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ORIGINAL CONTRIBUTION

Crystallization of titania ultra-fine particles from peroxotitanic acid in aqueous solution in the present of polymer and incorporation into poly(methyl methacylate) via dispersion in organic solvent

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Abstract We report a novel strategy for incorporation of titanium dioxide (TiO_2) particles, which were crystallized from peroxotitanic acid in the presence of hydrophilic polymer by hydrothermal treatment in aqueous solution, into poly(methyl methacrylate) (PMMA) via dispersion into chloroform. Dispersion of TiO_2 particles into chloroform was achieved by solvent change from water to chloroform in aid of amphiphilic polymer dispersant, poly(*N*-vinyl pyrrolidone) (PVP), poly(*N*-vinyl pyrrolidone-*co*-methyl methacrylate) (PVP-*co*-PMMA), poly(*N*-vinyl pyrrolidone-*block*-methyl methacrylate) (PVP-*b*-PMMA) through azeotropical removal of water. Incorporation of TiO_2 particles into PMMA was carried out by a casting process of a mixture of TiO_2 particles dispersed with PVP_{154}-*b*-$PMMA_{156}$ in chloroform and PMMA on a glass substrate. Resultant hybrid film containing TiO_2 less than 10 wt.% showed high transparency in visible region attributable to homogeneous dispersion into PMMA matrix. The refractive index of the hybrid films increased with TiO_2 content and agreed with the calculated values.

Keywords Titania · Particle · Dispersion · Dispersant · Refractive index

Introduction

Recently, organic–inorganic hybrid material, which are composed of polymer matrix dispersed inorganic particles of the size less than one-tenth of visible light wavelength, has attracted attention as new functional materials in various areas, because of exhibiting improvement of mechanical and physical properties [1]. One of the concerned applications of hybrid composed of fine inorganic particles is fabrication of high refractive optical materials, because it is difficult to prepare materials with the index value higher than 1.7 from polymer. In this sense, so far, there are some reports [2–4] in aims of fabrication of high refractive and transparence organic–inorganic hybrid material, such as an optical waveguide. On the other hand, titanium dioxide, TiO_2, is a stable and nontoxic inorganic compound with relatively high refractive index, 2.74 and 2.54 of respective rutile and anatase. Thus, some approaches of TiO_2/polymer hybrid material syntheses to fabricate high refractive polymer films were reported [5–6]. However, since TiO_2 particles generally tend to aggregate due to high surface energy in organic solvents or polymers. In this respect, so far, there are some reports for dispersion of TiO_2 particles into organic solvent using organic surfactant, dodecylbenzenesulfonic acid [7], dodecylamine [8], oleic acid [9], and stearic acid [10]. Nakayama et al. [11] reported

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dispersion of TiO_2 particles into several organic solvents by two-step chemical modification using a mixture of propionic acid and *n*-hexylamine.

Regarding synthesis of TiO_2 particles in aqueous solution, Chemseddine et al. [12–13] reported highly crystalline anatase TiO_2 particles with different size and shape could be obtained via hydrothermal treatment of titanium alkoxide in the presence of triethylammonium hydroxide. Sugimoto et al. [14–16] reported synthesis of shape-controlled TiO_2 particles from $Ti(OH)_4$ solution which was prepared by mixing titanium isopropoxide with triethanolamine, in the presence of ammonia as shape controller by hydrothermal treatment. In these cases, shape control was proposed by taking place due to adsorption of shape controller onto specific plane of TiO_2 crystal. We previously reported that selective crystallization of TiO_2 particles from peroxotitanic acid in the presence of hydrophilic polymer by hydrothermal treatment in aqueous solution [17]. In this case, TiO_2 particles stably dispersed in aqueous solution due to protective effects of hydrophilic polymer adsorbed on the particle surface. In this paper, we report a strategy for dispersion of TiO_2 particles which were prepared by hydrothermal process in the presence of hydrophilic polymer, into organic solvents in aid of amphiphilic polymer dispersant; poly(*N*-vinyl pyrrolidone) (PVP), poly(*N*-vinyl pyrrolidone-*co*-methyl methacylate) (PVP-*co*-MMA) or poly(*N*-vinyl pyrrolidone-*block*-methyl methacrylate) (PVP-*b*-PMMA), and for preparation of homogeneously TiO_2-dispersed PMMA film. Our final goal is the fabrication of transparence and high refractive materials by hybridization of inorganic fine particles and polymer.

Experimental

Materials

Tetraethylorthotitanate was purchased from Merck, Germany. Polymers, poly(acrylic acid) (PAAc) of number-average molecular weight (M_n) 5,000, poly(vinyl alcohol) (PVA) of M_n 22,000 and poly(ethylene glycol) (PEG) of M_n 4,000, poly(ethyleneimine) (PEI) of M_n 10,000 and other reagents, hydrogen peroxide, ammonium peroxodisulfate (APS), methacrylic acid (MAA), methyl methacrylate (MMA), *N*-vinyl pyrrolidone (VP), benzyl chloride, sodium *N*,*N*-diethyl dithiocarbamate trihydrate and 2,2-azobis (butyronitrile) (AIBN), were obtained from Wako Pure Chemical Industries, Ltd., Japan. Vinyl monomers were purified by distillation under reduced presser before use. Poly(methyl methacrylate) (PMMA) was synthesized by radical polymerization using AIBN in THF; M_n=2,000, M_w/M_n=1.89.

