

ORIGINAL ARTICLE

Preparation and properties of organic–inorganic hybrid polymer films using $[\text{Ti}_4(\mu_3\text{-O})(\text{O}^i\text{Pr})_5(\mu\text{-O}^i\text{Pr})_3(\text{PhPO}_3)_3]\cdot\text{thf}$

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A titanium phosphonate cluster with the formula of $[\text{Ti}_4(\mu_3\text{-O})(\text{O}^i\text{Pr})_5(\mu\text{-O}^i\text{Pr})_3(\text{PhPO}_3)_3]\cdot\text{thf}$ was synthesized. Titanium tetraisopropoxide and phenylphosphonic acid were mixed in tetrahydrofuran and subjected to hydrolysis to provide a white crystal of titanium phosphonate. The titanium phosphonate was mixed with poly(methyl methacrylate) (PMMA) to form a hybrid film. The titanium phosphonate content in the resulting mixture was < 30 wt% and the obtained material was yellow. The degradation temperature increased by ~ 30 °C owing to the hybridization of the titanium phosphonate cluster with PMMA. In another approach, titanium phosphonate was mixed with poly(vinyl alcohol) (PVA) to form a hybrid film. The titanium phosphonate content in the mixture was < 50 wt% and the obtained material was colorless. Isopropyl alcohol was formed in this reaction, suggesting the formation of a titanium phosphonate/PVA hybrid by the reaction of PVA with an isopropoxy group in titanium phosphonate.

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INTRODUCTION

Metal oxide clusters are unique compounds composed of metal–oxygen bonds as a main chain bearing side chains, such as organic groups, hydrides or halogens. Polysilsesquioxane cages¹ are well-known compounds with silicon and oxygen atoms in the main framework. Oxo-titanium clusters² composed of titanium and oxygen atoms are also examples of well-studied metal oxide clusters. Recently, organic–inorganic hybrid polymers prepared using these clusters were found to improve both the thermostability and wear resistivity relative to the corresponding organic polymers.^{3–7} Organic–inorganic hybrid materials are divided into two classes based on their bonding type. Class I comprises the polymers that are bonded by weak interactions, such as van der Waals force and hydrogen bonding. Class II comprises the polymers that are mixed by strong interactions, such as covalent bonding, or the ionic bonding between organic and inorganic components.⁸ For example, Chujo⁴ reported that the hybrid materials of polysulfide-bridged polyhedral oligosilsesquioxane (POSS) with poly(methyl methacrylate) (PMMA) or polystyrene (class I) showed a high thermal stability and high refractive indices compared with the calculated values.⁹ Schubert reported that PMMA cross-linked with $\text{Ti}_4\text{O}_2(\text{O}^i\text{Pr})_6(\text{OMc})_6$ (OMc = methacrylate) (class II) exhibits a high thermal stability.^{3–7} Therefore, organic–inorganic hybrid materials are very interesting because we can expect that the improvement of their physical properties will open new applications in materials science.

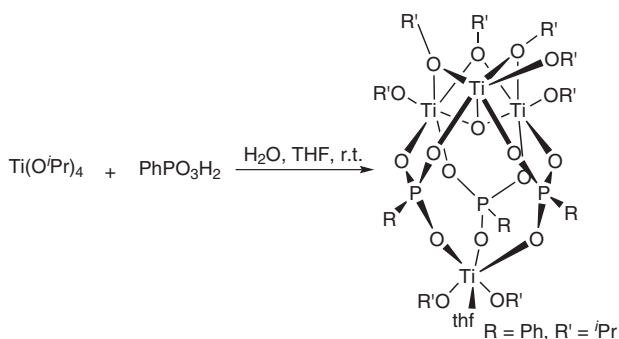
Clusters containing three components are being reported in current research. Titanium phosphonate clusters formed by titanium, oxygen and phosphorus have the potential for high chemical and thermostable properties owing to the presence of Ti–O–P bonds. The interactions among organophosphonate groups are easily controlled by changing the organic groups on titanium or phosphorus atoms. Organic–inorganic hybrid materials containing titanium phosphonate clusters would be prepared by an alcohol exchange reaction or the sol-gel process¹⁰ owing to the presence of an alkoxy group on the titanium atom. Although the synthesis of titanium phosphonate clusters has been reported,^{11–16} the synthesis of organic–inorganic hybrid materials containing these clusters has not been investigated. The use of dimethylsulfoxide (DMSO) as the coordinating solvent is one of the problems encountered in the previous preparation of hybrid materials using clusters. DMSO has strong coordinating properties compared with solvents, such as tetrahydrofuran (THF), which is a common coordinating solvent. Therefore, we expected that a new titanium phosphonium cluster with THF will be useful for the preparation of organic–inorganic hybrid materials because exchange reactions between THF and the ester groups of PMMA or the hydroxyl groups in poly(vinyl alcohol) (PVA) will occur easily. In this work, we report the synthesis and structure of a novel titanium phosphonate cluster, $[\text{Ti}_4(\mu_3\text{-O})(\text{O}^i\text{Pr})_5(\mu\text{-O}^i\text{Pr})_3(\text{PhPO}_3)_3]\cdot\text{thf}$ (TiOPPh), shown in Scheme 1. We also prepared PMMA or PVA hybrid materials

