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ORIGINAL ARTICLE

Organic–inorganic hybrids based on poly(bisphenol A-*co*-epichlorohydrin) containing titanium phosphonate clusters

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Abstract

Organic–inorganic hybrid films were prepared by transalkoxylation of poly(bisphenol A-*co*-epichlorohydrin) (PBE) and titanium phosphonate clusters, such as $[Ti_4(\mu_3\text{-}O)(O\textit{i}Pr)_5(\mu\text{-}O\textit{i}Pr)_3(O_3PPh)_3]\cdot$thf ($Ti_4P_3$), $[Ti(O\textit{i}Pr)(acac)(O_3PPh)]_4$ (Ti_4P_4; acac = acetylacetonato), and $Ti_7(\mu_3\text{-}O)_2(O\textit{i}Pr)_6(\mu\text{-}O\textit{i}Pr)_6(O_3PBnBr)_6$ (Ti_7P_6). The formation of covalent bonds between PBE and clusters was confirmed by the appearance of $\nu_{C\text{–}O\text{–}Ti}$ in the Fourier transform infrared spectra. In addition, the acetylacetonato group in Ti_4P_4 was dissociated by the hydroxyl group in PBE. The structure of the clusters in PBE was verified by a model reaction of these clusters with alcohols, such as ethanol and isopropyl alcohols, as monitored by nuclear magnetic resonance spectroscopy. The influence of the cluster structure was estimated based on the transmittance, thermal stability, and swelling tests with tetrahydrofuran. The transmittance of the hybrid films was worse than that of pure PBE. The temperature of 5% weight loss (T_{d5}) of the hybrid films was lower than that of pure PBE because Ti–O–C bonding was formed. The solvent uptake of the hybrid films was clearly dependent on the clusters. The swelling ratio increased in the order of $Ti_7P_6 < Ti_4P_4 < Ti_4P_3$; hence, Ti_7P_6 showed the highest cross-linking efficiency.

Introduction

Organic–inorganic hybrids containing molecular clusters have been developed in the field of material chemistry because they show excellent performance, such as improved mechanical and thermal properties. Clusters have advantages such as good solubility in organic solvents and their definite structures compared with those of nanoparticles [1]. Organic–inorganic hybrids containing titanium-oxo clusters, which are composed of titanium and oxygen atoms in the main framework, have been reported to show high thermal stabilities [2, 3], high mechanical properties [4–7], and high refractive indices [8]. However, the syntheses of titanium-oxo clusters require delicate techniques.

We focused on titanium phosphonate clusters, which are composed of phosphatitanoxane bonds (Ti–O–P) with alkoxyl groups, because these clusters are easily synthesized by the reaction of titanium tetraisopropoxide ($Ti(O\textit{i}Pr)_4$) with organophosphonic acid under room temperature and pressure [9–12]. Previously, hybrid materials containing $[Ti_4(\mu_3\text{-}O)(O\textit{i}Pr)_5(\mu\text{-}O\textit{i}Pr)_3(O_3PPh)_3]\cdot$thf ($Ti_4P_3$) were reported to show good thermal and mechanical properties [13, 14] and refractive indices [15]. Their glass transition temperatures and surface hardness are higher than those of the original polymers because the cluster acts as a good crosslinker [13]. Moreover, we previously reported the syntheses of titanium phosphonate clusters having another structure [12]. The properties of $[Ti(O\textit{i}Pr)(acac)(O_3PPh)]_4$ (Ti_4P_4) and $Ti_7(\mu_3\text{-}O)_2(O\textit{i}Pr)_6(\mu\text{-}O\textit{i}Pr)_6(O_3PBnBr)_6$ (Ti_7P_6) are different than those of Ti_4P_3. The solubilities and thermal stabilities of the clusters depend on the intermolecular polarity, the absence of a coordinated solvent, and the structure and number of substituted organic groups.