Measurements

Particles size and distribution were determined by a dynamic light scattering (DLS) method on DLS-7000DL, Otsuka Electronics Co., LtSd., Japan, with a He–Ne laser, at a reflection angle of 90°. Number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of polymer were determined by a gel permeation chromatography on straightly connected-columns, PL-gel MIXED-C and PL-gel MIXED-D, Polymer Lab. Co. Ltd., at 60°C using DMF containing 10 mM LiBr as an eluent at flow rate 0.8 mL/min, calibrated with poly(ethylene glycol) standard. ^1H NMR spectra were obtained on Bruker AVNACE 400, Germany. FT-IR spectra were recorded with KBr disk on JEOL JIR-5500, Japan. Thermogravimetric analysis was performed on Shimadzu TG-50, Japan, under nitrogen atmosphere in the range from room temperature to 800°C at rate 10°C/min. Absorption spectra were recorded on JASCO V-520, Japan. Scanning electron microscope (SEM) observation was performed on JEOL JSM 6320F, Japan. Transmission electron microscope (TEM) observation was carried out on Hitachi H-800, Japan, with acceleration voltage of 100 kV. The sample for TEM observation was prepared by evaporating the suspension on a carbon-coated cupper grid. In the case of TiO_2/PMMA hybrid film, the sample was prepared by sliced the film embedded with epoxy resin by a microtome. The refractive index of TiO_2/PMMA hybrid film was determined at 589 nm on NAR-2T, ATAGO Co., Ltd., Japan. X-ray reflection analyses were carried out on JEOL JDX-3500K, Japan.

Determination of crystal morphs fraction

The weight fraction of respective anatase- and rutile-type crystal in TiO_2 particles was determined by the following equation as a function of the strongest reflection, I_A and I_R for anatase (101) and rutile (110) at the Bragg angles 12.68° and 13.73°for CuKα radiation, respectively [18].

$$\text{Fraction of anatase (wt\%)} = 100 \times I_A / (I_A + 1.2651\, I_R) \tag{1}$$

Synthesis of poly(methacrylic acid) (PMA)

A mixture of MAA (5 cm^3, 11.7 mmol) and APS (15 mg, 0.056 mmol) was added into 50 cm^3 distilled water, and then the aqueous solution was heated at 100°C under nitrogen atmosphere for 24 h. The polymer formed was precipitated by addition of 2 N hydrochloride (HCl) from the reaction mixture. After filtration, polymer was dried under reduced pressure; yield 3.89 g, M_n 6,000, M_w/M_n=2.00.

Synthesis of TiO_2 particles in the presence of polymer

A typical run was as follows. To 3 mL tetraethylorthotitanate and 100 mL ethanol was gradually added 3 mL distilled water, and then the mixture was stirred for 30 min at room temperature. Resulting precipitate was centrifugally separated from the solution and dried under reduced pressure. One hundred twenty milligrams of the obtained TiO_2 solution was added to a mixture of 10 mL distilled water and 15 mL 30% hydrogen peroxide and then the solution was sonicated by ultrasonic wave for 1 h to give peroxotitanic acid solution. Fifty milligrams PAAc was added to the peroxotitanic acid solution and then stirred at 60°C for 48 h; eventually, the solution was heated in an autoclave at 200°C for 5 h.

Synthesis of PVP

Fifteen milligrams (91.3 μmol) AIBN, 3 mL (28.2 mmol) VP and 3 mL ethanol were put into a 50 mL flask, and the mixture heated at 70°C under nitrogen atmosphere for 24 h. The resulting mixture was dissolved in 5 mL of tetrahydrofuran. The polymer formed was precipitated with 200 mL diethyl ether and then dried under vacuum at 60°C for 24 h; yield 2.75 g, M_n 4,000, M_w/M_n=1.93.

Synthesis of Poly(VP-*co*-MMA)

Copolymerization of VP with MMA was carried out by the same procedure described above.