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Scheme 1 Synthesis of TiOPPh. TiOPPh, $\text{Ti}_4(\mu_3\text{-O})(\text{O}i\text{Pr})_5(\mu\text{-O}i\text{Pr})_3(\text{PhPO}_3)_3\cdot\text{thf}$.

containing the cluster and investigated the properties of these materials.

EXPERIMENTAL PROCEDURE

Measurements

NMR spectra were recorded using a JEOL Resonance JNM-ECP 500 spectrometer (JEOL, Akishima, Japan), (^1H at 500.16 MHz, ^{13}C at 125.77 MHz and ^{31}P at 202.46 MHz) at 24 °C. The chemical shifts were reported in p.p.m. relative to CDCl_3 used as an internal standard (for ^1H : 7.26 p.p.m. in residual CHCl_3 , ^{13}C : 77.16 p.p.m.) and H_3PO_4 as an external standard (for ^{31}P : 0.00 p.p.m.). Infrared spectra were recorded on a JASCO FT/IR-6100 FT-IR spectrophotometer (JASCO, Hachioji, Japan) using attenuated total reflectance (ZnSe prism, JASCO ATR PRO 0450-S). Thermogravimetric-differential thermal analysis was performed using a NETZSCH JAPAN, TG-DTA 2000SE analyzer (Yokohama, Japan). The samples were heated to 1000 °C under an airflow at the rate of 10 °C per min. Transmittance spectra were recorded using a JASCO V-670 spectrophotometer equipped with an integrating-sphere photometer (JASCO ISN-470 type) in the 200–800 nm wavelength range. Refractive indices were determined using an Otsuka Electronics FE-3000 refractive film thickness monitor (Osaka, Japan).

X-ray structure analyses

For structural determination, crystal data were collected using a Bruker AXS, SMART APEX CCD X-ray diffractometer (Yokohama, Japan) equipped with a rotating-anode X-ray generator emitting graphite-monochromatic $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 77 K. Empirical absorption corrections using equivalent reflections and Lorentzian polarization correction were performed using the SADABS program.¹⁷ All data were collected using SMART and Bruker SAINTPLUS (Version 6.45) software (Bruker AXS Inc., Madison, WI, USA). The structures were solved using the SHELXS-97 program¹⁸ and refined against F^2 using SHELXL-97.¹⁹ CCDC 1487366 contains the supplementary crystallographic data for TiOPPh. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

Materials

All solvents were purified by a standard process²⁰ and stored over activated molecular sieves. Titanium tetraisopropoxide and PVA (degree of polymerization, 500) were purchased from Wako Pure Chemical Industries, Tokyo, Japan. Phenylphosphonic acid was purchased from Tokyo Chemical Industry and PMMA ($M_w = 997\,000 \text{ g mol}^{-1}$) was purchased from Sigma-Aldrich (Tokyo, Japan). All reagents were used as received.

Synthesis of TiOPPh

The synthesis reaction was carried out in an argon atmosphere. Titanium tetraisopropoxide (36 ml, 0.12 mol) was added to PhPO_3H_2 (9.56 g, 60.5 mmol) and H_2O (0.36 ml, 20 mmol) in 48 ml THF at room temperature, with white precipitation appearing shortly afterward. After several hours of stirring, the mixture became a colorless solution, whereupon the stirring was