In this work, we prepared organic–inorganic hybrid films containing titanium phosphonate clusters of Ti_4P_3, Ti_4P_4, and Ti_7P_6 based on poly(bisphenol A-*co*-epichlorohydrin) (PBE), as shown in Scheme 1. PBE was selected because of (i) the hydroxyl group in the side

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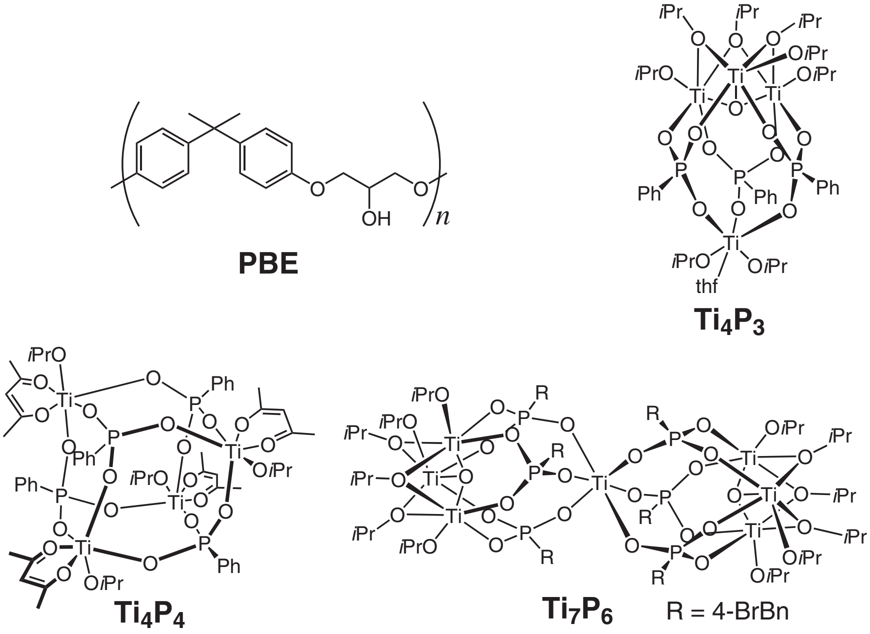
Scheme 1 Chemical structures of PBE and titanium phosphonate clusters



chain, (ii) easy film formation, and (iii) the similar solubility parameters for titanium phosphonate clusters. The hybrid films were characterized by fourier transform infrared (FTIR) spectra; the structures of the clusters in PBE were estimated from the model reaction of the clusters with alcohols. Additionally, the hybrid films were examined by transmittance, thermal stability, and swelling in tetrahydrofuran (THF).

Experimental section

Measurements

FTIR spectra were recorded using an FT/IR-6100 spectrophotometer (JASCO, Hachioji, Japan) equipped with attenuated total reflectance (JASCO ATR PRO 0450-S, ZnSe prism). All nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECP500 spectrometer (^{13}C at 125.77 MHz and ^{31}P at 202.46 MHz) at ~23 °C. $^{13}C\{^1H\}$ NMR spectra were recorded using the chloroform-*d* peak as the internal standard (77.0 ppm). $^{31}P\{^1H\}$ NMR spectra were recorded using 85% phosphoric acid as the external standard (0.0 ppm). When the reaction was followed by $^{31}P\{^1H\}$ NMR spectroscopy, the reaction solution was transferred into an NMR tube, and a capillary containing H_3PO_4 dissolved in D_2O was used as the external standard to lock the signal. Thermal gravimetric analysis (TGA) was performed using a TG-DTA analyzer (2000SE, Netzsch Japan, Yokohama, Japan) under nitrogen flow. The samples were heated to 180 °C for 30 min to remove absorbed water, followed by heating to 1000 °C at a rate of 5 °C/min. Transmittance spectra were recorded using a JASCO V-670 spectrophotometer equipped with an integrating-sphere photometer ISN-470 type (JASCO) in the wavelength range 300–800 nm. Small-angle X-ray scattering (SAXS) measurements were recorded using an SAXSess camera (Anton Paar Japan, Shinagawa, Japan) equipped with a PANalytical PW3830 laboratory X-ray generator with Cu Kα radiation (0.154 nm, 40 kV, 50 mA) as the X-ray source. The swelling test was evaluated using the solvent uptake per gram of the film after storage in THF at 23 ± 2 °C for 3 days.