Synthesis of benzyl *N*,*N*-diethyl dithiocarbamate (BDDC)

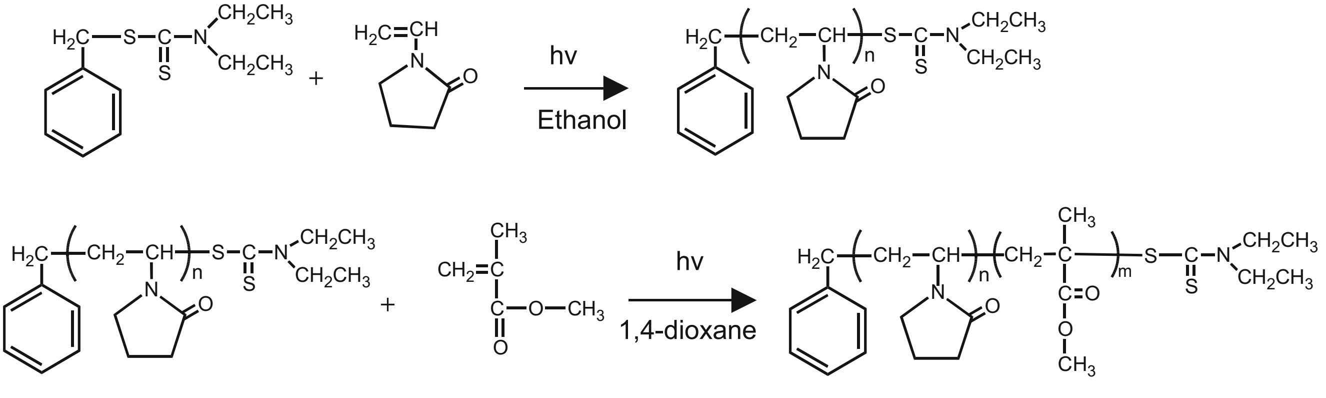
To 30 mL ethanol solution, in which 5.21 g (23.1 mmol) sodium *N*,*N*-diethyl dithiocarbamate trihydrate was dissolved, 2 mL (17.4 mmol) benzyl chloride was slowly added at 0°C, and then the mixture was stirred for 12 h at room temperature. The resulting mixture was filtrated to remove the inorganic precipitate. After evaporation of ethanol and addition of 40 mL distilled water, yellow product was extracted with 20 mL diethyl ether three times. The organic phase was dried on anhydrous sodium sulfate and evaporation of diethyl ether afforded the product. Yield: 3.75 g (90%), ^1H NMR ($CDCl_3$, 400 MHz); δ: 1.28 (q, 6H, $N(CH_2CH_3)_2$), 3.72 (q, 2H, $N(CH_2CH_3)_2$), 4.05 (q, 2H, $N(CH_2CH_3)_2$), 4.53 (s, 2H, CH_2Ph), 7.2–7.5 (m, 5H, Ph) ppm.

Synthesis of PVP-*b*-PMMA via a photo iniferter

A typical run was as follows: to a test tube was added 30 mg (0.125 mmol) BDDC, 3 mL (28.2 mmol) VP, and 3 mL ethanol. The reaction mixture was purged with high-grade nitrogen for 1 h to remove traces of oxygen and then was carefully degassed by three freeze–pump–thaw cycles. Finally, the test tube was sealed off under reduced pressure and irradiated for 5 h employing a high pressure mercury lamp. Resulting polymer was precipitated with diethyl ether and dried at 50°C under vacuum; yield: 1.92 g (68%), M_n: 16,700, M_w/M_n: 1.16. Two grams of PVP iniferter, 3 mL (28.2 mmol) MMA and 5 mL 1,4-dioxane was added to a test tube and then the polymerization was carried out as described above. Resulting polymer was precipitated with diethyl ether and then dried at 50°C under vacuum for 24 h; yield: 4.32 g, M_n: 32,000, M_w/M_n: 1.58. ^1H NMR (D_2O) for PVP; δ: 1.28 (m, $N(CH_2CH_3)_2$), 3.25 (m, $N\text{-}CH_2$), 7.2–7.5 (m, Ph) ppm. ^1H NMR ($CHCl_3$, 400 MHz) for VP and MMA block polymer; δ: 1.28 (m, $N(CH_2CH_3)_2$), 3.25 (m, $N\text{-}CH_2$), 3.67 (m, OCH_3), 7.2–7.5 (m, Ph) ppm. Molar fractions of MMA block in the block copolymer were determined by ^1H NMR spectroscopy (Scheme 1).

Solvent exchange of aqueous TiO_2 suspension with chloroform

A typical run was as follows. Ten milliliters of TiO_2 particles suspension was slowly added to the 100 mL of the mixture of ethanol and acetonitrile (1:1 vol.) containing100 mg PVP.



Scheme 1 The procedure for the synthesis of block copolymer via photo iniferter

Table 1 Crystal structure and size of TiO_2 particles synthesized with water-soluble polymer

Polymer	M_n	Polymer addition/mg	Fraction/wt.% anatase: rutile	Particles size/nm
–	–	–	20:80	200–300[a]
PMA	6,000	25	60:40	50±5[b]
		50	100:0	50±5[b]
PAAc	5,000	25	100:0	20±5[b]
		50	100:0	20±5[b]
PVA	22,000	50	100:0	50±10[b]
PEG	5,000	25	5:95	100–200[a]
		100	0:100	
PEI	10,000	100	10:90	100–200[a]

[a] Determined by TEM

[b] Determined by DLS

Resulting solution was stirred at room temperature for 1 h, and then sonicated for 1 h. The solution was concentrated by evaporation of ethanol and water as azeotrope to give 20 mL suspension, and then TiO_2 particles were collected by centrifugation. Resulting wet TiO_2 particles was put into 40 mL chloroform and the solution was sonicated to be dispersed.

