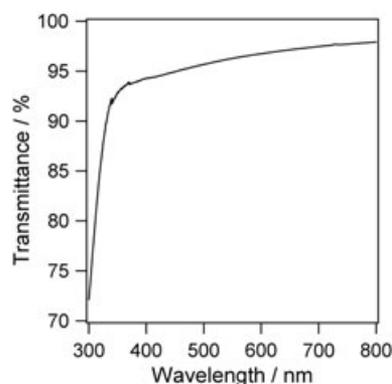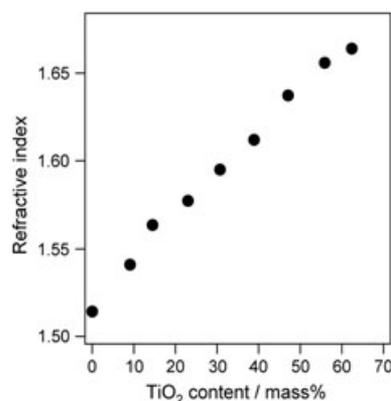

Figure 5. Variations in the refractive indices of TiO₂/epoxy hybrid films at 633 nm with the TiO₂ content.

monotonously from 1.51 (0 mass%) to 1.66 (62.4 mass%) with an increase in TiO₂ content. The refractive index of amorphous TiO₂ NPs modified by OPA is estimated to be 1.7. This value is lower than that of crystalline TiO₂, partly due to the presence of OPA moieties, but higher than that of the pure polymer: 1.51. The incorporation of TiO₂ NPs into epoxy resin matrices therefore results in an increase in the refractive indices of hybrid films. In another study of the preparation of TiO₂ (anatase)/epoxy hybrids,[5] the refractive indices of the epoxy hybrids increased from 1.58 for the pure polymer to 1.73 for 60 mass% TiO₂ content – a similar variation in refractive index with an increase in TiO₂ content.

Conclusions

TiO₂ NPs were synthesized via a non-hydrolytic sol–gel route using diisopropyl ether as an oxygen donor, and their surfaces were modified with *n*-octylphosphonic acid to produce organophilic TiO₂ NPs. Transparent TiO₂/epoxy hybrid films with high refractive indices have been prepared by incorporating modified TiO₂ NPs into epoxy resin matrices. The refractive indices of prepared TiO₂/epoxy hybrid films increased monotonously from 1.51 to 1.66 at 633 nm as the OPA-modified TiO₂ content increased. It should be noted that this study reveals the possibility of obtaining a transparent hybrid film with high refractive index by using organophilic TiO₂ NPs via a non-hydrolytic sol-gel route and subsequent surface modification.

Acknowledgments

References

[1] L. L. Beecroft, C. K. Ober, *Chem. Mater.* **1997**, *9*, 1302.
[2] W. Caseri, *Chem. Eng. Commun.* **2009**, *196*, 549.
[3] N. Kambe, S. Kumar, S. Chiruvolu, B. Chaloner-Gill, Y. D. Blum, D. B. MacQueen, G. W. Faris, *Mater. Res. Soc. Symp. Proc.* **2001**, 676.
[4] C. M. Chang, C. L. Chang, C. C. Chang, *Macromol. Mater. Eng.* **2006**, *291*, 1521.
[5] N. Nakayama, T. Hayashi, *J. Appl. Polym. Sci.* **2007**, *105*, 3662.
[6] R. J. Nussbaumer, W. R. Caseri, P. Smith, T. Tervoort, *Macromol. Mater. Eng.* **2003**, *288*, 44.
[7] H. Althues, J. Henle, S. Kaskel, *Chem. Soc. Rev.* **2007**, *36*, 1454.
[8] C. Guan, C. L. Lu, Y. F. Liu, B. Yang, *J. Appl. Polym. Sci.* **2006**, *102*, 1631.
[9] P. H. Mutin, A. Vioux, *Chem. Mater.* **2009**, *21*, 582.
[10] M. Niederberger, G. Garnweitner, *Chem. Eur. J.* **2006**, *12*, 7282.
[11] A. Aboulaich, B. Boury, P. H. Mutin, *Chem. Mater.* **2010**, *22*, 4519.
[12] P. H. Mutin, G. Guerrero, A. Vioux, *J. Mater. Chem.* **2005**, *15*, 3761.
[13] M. A. Neouze, U. Schubert, *Monatsh. Chem.* **2008**, *139*, 183.
[14] Y. Imai, A. Terahara, Y. Hakuta, K. Matsui, H. Hayashi, N. Ueno, *Eur. Polym. J.* **2009**, *45*, 630.
[15] G. J. Ruiterkamp, M. A. Hempenius, H. Wormeester, G. J. Vancso, *J. Nanopart. Res.* **2011**, *13*, 2779.
[16] G. Guerrero, P. H. Mutin, A. Vioux, *Chem. Mater.* **2001**, *13*, 4367.
[17] P. H. Mutin, G. Guerrero, A. Vioux, *C. R. Chim.* **2003**, *6*, 1153.
[18] P. H. Mutin, V. Lafond, A. F. Popa, M. Granier, L. Markey, A. Dereux, *Chem. Mater.* **2004**, *16*, 5670.
[19] H. Wang, P. Xu, W. Zhong, L. Shen, Q. Du, *Polym. Degrad. Stabil.* **2005**, *87*, 319.
[20] H. C. Kuan, S. L. Chiu, C. H. Chen, C. F. Kuan, C. L. Chiang, *J. Appl. Polym. Sci.* **2009**, *113*, 1959.
[21] S. F. Wang, Y. R. Wang, K. C. Cheng, S. H. Chen, *J. Mater. Sci. Mater. Electron.* **2010**, *21*, 104.
[22] D. Morselli, M. Messori, F. Bondioli, *J. Mater. Sci.* **2011**, *46*, 6609.
[23] X. Song, X. Wang, H. Wang, W. Zhong, Q. Du, *Mater. Chem. Phys.* **2008**, *109*, 143.
[24] A. Aboulaich, O. Lorret, B. Boury, P. H. Mutin, *Chem. Mater.* **2009**, *21*, 2577.
[25] D. Morselli, F. Bondioli, M. Sangermano, M. Messori, *Polymer* **2012**, *53*, 283.
[26] D. F. Shriver, M. A. Drezdzon, The Manipulation of Air-Sensitive Compounds, 2nd edn, Wiley-Interscience, New York, **1986**.
[27] A. Shimada, Y. Yoneyama, S. Tahara, P. H. Mutin, Y. Sugahara, *Chem. Mater.* **2009**, *21*, 4155.
[28] T. Busani, R. A. B. Devine, *Semicond. Sci. Technol.* **2005**, *20*, 870.
[29] W. Gao, L. Reven, *Langmuir* **1995**, *11*, 1860.
[30] F. Brodard-Severac, G. Guerrero, J. Maquet, P. Florian, C. Gervais, P. H. Mutin, *Chem. Mater.* **2008**, *20*, 5191.
[31] P. Innocenzi, A. Sassi, G. Brusatin, M. Guglielmi, D. Favretto, R. Bertani, A. Venzo, F. Babonneau, *Chem. Mater.* **2001**, *13*, 3635.
[32] J. McElwee, R. Helmy, A. Y. Fadeev, *J. Colloid, Interf. Sci.* **2005**, *285*, 551.
[33] F. W. Mclafferty, Interpretation of Mass Spectra, W. A. Benjamin, Inc., New York, **1966**, pp. 83–85.