Materials

All solvents were purified using a standard process [16] and stored over activated molecular sieves. PBE (M_w = 40,000 g/mol) was purchased from Sigma–Aldrich (Tokyo, Japan) and dried at 60 °C under vacuum (~1 mmHg) for >3 h. Ti_4P_3, Ti_4P_4, and Ti_7P_6 were prepared as described previously [12]; the details of syntheses and characterization are shown in the supporting information.

Preparation of the hybrid films

A solution of titanium phosphonate clusters in 2 mL of THF was added to 0.12 g of PBE dissolved in 5 mL of THF, followed by stirring at 23 ± 2 °C for 2 h. The solution was filtrated, cast into a 50*ϕ* Teflon petri dish, dried at room temperature in a desiccator over silica gel for 1 day, and finally cured at 120 °C for 1 day.

Reaction of Ti_7P_6 with ethanol (Ti_7P_6-OEt)

The Ti_7P_6 cluster (200 mg, 78 μmol) was dissolved in 1 mL THF. A 5 mL aliquot of ethanol (89 mmol) was added to the solution followed by reflux for 1 h. The colorless crystals ($[Ti_7(\mu_3\text{-}O)_2(OEt)_6(\mu\text{-}OEt)_6(O_3PBnBr)_6]$: Ti_7P_6-OEt) were obtained after 1 day.

Reaction of Ti_4P_4 with isopropyl alcohol

The Ti_4P_4 cluster (200 mg, 134 μmol) was dissolved in 2 mL THF followed by the addition of isopropyl alcohol (5 mL, 65 mmol). The mixture was refluxed for 1 h; an insoluble pale-yellow powder (~10 mg) was filtered. Alkoxylated-Ti_4P_4 was obtained as a solution. Acetylacetone (1 mL, 10 mmol) was added to the solution, and the mixture was stirred at room temperature for 1 day.

Results and discussion

Preparation of the hybrid films

Clusters and PBE were soluble in THF and chlorinated hydrocarbons and insoluble in hexane and isopropyl alcohol. In particular, the solubilities of Ti_4P_4 and Ti_7P_6 were similar to that of PBE. The precursors of the films were prepared by the transalkoxylation reaction between the titanium phosphonate clusters and the hydroxyl group in PBE. The hybrid films were yellow. The color became stronger with the increase in the amount of clusters. When the cluster amount was >40 wt%, the precursors for Ti_4P_3 and Ti_4P_4 gelled in <2 h because of rapid transalkoxylation. The precursors were cast into a Teflon petri dish followed by drying in a desiccator. (When the drying process was carried out in air, a heterogeneous film was obtained because the Ti–O–C bond is highly sensitive to moisture.) Homogeneous hybrid films were prepared after curing at 120 °C. The films were still homogeneous when stored in water for 1 week.

Characterization of hybrid films by FTIR spectroscopy

The hybrid films were characterized by FTIR spectroscopy using ATR analysis, and all films showed absorption bands owing to $\nu_{O\text{–}H}$ at 3400–3500 cm^{-1}. The FTIR spectra of pure PBE and PBE–30 wt% hybrids in the region of 600–1700 cm^{-1} are shown in Fig. 1. The absorption bands owing to $\nu_{C=C\text{–}H}$ at 1606, 1581, and 1505 cm^{-1} [17, 18]; $\delta_{H\text{–}C\text{–}H}$ at 1458 and 1361 cm^{-1} [19]; $\nu_{C\text{–}O\text{–}H}$ at 1413 cm^{-1} [19, 20]; $\nu_{C\text{–}C\text{–}O\text{–}C}$ at 1230 and 1179 cm^{-1} [19]; $\nu_{C\text{–}O\text{–}C}$ at 1036 cm^{-1} [19] and $\nu_{C=C\text{–}H}$ at 824 cm^{-1} [19] were derived from PBE. The stretching vibrations of P–C were observed at 1438 and 1140 cm^{-1} [21–23] for Ti_4P_3 and Ti_4P_4 and at 1412 (overlapped with $\nu_{C\text{–}O\text{–}H}$ in PBE) and 703 cm^{-1} [24, 25] for Ti_7P_6. In the region of 1000–1050 cm^{-1}, stretching vibrations due to P–O, C–O, and O–C–O appeared, but these bands overlapped. The band for $\nu_{C\text{–}O\text{–}Ti}$ appeared at ~991 cm^{-1} [26, 27]; therefore, transalkoxylation between titanium phosphonate clusters and PBE was proven by the FTIR analysis. Interestingly, the intensity of the band owing to $\nu_{C=C}$ in the acetylacetonato group of Ti_4P_4 at 1529 cm^{-1} [28] was very weak. These phenomena can be explained by the alcoholysis of the acetylacetonato group, similar to the reaction of zirconium tetrakis(acetylacetonato) [29] and zinc bis(acetylacetonato) [30] with alcohol. Hence, most of the acetylacetonato groups of Ti_4P_4 are likely dissociated in PBE.