Preparation of TiO_2/PMMA hybrid film

The required amount of chloroform suspension of TiO_2 particle were put into 2 ml of PMMA chloroform solution containing 30 mg PMMA (1.0 wt.%). After sonication for 1 h, the mixture was put into a glass Petri dish of 5 cm in diameter. Drying up at room temperature and followed by heating at 100°C for 30 min gave the film. The weight fraction of TiO_2 in the hybrid film was evaluated by weight reduction during elevating temperature from 200°C to 800°C by thermogravimetric analysis.

Table 2 Effects of pH of peroxotitanic acid solution on crystal structure and particle size

Polymer	The amount of doped polymer (mg)	pH of solution	Fraction wt.% anatase:rutile	Particle size[a] (nm)
PAAc	25	1.5	100:0	20±5
	25	4.0	100:0	20±5
	25	7.5	100:0	20±5
	25	9.0	100:0	20±5
	25	10.5	100:0	20±5

[a] Determined by DLS

Results and discussion

Effects of polymer addition on TiO_2 crystallization

As reported previously [17], additives of hydrophilic polymer in crystallization of TiO_2 from peroxotitanic acid affected crystal morphs and particle shape. In Table 1, polymer additive effects on crystallization of TiO_2 were summarized. The hydrothermal treatment of peroxotitanic acid solution without polymer afforded a mixture of anatase and rutile-type particles in the weight ratio of 20/80. Addition of hydrophilic polymer, such as PMAA, PAAc and PVA with carboxylic acid or hydrophilic acid on the side chain to the reaction mixture led to formation of anatase-rich TiO_2 particles, while PEG and PEI gave rutile-

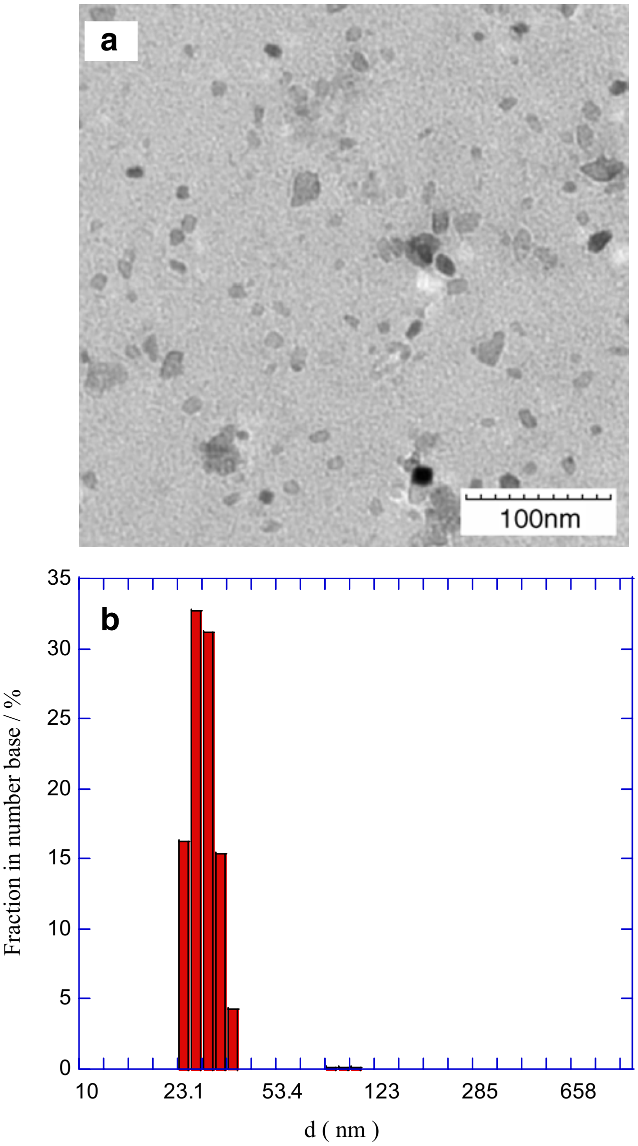
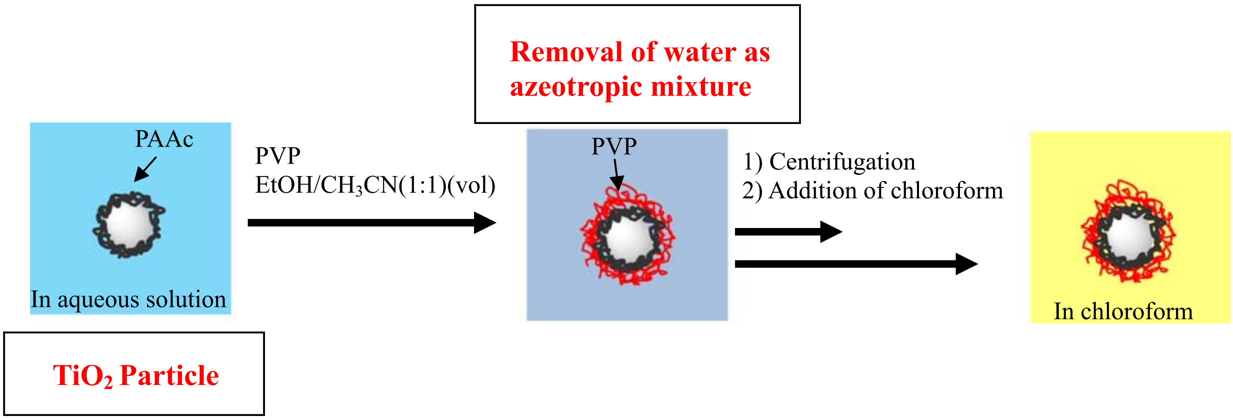