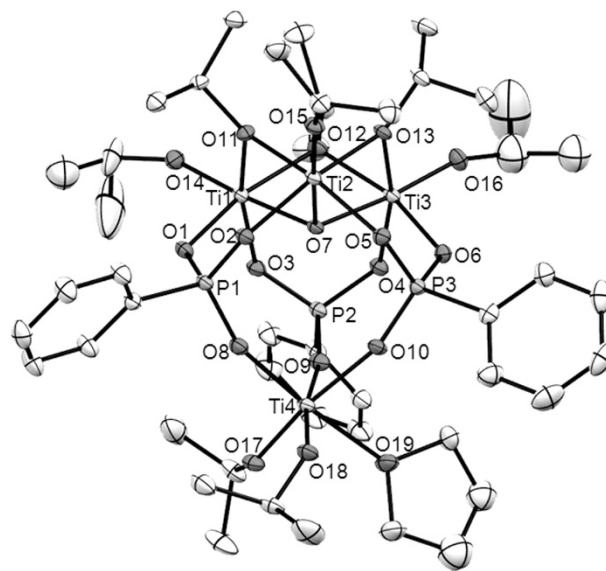


Figure 1 ORTEP drawing of TiOPPh with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and bond angles (°) are as follows: Ti(1)–O(1) 1.972(6), Ti(1)–O(7) 1.962(4), Ti(1)–O(11) 2.010(5), Ti(1)–O(14) 1.779(5), Ti(4)–O(8) 1.924(6), Ti(4)–O(17) 1.820(7), Ti(4)–O(19) 2.162(6), P(1)–O(1) 1.536(4); O(1)–Ti(1)–O(3) 90.7(2), O(1)–Ti(1)–O(11) 87.5(2), O(7)–Ti(1)–O(14) 175.4(2), O(8)–Ti(4)–O(9) 94.5(2), O(8)–Ti(4)–O(19) 174.3(3), O(1)–P(1)–O(2) 111.4(3), O(1)–P(1)–O(8) 110.9(3). TiOPPh, $\text{Ti}_4(\mu_3\text{-O})(\text{O}i\text{Pr})_5(\mu\text{-O}i\text{Pr})_3(\text{PhPO}_3)_3\cdot\text{thf}$. A full color version of this figure is available at the *Polymer Journal* journal online.

stopped. Colorless block crystals from the solution appeared after several weeks, and were then filtrated and dried *in vacuo*. White block crystals were obtained in a yield of 8.25 g (34%).

^1H NMR (500 MHz, $\text{CDCl}_3/7.26 \text{ p.p.m.}$): $\delta = 1.06$ (d, $J = 5.5 \text{ Hz}$, 12H), 1.37 (d, $J = 6.0 \text{ Hz}$, 18H), 1.44 (d, $J = 6.0 \text{ Hz}$, 18H), 1.75–1.81 (m, 6H), 3.79–3.82 (m, 6H), 4.69 (sept, $J = 6.0 \text{ Hz}$, 3H), 4.94 (br-s, 2H), 5.03 (sept, $J = 6.0 \text{ Hz}$, 3H), 7.30–7.38 (m, 9H), 7.88 (dd, $J = 7.5 \text{ Hz}$, $^3J_{\text{P-H}} = 12.0 \text{ Hz}$, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, $\text{CDCl}_3/77.16 \text{ p.p.m.}$): $\delta = 24.51$, 24.83, 25.36, 68.84, 78.45, 79.14, 79.40, 127.31 (d, $^2J_{\text{P-C}} = 14.4 \text{ Hz}$), 129.72 (d, $^4J_{\text{P-C}} = 2.9 \text{ Hz}$), 131.05 (d, $^3J_{\text{P-C}} = 9.6 \text{ Hz}$), 134.44 (d, $^1J_{\text{P-C}} = 203.9 \text{ Hz}$); $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, $\text{CDCl}_3/\text{p.p.m.}$): $\delta = 9.2$. Ceramic yield: 40.4% (calcd. for $\text{Ti}_4\text{P}_3\text{O}_{16}$ 41.7%).

Preparation of free-standing hybrid films

PMMA–TiOPPh hybrid films. 5 ml of PMMA in toluene (50 g l^{-1}) was added to TiOPPh in toluene (31 g l^{-1}), and the mixture was stirred at room temperature overnight. The solution was poured into a 60 mm ϕ glass petri dish followed by curing at 50 °C for 1 day and then at 120 °C for 1 day in an air atmosphere. The thickness of the films was $\sim 85 \mu\text{m}$.

PVA–TiOPPh hybrid films. 0.12 g of PVA dissolved in 10 ml of DMSO was added to TiOPPh dissolved in 1 ml of THF and the mixture was stirred at room temperature overnight. The solution was poured into a 50 mm Teflon petri dish followed by curing at 50 °C for 1 day and then at 120 °C for 1 day in an air atmosphere. The thickness of the films was $\sim 60 \mu\text{m}$.