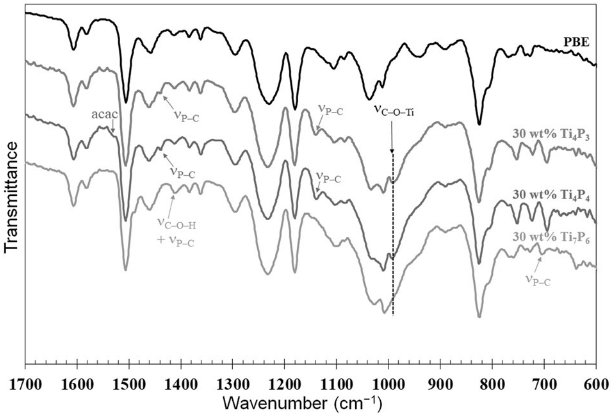


Fig. 1 FTIR spectra of PBE and PBE–30 wt% clusters

NMR spectroscopy of the modeling reaction

To confirm that the structure of titanium phosphonate clusters is maintained in PBE, we examined the model reaction of the titanium phosphonate clusters with alcohols. When Ti_4P_3 or Ti_7P_6 was refluxed in ethanol and followed by cooling, colorless crystals were grown and collected. The transalkoxylation of Ti_4P_3 was reported in a previous paper [13], and the core structure was maintained. The $^{13}C\{^1H\}$ NMR spectrum of Ti_7P_6 clearly show the structure of the ethoxylated-titanium phosphonate cluster, as shown in Fig. 2. Based on the results, Ti_4P_3 and Ti_7P_6 must account for the structural preservation of the main framework in PBE. However, the reaction of Ti_4P_4 with ethanol is very complicated because the isopropoxyl and acetylacetonato groups are exchanged with the ethoxyl group. Hence, we used isopropyl alcohol; the $^{31}P\{^1H\}$ NMR spectra of the reaction solution of Ti_4P_4 and isopropyl alcohol is shown in Fig. 3. The new signals appeared in the lower magnetic field (−2 to 7 ppm). The signals in the region of 4–7 ppm can