Fig. 1 TEM image (**a**) and particle size distribution of TiO_2 particle synthesized with PAAc at pH 10.5 in the aqueous solution (**b**)



Scheme 2 The procedure for the dispersion of TiO_2 particles into chloroform

rich particles. In most cases, increase of polymer addition resulted in completely controlled crystallization. Therefore, these results suggest that coordination of carboxylic or hydroxyl group to peroxotitanic or titanic acid play an important role in the stage of crystalline nucleation during dehydration or deoxygenation of peroxotitanic acid. However, detail mechanism of controlled crystallization is still unclear. On the other hand, addition of PEG to the reaction system gave TiO_2 particles of around 200 nm, while PAAc, PMA, and PVA addition resulted in formation of the particles around 20 nm. Thus, carboxyl and hydroxyl groups are certainly favorable for preventing from aggregation between the particles during crystallization. The initial pH of peroxotitanic acid formed by the reaction of TiO_2 sol with H_2O_2 was around 1.5. Sugimoto et al. [19] reported that crystallization of TiO_2 from titanium isopropoxide in the presence of amino acid or aliphatic carboxylic acid depended on pH of the starting solution. Therefore, we investigated effects of pH on crystallization of TiO_2 particles in the presence of PAAc. The pH of peroxotitanic acid solution was adjusted with NH_4OH aqueous solution in the range of pH from 1.5 to 10.5. The results are listed in Table 2. TiO_2 particles formed in this pH range were anatase-type. However, it was observed that fraction of small size particles around 20 nm increased with elevating pH of the starting solution. Eventually, TiO_2 particles formed at pH 10.5 were stably suspended for a long time. A TEM image and particle size distribution of TiO_2 particles formed at pH 10.5 was shown in Fig. 1(a) and (b), respectively.

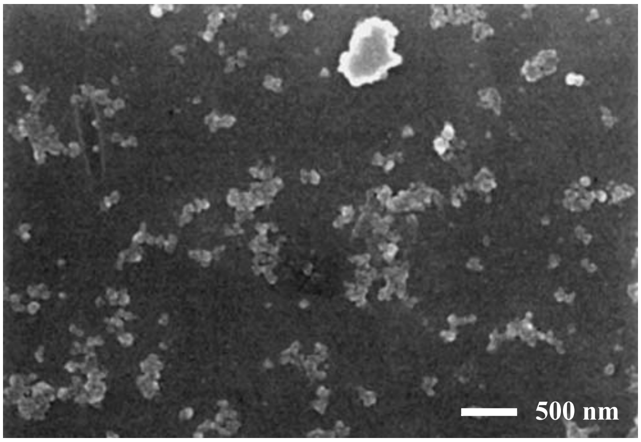


Fig. 2 SEM image of PMMA film containing PVP-modified TiO_2 with 1.0 wt.% TiO_2 on the glass substrate

Dispersion of TiO_2 particles into chloroform

In the present crystallization, TiO_2 particles are formed in aqueous solution, so that it is so difficult to supply them directly to fabrication of functional materials. Thus, we examined dispersion of TiO_2 particles into chloroform using amphiphilic polymer, PVP, as a polymer dispersant via solvent exchange. Solvent exchange process of TiO_2 particles formed in the presence of PAAc at pH of 10.5 using the dispersant is shown in Scheme 2. A key point of the exchange process is removal of water from the TiO_2 aqueous suspension through azeotropical evaporation, and outline of the procedure is as follows. After addition of PVP ethanol/acetonitrile solution to aqueous TiO_2 suspen-

Table 3 Effect of copolymer addition on particle size in chloroform solution

	Fraction of copolymer (VP/MMA)	M_n	M_w/M_n	Particle size[a] (nm)
PVP		4,000	1.93	20±5
Poly(VP-*co*-MMA)	1/18	5,500	2.10	300±10
	1/11	7,000	1.87	130±15
	1/5	4,600	1.95	80±10
	1/3	4,000	1.78	40±10
	1/1	5,000	1.89	20±5