Preparation of hybrid thin films

A solution of 0.12 g of PVA in 5 ml of deionized water was added to TiOPPh in 5 ml of THF and the mixture was stirred at room temperature overnight. Hybrid thin films were prepared by spin-coating of the solution on a silicon wafer at 1000 r.p.m. for 20 s and then heating at 120 °C for 2 min in air.

RESULTS AND DISCUSSION

Characterization of TiOPPh

TiOPPh was synthesized by the reaction of titanium tetraisopropoxide with PhPO_3H_2 and water in THF. The formation of this cluster was confirmed using various NMR spectra, Fourier transform infrared (FT-IR) spectra and single-crystal X-ray structural analysis. Single-crystal X-ray structural diffraction showed that TiOPPh is composed of four titanium atoms, three PhPO_3 groups, five terminal O^iPr , three bridged O^iPr , one $\mu_3\text{-O}$ and one THF molecule (Figure 1, Table 1). The main TiOPPh framework consisted of three bridged RPO_3 between one Ti atom coordinated by THF and one Ti_3O containing a $\mu_3\text{-O}$ atom. Three phosphonates are arranged in one direction, one on top of the other and are capped by a THF-coordinated Ti atom. This structure is very similar to that of TiOPPh-dmsol.^{11,12} In the ^1H NMR spectrum, three doublet signals attributed to the CH_3 in the isopropoxy group were found at 1.06, 1.37 and 1.44 p.p.m. with respective integration ratios of 12H, 18H and 18H. These signals are assigned to the terminal isopropoxy group on the Ti coordinated by

Table 1 Crystal data for TiOPPh

Empirical formula	$\text{C}_{46}\text{H}_{79}\text{O}_{19}\text{P}_3\text{Ti}_4$
Formula weight	1220.6
Crystal system	Triclinic
Space group	P-1
a (Å)	12.3418 (11)
b (Å)	13.7751 (12)
c (Å)	20.2975 (17)
α (°)	90.957 (1)
β (°)	105.730 (1)
γ (°)	114.034 (1)
Z	2
V (Å ³)	3001.7 (5)
$D_{\text{calcd.}}$ (g cm ⁻³)	1.35
$R1$ ($I > 2\sigma(I)$)	0.0707
$wR2$	0.2199
S	1.062

Abbreviation: TiOPPh, $\text{Ti}_4(\mu_3\text{-O})(\text{O}^i\text{Pr})_5(\mu\text{-O}^i\text{Pr})_3(\text{PhPO}_3)_3\cdot\text{thf}$.

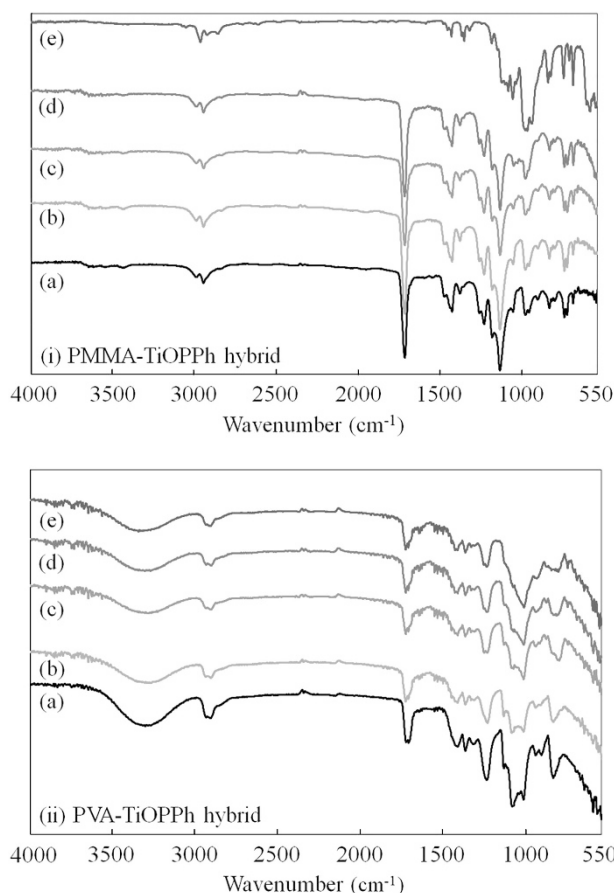


Figure 3 FT-IR spectra of (i) PMMA-TiOPPh hybrid films: (a) PMMA only, (b) PMMA-2.5 wt% TiOPPh, (c) PMMA-10 wt% TiOPPh, (d) PMMA-20 wt% TiOPPh and (e) TiOPPh only; and (ii) PVA-TiOPPh hybrid films: (a) PVA only, (b) PVA-2.5 wt% TiOPPh, (c) PVA-10 wt% TiOPPh, (d) PVA-20 wt% TiOPPh and (e) PVA-40 wt% TiOPPh. PMMA, poly(methyl methacrylate); PVA, poly(vinyl alcohol); TiOPPh, $\text{Ti}_4(\mu_3\text{-O})(\text{O}^i\text{Pr})_5(\mu\text{-O}^i\text{Pr})_3(\text{PhPO}_3)_3\cdot\text{thf}$. A full color version of this figure is available at the *Polymer Journal* journal online.