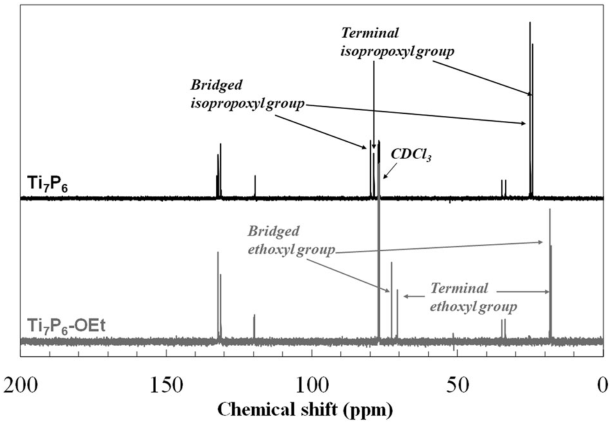


Fig. 2 $^{13}C\{^{1}H\}$ NMR spectra of Ti_7P_6 and Ti_7P_6-OEt in $CDCl_3$

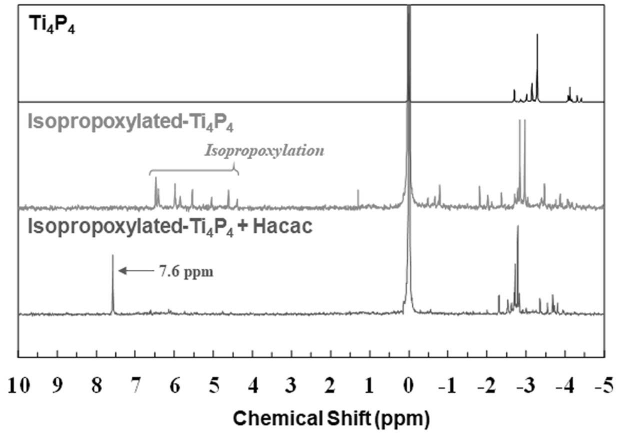


Fig. 3 $^{31}P\{^{1}H\}$ NMR spectra of Ti_4P_4 (in THF), isopropoxylated-Ti_4P_4, and addition of Hacac (in *i*PrOH+THF)

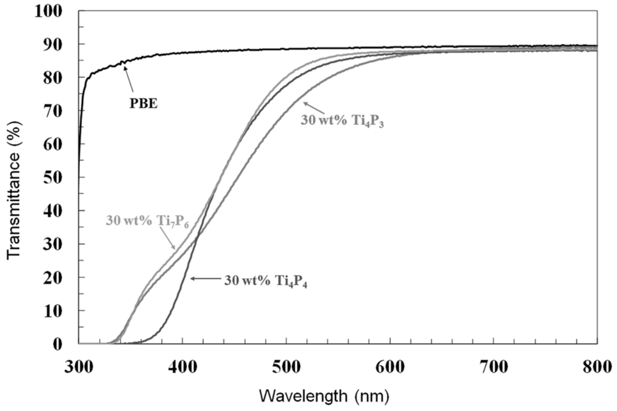


Fig. 4 UV–Vis transmittance spectra of PBE and PBE–30 wt% clusters

Table 1 Transmittance, T_{d5}, and solvent uptake in THF of pure PBE and hybrid films

Cluster	Cluster proportion (wt%)	Thickness (μm)	$T_{500\ nm}$ [a] (%)	T_{d5} [b] (°C)	Swelling to THF[c] (solvent [g]/film [g])
None	–	41	88	354	–[d]
Ti_4P_3	10	34	83	333	4.58
	20	39	81	325	1.39
	30	36	70	312	0.86
Ti_4P_4	10	32	83	330	4.64
	20	41	78	322	1.16
	30	49	77	314	0.46
Ti_7P_6	10	61	79	329	3.32
	20	41	85	334	0.49
	30	45	80	330	0.34

[a] Measured by UV−Vis spectrometry at 500 nm

[b] Measured by TGA

[c] The solvent uptake per gram of the hybrids after storage in THF for 3 days

Solvent uptake = (swelled film [g] − former film [g])/former film [g] = absorption solvent [g]/former film [g]

[d] Dissolution

possibly be assigned to the phosphonate group bearing titanium atoms and no acetylacetonato group because these signals appeared in the region of the reaction solution of Ti(O*i*Pr)$_4$ with $PhPO_3H_2$ (see Figure S1). On the other hand, the signals in the region of −2 to 1 ppm can be assigned to the phosphonate group binding titanium atoms with acetylacetonato groups. Hence, we suggest the formation of cubic structures such as $[Ti(OiPr)_2(O_3PPh)]_4$ and $[Ti(OiPr)_{1+x}(acac)_{1-x}(O_3PPh)]_4$. Therefore, we added acetylacetone to this solution to confirm reversal to Ti_4P_4. From the results, the signals at −2 to 7 ppm disappear and support the reverse reaction of Ti_4P_4 (the chemical shift value of $^{31}P\{^{1}H\}$ NMR slightly differed owing to the solvent effect); however, a signal at 7.6 ppm appeared. This signal at 7.6 ppm was confirmed when acetylacetone was added to the reaction solution of Ti(O*i*Pr)$_4$ and $PhPO_3H_2$ [31]. This behavior is presumed to indicate cleavage of the cubic structures by acetylacetone, which acts as a very strong ligand, similar to the zirconium-oxo cluster [32]. As a result, Ti_4P_4 was exchanged with alcohol from the acetylacetonato group and might have maintained the core structure.