[a] Determined by DLS

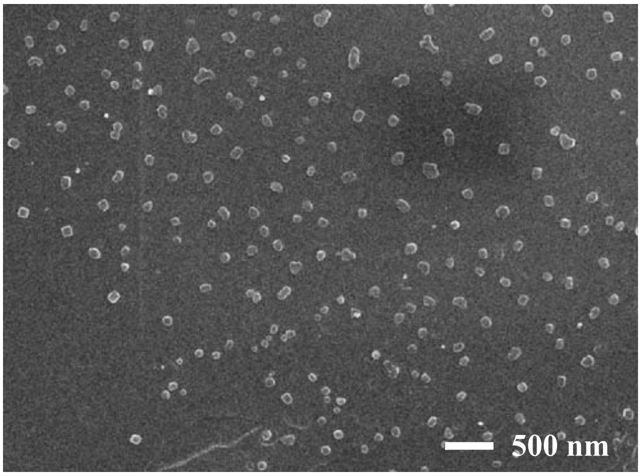


Fig. 3 SEM image of PMMA film containing poly(VP-*co*-MMA), of VP/MMA ratio 1/1, -modified TiO_2 with 1.0 wt.% TiO_2 on the glass substrate

sion, the mixture was heated to evaporate water as an azeotropic mixture with ethanol. Following addition of chloroform to the solution made the TiO_2 particles dispersed in chloroform. An FT-IR spectrum of dried particles obtained by evaporation of chloroform from the suspension showed the absorption peak around 1,650 cm^{-1}, which was assignable to amide carbonyl group of PVP. These results suggested that PVP was absorbed on the surface by the strong interaction between the amide carbonyl and hydroxyl groups onTiO_2. Therefore, the strong adsorption and consequent protecting colloidal effects of adsorbed PVP possibly prevented from aggregation of the particles in chloroform.

Incorporation of TiO_2 particles into PMMA film

PMMA films containing TiO_2 particles were prepared by a spin coating of mixture of PVP-adsorbed TiO_2 chloroform suspension and PMMA on glass substrate. A typical SEM image of PMMA film composed of 1.0 wt.% TiO_2 are shown in Fig. 2. In the film, TiO_2 particles of more than 100 nm size were observed. This result indicated the particles were aggregated during the drying process due to low affinity between PVP and PMMA. In this case, therefore, an affinity between PVP adsorbed on TiO_2 surface and PMMA matrix was an important factor to prevent from aggregation of TiO_2 particles. In order to enhance the affinity between dispersant polymer and PMMA, preparation of TiO_2-dispersed PMMA films was examined by using dispersant copolymer of VP and MMA, VP/MMA mole ratio of which was in the range from the 1/18 to 1/1. In this copolymer synthesis, unfortunately, it was impossible to synthesize copolymers of high PV fraction more than 50 mol% by radical polymerization, because of low copolymerization reactivity between PV and MMA. Particles size of TiO_2 particles dispersed in chloroform using poly(VP-*co*-MMA) dispersant decreased with increasing of VP fraction in copolymer and attained 20 nm when the copolymer of VP/MMA mole ratio 1/1 was employed (Table 3). These results suggested that adsorption of VP moiety on TiO_2 particles plays an important role for dispersion of the particles in low polar solvent without aggregation. However, incorporation of TiO_2 into PMMA

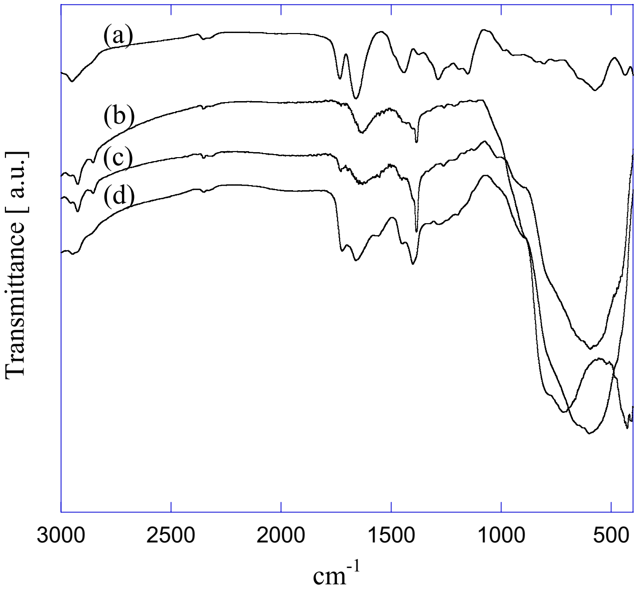


Fig. 4 FT-IR spectra of PVP_{154}-*b*-$PMMA_{156}$ block copolymer (**a**), TiO_2 particle synthesized without polymer (**b**), TiO_2 particles synthesized in the presence of PAAc (**c**), TiO_2 particles dispersed in chloroform using block copolymer (**d**). All spectra were taken after drying under reduced pressure