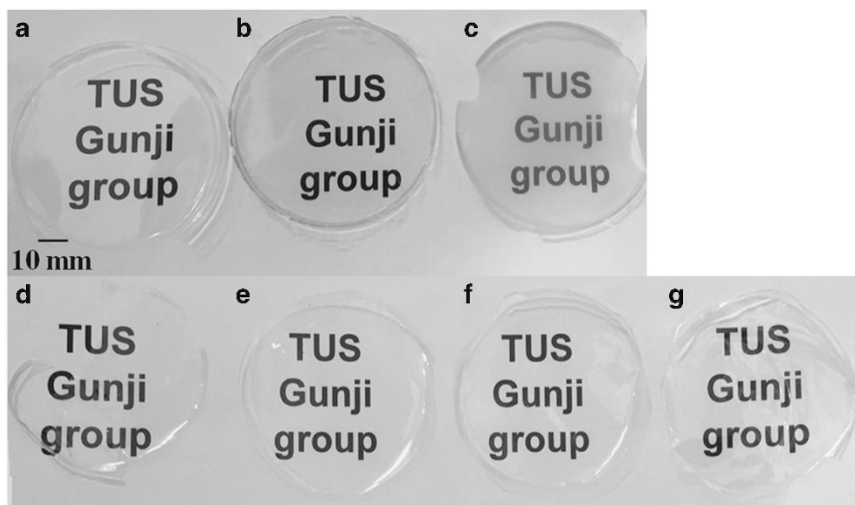


Figure 2 Photograph of hybrid films. (a) PMMA only, (b) PMMA-10 wt% TiOPPh, (c) PMMA-20 wt% TiOPPh, (d) PVA only, (e) PVA-10 wt% TiOPPh, (f) PVA-20 wt% TiOPPh and (g) PVA-40 wt% TiOPPh. PMMA, poly(methyl methacrylate); PVA, poly(vinyl alcohol); TiOPPh, $\text{Ti}_4(\mu_3\text{-O})(\text{O}^i\text{Pr})_5(\mu\text{-O}^i\text{Pr})_3(\text{PhPO}_3)_3\cdot\text{thf}$. A full color version of this figure is available at the *Polymer Journal* journal online.

THF, the terminal isopropoxy group on the Ti_3O unit and the bridged isopropoxy group, respectively. CH in the isopropoxy group shows signals at 4.69, 4.94 and 5.03 p.p.m. The signals derived from the phenyl group shown at 7.30–7.38 p.p.m. as a multiplet are assigned to

the overlapping signals of *m*- and *p*-CH in the phenyl group, and the double doublet signal observed at 7.88 p.p.m. was assigned to *o*-CH in the phenyl group. The ^{13}C NMR spectrum shows signals owing to CH_3 at 24.51 and 24.83 p.p.m., owing to THF at 25.36 and