Properties of the hybrid films

Transmittance

The transmittance in the region of 300–800 nm of the hybrid films is shown in Fig. 4 and summarized in Table 1. The transmittances of all hybrid films decreased with increasing concentrations of titanium phosphonate clusters. The transmittance of the PBE–10 wt% Ti_7P_6 hybrid film was lower than that of the higher proportion films of Ti_7P_6 because the 10 wt% Ti_7P_6 hybrid film was 1.4 times as thick as the other Ti_7P_6 hybrid films. The transmittance edge values of the Ti_4P_3 and Ti_7P_6 hybrid films were approximately 315 nm; their values were attributed to the nature of Ti_4P_3 and Ti_7P_6. Although the absorption edge value of Ti_4P_4 is 420 nm [12], the transmittance edge value of the Ti_4P_4 hybrid film was ~350 nm. The absorption of Ti_4P_4 was caused by the ligand-to-metal charge transfer (LMCT) transition between titanium atoms and the acetylacetonato groups [27, 33–35]; many acetylacetonato groups of Ti_4P_4 were obviously dissociated by PBE. The transmittance of the Ti_4P_3, Ti_4P_4, and Ti_7P_6 hybrid films began to decrease at 600, 560, and 540 nm, respectively. One of the reasons for absorption in the visible range is the LMCT transition between the titanium atom and the phenoxy moiety in PBE. Another reason is light scattering due to the aggregation of clusters. To investigate whether visible light absorption is caused by the LMCT transition, PBE–30 wt% cluster hybrid solutions, which were mixed at room temperature for 2 h, were measured by UV–Vis spectroscopy in CH_2Cl_2. However, no absorption band owing to the LMCT transition was observed; the UV–Vis spectra exhibited a mixture of PBE and titanium phosphonate clusters. Moreover, the hybrid solutions were deposited onto silicon wafers by drop-coating followed by curing at 110 °C for 2 min. The coating films were examined by FTIR spectroscopy, but the intensities of ν_{C-O-Ti} were very weak. Furthermore, the PBE–Ti_4P_4 hybrid solution confirmed a strong absorption band owing to the acetylacetonato group. Therefore, the LMCT transition of the hybrid films could not be observed unlike the hybrid solutions because the state of the films and solutions is very different.

The aggregation of clusters in 20 wt% hybrid films was determined by SAXS measurements (see Figure S2). The titanium phosphonate clusters were well dispersed into PBE, but the small aggregation of several molecules was observed. (The sizes of Ti_4P_3, Ti_4P_4, and Ti_7P_6 were 4.8 Å, 5.7 Å, and 9.6 Å, respectively, which were calculated from the single-crystal X-ray structural analysis. Ti_4P_3: CCDC-1487366, Ti_4P_4: CCDC-1561995, Ti_7P_6: CCDC-1553149.) However, large aggregates (<10 nm) were not confirmed; hence, the loss of transmittance observed by UV–Vis spectroscopy was not caused by light scattering.

In our previous study, poly(vinyl alcohol)– and poly(styrene-*co*-allyl alcohol)–Ti_4P_3 hybrids showed high transparency [13, 15]. On the other hand, the poly(vinylphenol)–Ti_4P_3 hybrid was orange red [13] because of the LMCT transition from the phenoxy groups in poly(vinylphenol) to titanium atoms, as in $[Ti(OPh)_4(HOPh)]_2$ [36].

Although the cause of the decreasing transmittance could not be identified, the loss of transmittance may be caused by the presence of a phenoxy moiety in PBE.