Table 4 Characterization of block copolymer and effect of polymer addition on particle size in chloroform solution

	PVP /g mol^{-1}	M_w/M_n of PVP	PMMA /g mol^{-1}	M_w/M_n of block copolymer	Particle size [a]/nm
PVP_{24}-*b*-$PMMA_{28}$	2,700	1.32	2,800	1.48	80±15
PVP_{52}-*b*-$PMMA_{56}$	5,800	1.26	5,600	1.45	20±5
PVP_{102}-*b*-$PMMA_{107}$	11,700	1.23	10,700	1.67	20±5
PVP_{154}-*b*-$PMMA_{156}$	17,200	1.16	15,600	1.58	20±5

[a] Determined by DLS

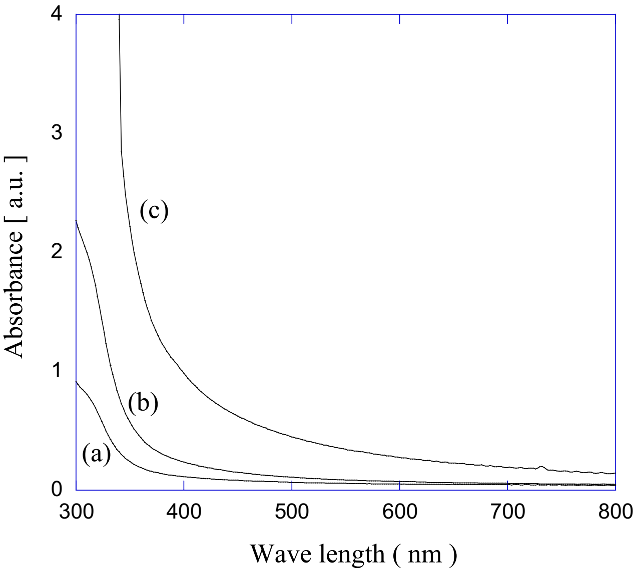


Fig. 5 UV–vis spectra of TiO_2/PMMA film (**a**) 2.0 wt.%, (**b**) 5.0 wt.%, (**c**) 10.0 wt.%

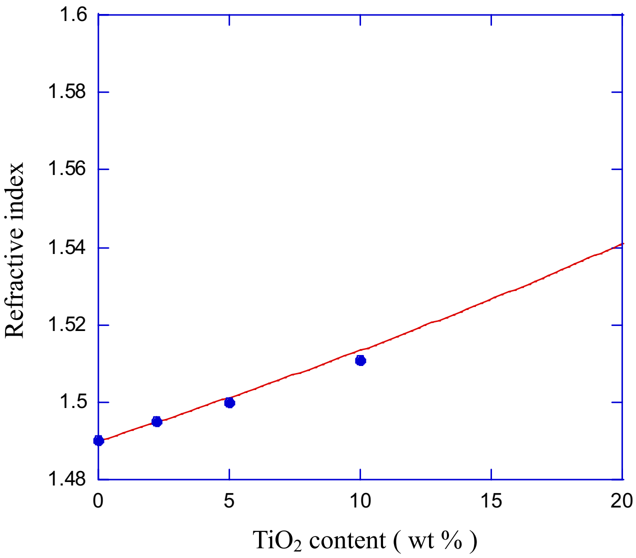


Fig. 7 Plots of TiO_2 content vs. refractive index of hybrid film prepared using PVP_{154}-*b*-$PMMA_{156}$: *solid line* represents calculated values