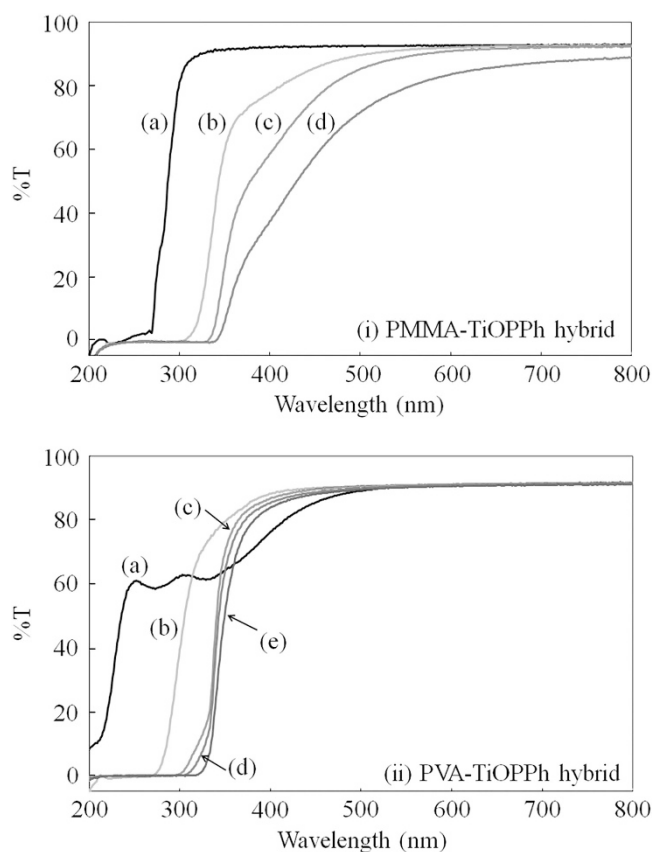


Figure 4 UV-Vis transmission spectra of (i) PMMA-TiOPPh hybrid films: (a) PMMA only, (b) PMMA-2.5 wt% TiOPPh, (c) PMMA-10 wt% TiOPPh and (d) PMMA-20 wt% TiOPPh; and (ii) PVA-TiOPPh hybrid films: (a) PVA only, (b) PVA-2.5 wt% TiOPPh, (c) PVA-10 wt% TiOPPh, (d) PVA-20 wt% TiOPPh and (e) PVA-40 wt% TiOPPh. PMMA, poly(methyl methacrylate); PVA, poly(vinyl alcohol); TiOPPh, $\text{Ti}_4(\mu_3\text{-O})(\text{O}^i\text{Pr})_5(\mu\text{-O}^i\text{Pr})_3(\text{PhPO}_3)_3\cdot\text{thf}$; UV-Vis, ultraviolet-visible. A full color version of this figure is available at the *Polymer Journal* journal online.

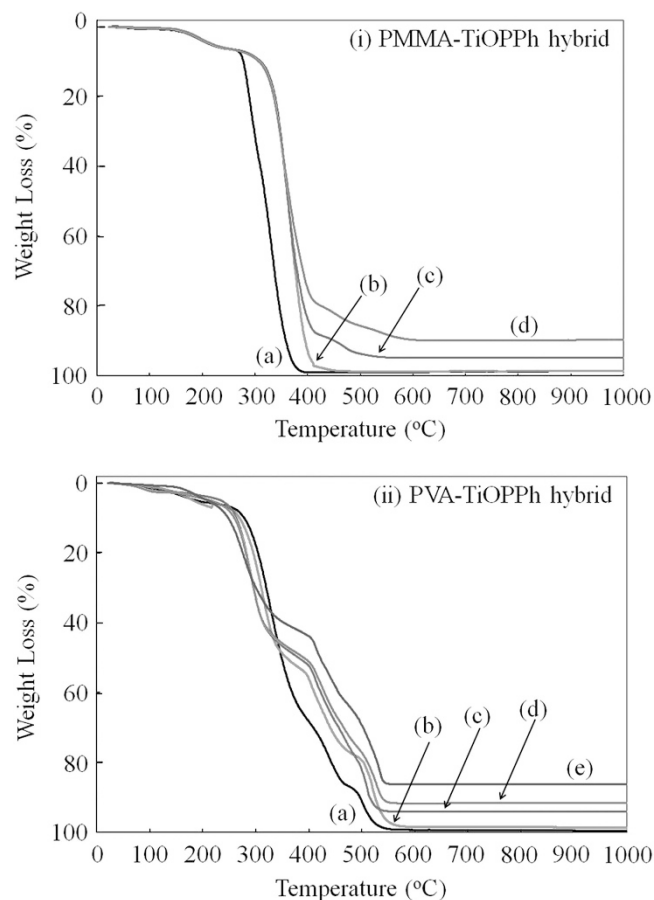


Figure 5 Thermogravimetric analysis traces of (i) PMMA-TiOPPh hybrid films: (a) PMMA only, (b) PMMA-2.5 wt% TiOPPh, (c) PMMA-10 wt% TiOPPh and (d) PMMA-20 wt% TiOPPh; and (ii) PVA-TiOPPh hybrid films: (a) PVA only, (b) PVA-2.5 wt% TiOPPh, (c) PVA-10 wt% TiOPPh, (d) PVA-20 wt% TiOPPh and (e) PVA-40 wt% TiOPPh. PMMA, poly(methyl methacrylate); PVA, poly(vinyl alcohol); TiOPPh, $\text{Ti}_4(\mu_3\text{-O})(\text{O}^i\text{Pr})_5(\mu\text{-O}^i\text{Pr})_3(\text{PhPO}_3)_3\cdot\text{thf}$. A full color version of this figure is available at the *Polymer Journal* journal online.