Thermal stabilities

Thermal analyses of the hybrid films were performed by TGA under a nitrogen atmosphere. The results for PBE and 30 wt% hybrids in the region of 200–600 °C are shown in Fig. 5, and the temperatures of 5% weight loss (T_{d5}) are summarized in Table 1. For pure PBE, a weight loss of 4.5% appeared at 240–300 °C. This weight loss was assigned to the dehydration of the hydroxyl group, similar to that of poly(vinyl alcohol) [37, 38]. Hybrid films gently decomposed by dehydration at 200–300 °C. The behavior was caused by (i) the decreasing amount of hydroxyl group and (ii) the suppressed mobility of the PBE chain. However, the T_{d5} values of the hybrids were lower than that of pure PBE. This difference is caused by the decomposition of the PBE main chain through the cleavage of the Ti–O–C bond; for example, titanium tetraisopropoxide decomposes while eliminating organic molecules and forming a radical species at higher than 280 °C [39, 40]. Moreover, the thermal degradation of poly(vinyl alcohol) [37] and the photodegradation of PBE [41] were proposed to be owing to to cleavage of the main chain though radical formation. Therefore, we propose that thermal degradation of the PBE hybrids proceeds by (i) aliphatic Ti–O–C bond cleavage to form a radical species and (ii) radical transfer to PBE followed by degradation of the PBE main chain. Hence, hybrids composed of aliphatic Ti–O–C bonds have lower thermal stabilities.

Solvent uptake

The difference in titanium phosphonate clusters was obviously confirmed by the swelling tests of hybrid films, which were carried out during storage in THF at 23 ± 2 °C for 3 days. The solvent uptake after storage in THF is shown in Table 1. The swelling behaviors of the hybrids

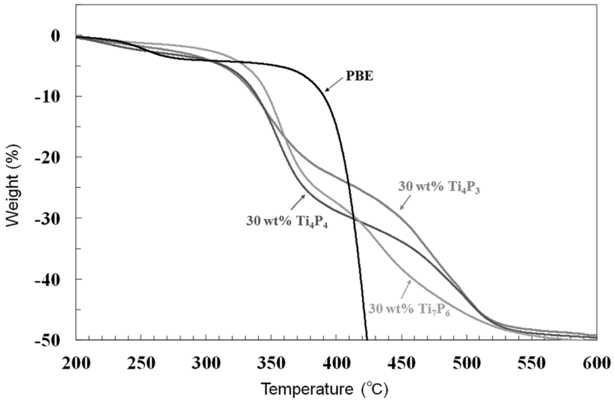


Fig. 5 TGA traces of PBE and PBE–30 wt% clusters under nitrogen atmosphere

depended on the proportion and structures of the clusters, as with cluster–PMMA hybrids such as titanium, zirconium, and tantalum-oxo clusters [3, 42–44]. The solvent uptake of the hybrids decreased in the order of $Ti_7P_6 < Ti_4P_4 < Ti_4P_3$. Because the solvent uptake is strongly dependent on the cross-linking density, Ti_7P_6 was estimated to have the highest cross-linking efficiency.

Conclusion

Organic–inorganic hybrid films were prepared by the transalkoxylation of PBE and titanium phosphonate clusters such as Ti_4P_3, Ti_4P_4, and Ti_7P_6. The hybrid films were characterized by FTIR spectroscopy; the formation of covalent bonds between PBE and the clusters was confirmed by the presence of $\nu_{C–O–Ti}$. Moreover, the acetylacetonato group in Ti_4P_4 dissociated owing to the alcoholysis reaction of PBE. From the SAXS results of the 20 wt% hybrid films, the titanium phosphonate clusters were well dispersed in PBE. Maintaining the structure of the clusters was presumed to be due to the reaction of these clusters with ethyl alcohol or isopropyl alcohol. The influence of the different structures of clusters was estimated by transmittance, thermal stability, and swelling tests in THF. The transmittance of the hybrid films was lower than that of pure PBE. In addition, the T_{d5} values of the hybrid films were lower than that of pure PBE because of the formation of Ti–O–C bonds. Finally, the solvent uptake of the hybrid films clearly differed among the clusters; the solvent uptake of the Ti_7P_6 hybrid film was the lowest of the cluster hybrid films. Therefore, Ti_7P_6 showed the highest cross-linking efficiency.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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