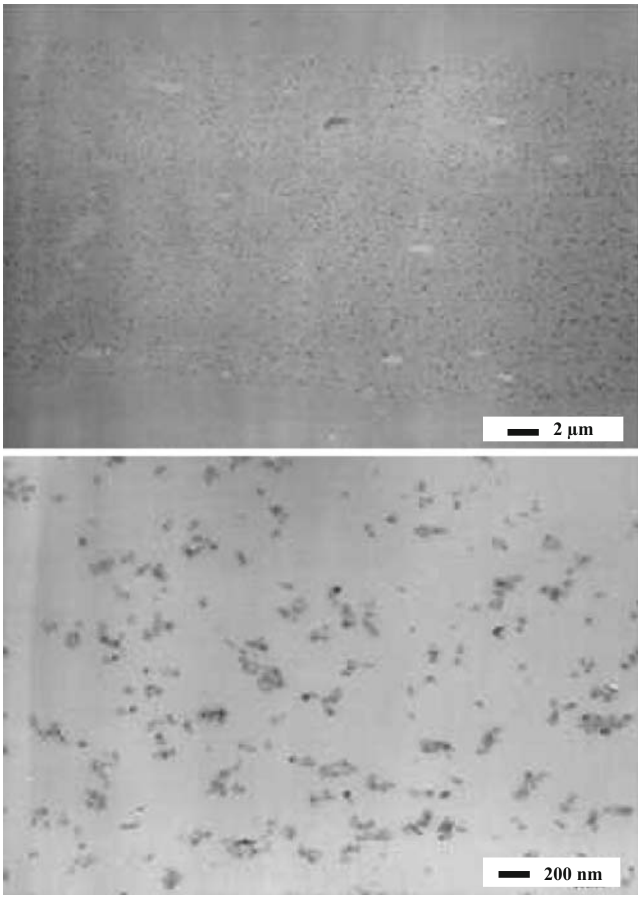


Fig. 6 Cross-sectional TEM image of PMMA film containing PVP_{154}-*b*-$PMMA_{156}$ block copolymer-modified TiO_2 with 10.0 wt.% of TiO_2

using the chloroform suspension, prepared by employing poly(VP-*co*-MMA), of VP/MMA mole ratio 1/1, gave the film composed of TiO_2 particles of around 80 nm size (Fig. 3). Probably, the aggregation of TiO_2 particles during PMMA film processing comes from low MMA mole faction in copolymer dispersant. Therefore, the chemical composition, which is mole ratio of VP to MMA in the present case, is significant to keep dispersion of TiO_2 particles in chloroform and PMMA film. In these polymers, the PVP moiety played a role as an adsorption unit on TiO_2 particles, while the PMMA layer brought about affinity with PMMA matrices. Therefore, it was expected that employing block polymer dispersant of VP and MMA gave rise to effective dispersion of TiO_2 not only in chloroform, but also in PMMA film.

In the present study, block copolymers of VP/MMA mole ratio 1/1, shown in Table 4, were examined for dispersion of TiO_2 in chloroform and incorporation into PMMA matrix. In the case of PVP_{24}-*b*-$PMMA_{28}$ addition, it was observed that addition of the polymer dispersant gave rise to aggregation of TiO_2 particles due to shorting of PMMA moiety. In addition of block copolymer of higher molecular weight than PVP_{24}-*b*-$PMMA_{28}$, TiO_2 particles were dispersed into chloroform without aggregation after solvent exchanging. Adsorption of the block polymer on TiO_2 particles after solvent exchanging was confirmed by appearance adsorption bands at 1,650 cm^{-1} assigned to amide carbonyl group of PVP moiety on IR spectra (Fig. 4). Incorporation of TiO_2 particle into PMMA film, around 60 µm in thickness, was carried out using TiO_2 particles dispersed in chloroform employing PVP_{154}-*b*-$PMMA_{156}$.

The resulting PMMA thin film exhibited a high transparency up to less than TiO_2 concentration of 10 wt.%. As shown in Fig. 5, however, UV–vis spectra indicated that absorbance in the visible light region increased with TiO_2 content from 2.0 to 10 wt.%, probably being due to light scattering on aggregated TiO_2 particles in the polymer matrices. In the TEM image of cross section of the film (Fig. 6), it was observed that TiO_2 particles were homogeneously dispersed in PMMA matrix, but some clusters around 100 nm were formed. The formation of the cluster probably led to increasing absorbance in visible region. However, the refractive index of PMMA hybrid film proportionally increased with TiO_2 content, and agreed with calculated values, as shown in Fig. 7. The values were calculated by following Lorentz–Lorenz equation [20];

$$\left(n^2-1\right)\Big/\left(n^2+2\right)=\sum v_i\left(n_i^2-1\right)/\left(n_i^2+2\right) \qquad (2)$$

where n is refractive index of hybrid film, v_i and n_i are volume fraction and refractive index of component i, respectively. In this case, refractive indexes of anatase TiO_2 and PMMA were employed following values of n= 2.52 and n=1.49, respectively. Therefore, it was shown that the refractive indexes of the hybrid film were independent upon formation of TiO_2 cluster less than around 100 nm. Consequently, in order to achieve high transparency of the hybrid film at visible light region, extremely high dispersion of TiO_2 nanoparticles, less than 20 nm in PMMA films should be attained. The effective dispersion of the particles in organic media is now in progress.

Conclusions

TiO_2 particles with diameter of 20 nm were synthesized from peroxotitanic acid in the presence of hydrophilic acid. Synthesis of TiO_2 particles in the presence of PAAc addition at high pH value gave stable aqueous suspension. The presence of hydrophilic polymer during crystallization of TiO_2 from peroxotitanic acid resulted in complete control of TiO_2 crystal morphs. Well-dispersed TiO_2 particles in chloroform were obtained by addition of amphiphilic polymer, PVP, poly(VP-*co*-MMA), or VP-MMA block copolymer as a dispersant. PVP_{154}-$PMMA_{156}$ dispersant addition led to high dispersion of TiO_2 particles of 20 nm in chloroform and effective incorporation into PMMA matrix to give high transparent films. The refractive index of the hybrid films proportionally increased with TiO_2 content less than 10 wt.%.

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