Table 2 Optical and thermal properties of TiOPPh hybrid films

Sample	Transmittance		Thermal analysis	
	T_{550} (%) ^a	T_{420} (%) ^b	T_{d10} (°C) ^c	Ceramic yield (wt%) ^d
Only PMMA	92.3	91.7	279	1.4
PMMA-2.5 wt% TiOPPh	90.9	79.6	312	1.4
PMMA-10 wt% TiOPPh	89.2	66.9	311	5.2
PMMA-20 wt% TiOPPh	78.6	42.9	308	10.3
Only PVA	90.4	81	278	0.4
PVA-2.5 wt% TiOPPh	90.9	89.6	270	1.3
PVA-10 wt% TiOPPh	91	88.4	264	5.9
PVA-20 wt% TiOPPh	90.6	87.3	259	8.4
PVA-40 wt% TiOPPh	90.3	86.4	249	13.9

Abbreviations: PMMA, poly(methyl methacrylate); PVA, poly(vinyl alcohol); TiOPPh, $\text{Ti}_4(\mu_3\text{-O})(\text{O}^i\text{Pr})_5(\mu\text{-O}^i\text{Pr})_3(\text{PhPO}_3)_3\cdot\text{thf}$; UV-Vis, ultraviolet-visible.

^aMeasured by UV-Vis spectroscopy at 550 nm.

^bMeasured by UV-Vis spectroscopy at 420 nm.

^cDetermined from the decomposition temperature with 10% weight loss.

^dWeight percent of the residue at 1000 °C.

68.84 p.p.m., and owing to CH at 78.45, 79.14 and 79.40 p.p.m. The signals derived from the phenyl group appear in the doublet because of the coupling between the phosphorus and the carbon atoms. The signals observed at 127.31, 129.72, 131.05 and 134.44 p.p.m. were assigned to *o*-CH, *p*-CH, *m*-CH and *ipso*-CH, respectively. The ^{31}P NMR spectrum shows signals at 9.26 p.p.m. in CDCl_3 ; in C_6D_6 , the ^{31}P shows signals at 6.8 p.p.m. with an integrated intensity of 2 and at 7.2 p.p.m. with an integrated intensity of 1.

The FT-IR spectrum of TiOPPh shows the following absorption bands: $\nu_{\text{C-H}}$ of phenyl at 3056 cm^{-1} , $\nu_{\text{C-H}}$ of the isopropoxy group at 2970 and 2928 cm^{-1} , $\nu_{\text{C-H}}$ of THF at 2862 cm^{-1} , $\nu_{\text{C=C}}$ of phenyl at 1439 cm^{-1} , $\delta_{\text{C-H}}$ at 1375 and 1362 cm^{-1} , $\nu_{\text{C-C}}$ at 1156 and 1132 cm^{-1} , $\nu_{\text{C-O}}$ and $\nu_{\text{P-O}}$ at 989 – 949 cm^{-1} overlapping with $\delta_{\text{C=C}}$ at 754 and 696 cm^{-1} assigned to the out-of-plane phenyl vibration, and $\nu_{\text{Ti-O}}$ at 614 – 558 cm^{-1} . The thermogravimetric-differential thermal analysis of TiOPPh shows weight losses at 80 – $250\text{ }^\circ\text{C}$ (41%) assigned to the decomposition of the isopropoxy group, THF and the carbons in phenyl, as well as at $450\text{ }^\circ\text{C}$ (8%) and $800\text{ }^\circ\text{C}$ (10%).

Preparation of free-standing hybrid films

PMMA hybrid films were prepared from a toluene solution, and PVA hybrid films were prepared from a solution of DMSO and THF. A photograph of the hybrid films is shown in Figure 2. The PMMA films changed from colorless to yellow as the TiOPPh concentration increased. However, colorless and transparent films were prepared by using PVA. We note that we have attempted to prepare hybrid films containing 30 wt% of PMMA and 50 wt% of PVA. Unfortunately, these films were not prepared because they were too rigid to retain the form of free-standing films.

FT-IR spectra are shown in Figure 3. All PMMA hybrid films show $\nu_{\text{C-H}}$ at 3000 – 2950 cm^{-1} , $\nu_{\text{C-H}}$ at 1723 cm^{-1} , and $\nu_{\text{C-O-C}}$ at 1190 and 1144 cm^{-1} . PMMA–TiOPPh hybrid films show new bands owing to $\nu_{\text{P=O}}$ at 1040 cm^{-1} and $\nu_{\text{Ti-O}}$ at $\sim 550\text{ cm}^{-1}$. However, the $\nu_{\text{P=O}}$ band could be observed only for the 20 wt% TiOPPh. The bands derived from PMMA were very similar, especially $\nu_{\text{C=O}}$ at 1723 cm^{-1} . These results indicated that the carbonyl groups of PMMA did not coordinate to the TiOPPh Ti atom via an exchange reaction between THF and the carbonyl groups. However, $\nu_{\text{C-O-C}}$ shifted from 1144 cm^{-1} (PMMA) to 1142 cm^{-1} (PMMA–TiOPPh hybrid). Therefore, PMMA and TiOPPh can be blended by using a weak interaction between the PMMA methoxy group and TiOPPh. However, all PVA hybrid films showed $\nu_{\text{O-H}}$ at 3300 cm^{-1} , $\nu_{\text{C-H}}$ at 2911 cm^{-1} and $\nu_{\text{C-C}}$ at 1421 cm^{-1} . The signal intensity owing to $\nu_{\text{P-O}}$ at 1000 cm^{-1} increased and that owing to $\nu_{\text{O-H}}$ decreased with increasing amount of TiOPPh. On the basis of these results, an alcohol exchange reaction between the hydroxy group in PVA and the isopropoxy group in TiOPPh was confirmed.

Transmittance spectra are shown in Figure 4 and the data are summarized in Table 2. As the TiOPPh concentration increased, the transparency of PMMA hybrid films in the visible region decreased significantly. Moreover, these TiOPPh–PMMA hybrid films were yellow. However, the transparency of the PVA hybrid films was high compared with that of the PVA films. The origin of the yellow color in PMMA films is assigned to the aggregation and/or polymerization of TiOPPh caused by the water in the air. In contrast, TiOPPh in PVA appears to be highly dispersed. Therefore, the PVA hybrid films were obtained as colorless films. These conclusions are also supported by the infrared (IR) spectroscopy results.

Thermogravimetric-differential thermal analysis thermograms of hybrid films are shown in Figure 5 and the data are summarized in Table 2. The temperatures of 10% weight loss (T_{d10}) were 279 and

$278\text{ }^\circ\text{C}$ for PMMA and PVA, respectively. The T_{d10} values for PMMA–TiOPPh hybrid films were $\sim 310\text{ }^\circ\text{C}$ and were $30\text{ }^\circ\text{C}$ higher than that of PMMA. TiOPPh improves the thermal stability of PMMA such that the weight loss is 40 wt% at $310\text{ }^\circ\text{C}$. The improvement of thermal stability was the same as that for other blend, or hybrid PMMA materials containing polysulfide-bridged POSS,⁹ zirconia nanocrystals modified with 3-(methacryloxy)propyl-trimethoxysilane²¹ and titania modified with 2-hydroxyethyl methacrylate²² that were reported in previous studies. However, the T_{d10} of the PVA–TiOPPh hybrid films decreased with increasing TiOPPh concentration, such that the T_{d10} of PVA-30 wt% of the TiOPPh hybrid film was decreased by $45\text{ }^\circ\text{C}$ compared with the value obtained for PVA. The T_{d10} decrease can be attributed to the reaction of the isopropoxy group in TiOPPh with the residual hydroxy group in PVA.

The refractive indices of PVA-hybrid thin films at 633 nm were measured. The refractive index of PVA only was 1.488, and those of PVA-2.5 wt% TiOPPh and PVA-10 wt% TiOPPh were 1.500 and 1.501, respectively. The increase of the refractive index values supports the formation of hybrids.

CONCLUSION

A titanium phosphonate cluster with a formula of TiOPPh was synthesized via the reaction of titanium tetraisopropoxide and phenylphosphonic acid in water and THF. Titanium phosphonate was mixed with PMMA to form a yellow hybrid film at a concentration of $<30\text{ wt}\%$. The degradation temperature increased by $\sim 30\text{ }^\circ\text{C}$ when the titanium phosphonate cluster was hybridized with PMMA. However, titanium phosphonate was mixed with PVA to form a hybrid film. The resulting content was $<50\text{ wt}\%$ and the obtained material was colorless. Isopropyl alcohol was detected after the formation of the hybrid films, confirming the reaction of PVA with the isopropoxy group in the titanium phosphonate cluster. The application of titanium phosphonate clusters for the preparation of hybrid materials is expected to be useful for the development of new organic–inorganic hybrid materials, including various reactive positions in a molecule.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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