PREPARATION OF TIO$_2$ NANOPARTICLES IN WATER-IN-CO$_2$ MICROEMULSIONS

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Absrtact: Titanium dioxide nanoparticles were produced by the controlled hydrolysis of titanium tetraisopropoxide (TTIP) in water-in-CO$_2$ (w/c) microemulsions stabilized with the surfactants ammonium carboxylate perfluoropolyether (PFPECOO$^-$NH$_4$) (Mw = 587), poly (ethylene oxide-*block*- 1H,1H perfluorooctyl methacrylate) (PEO$_{2K}$-*b*-PDHFOMA$_{13K}$), and poly (dimethyl amino ethyl methacrylate-*block*-1H,1H,2H,2H perfluorooctyl methacrylate) (PDMAEMA$_{1.4K}$-*b*-PTHFOMA$_{12K}$). Particle formation and aggregation have been investigated by dynamic light scattering. The crystallite structure after calcinations was examined by XRD and transmission electron microscopy. The crystallite size could be controlled by the water-to-surfactant molar ratio, w$_o$ which influences the hydrolysis rate, droplet size and intermicellar interactions. For the hydrolysis of TTIP in the w/c microemulsion (w$_o$ = 5) stabilized with PFPECOO$^-$NH$_4$ and PDMAEMA$_{1.4K}$-*b*-PTHFOMA$_{12K}$, the particles formed were stable and optically transparent for 24 h. In contrast, the particle aggregations were unstable by PEO$_{2K}$-*b*-PDHFOMA$_{13K}$ at the same condition, eventually leads to precipitates.

Introduction

There has been much interest both in nanometer sized particles and in procedures to prepare and stabilize uniform nanoparticles. Microemulsions provide a microheterogeneous medium for the generation of nanoparticles. The formation of particles in such systems is controlled by the reactant distribution in the droplets and by the dynamics of interdroplet exchange. The surfactant stabilized microcavities provide a cage-like effect that limits particle nucleation, growth and agglomeration.[1,2] Recently, water-in-oil (w/o) microemulsions have been utilized as templates to prepare TiO$_2$ nanoparticles,[3] which have attracted much attention as photocatalysts. The challenge has been to suppress uncontrolled particle aggregation in order to produce stable nanosized TiO$_2$ from titanium alkoxide which has very high reactivity toward water.[4-6] Previously, we reported briefly the use of w/c microemulsions to achieve particle size control for nanosized titanium dioxide.[7]

Carbon dioxide is an attractive alternative to organic solvents because it is nontoxic,

nonflammable, highly volatile, inexpensive, and environmentally benign. Water-in-CO_2 (w/c) microemulsions have been formed with specially designed surfactants containing 'CO$_2$-philic' fluorocarbon moiety.[8-11] In common with many w/o microemulsions, certain water-in-CO_2 (w/c) microemulsions exhibited a spherical droplet structure for which the droplet radius was directly proportional to the water-surfactant ratio, w_o.[9,10] Moreover they served as effective reaction vessels for inorganic,[11,12] organic,[13] and enzymatic reactions.[14] The objective of this work is to investigate the controlled formation of TiO_2 nanoparticles from direct reaction of titanium tetraisopropoxide (TTIP) with water solubilized in w/c microemulsions stabilized by low molecular weight and polymeric surfactants.

Experimental Section

Materials

THF was distilled from sodium naphthalide under reduced pressure prior to use. Methyl trimethylsilyl dimethylketene acetal (Aldrich) was purified by distillation at reduced pressure. 2-bromopropionyl chloride (BPC) (Aldrich) was distilled under vacuum. 2-(dimethylamino) ethyl methacrylate (DMAEMA) was distilled over CaH_2 prior to used. 1H,1H-perfluorooctyl methacrylate (DHFOMA) (SynQuest) and 1H,1H,2H,2H perfluorooctyl methacrylate (THFOMA) (SynQuest) were passed through a neutral alumina column to remove the inhibitor and then vacuum distilled. Methoxy polyethylene glycol 2000 (MPEO-OH, Sigma) was dried by azeotropic distillation with toluene. Trifluorotoluene (TFT) and benzene were distilled over CaH_2. Copper (I) Chloride (99.999 + %, Aldrich), 2,2'-bipyridine (bipy) (Aldrich), 1,1,2-trichlorotrifluoroethane (F-113) (Aldrich), ether, and chloroform were used as received. PEG macroinitiator (MPEG-Br) was prepared by condensation reaction between MPEO-OH and BPC[15].
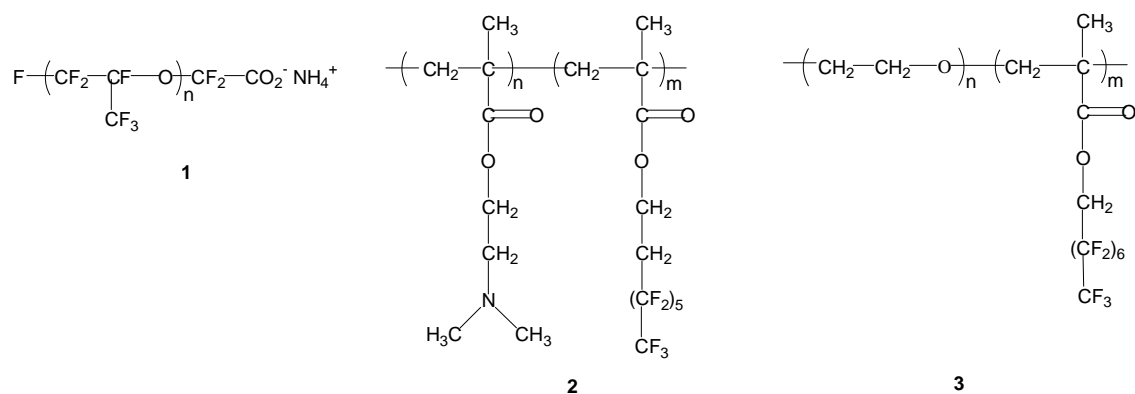

Figure 1. Structures of surfactants for w/c microemulsions

The structures of surfactants used in this work are shown in Figure 1. PFPECOO^{-+}NH$_4$ (M$_w$ = 587) (**1** in Figure 1) was prepared by neutralizing PFPE-COOH with NH$_4$OH.

Synthesis of PDMAEMA-*b*-PTHFOMA

PDMAEMA$_{1.4K}$-*b*-PTHFOMA$_{12K}$ (**2** in Figure 1) was prepared by sequential addition of DMAEMA and THFOMA via group transfer polymerization (GTP) according to previously reported[7].

Synthesis of PEG-*b*-PDHFOMA

PEG$_{2K}$-*b*-PDHFOMA$_{13K}$ (**3** in Figure 1) was synthesized in the mixed solvent of TFT and benzene by atom transfer radical polymerization of DHFOMA using MPEG-Br as macroinitiator[15].

Preparation of nanosized TiO$_2$

A variable volume view cell was used as a reaction vessel to prepare TiO$_2$ particles. CO$_2$ pressure was controlled using ISCO syringe pump. A surfactant was placed in the cell, followed by the addition of water to achieve the desired water-to-surfactant ratio (w$_o$). The cell was immersed in water bath and the temperature of cell was controlled precisely. The cell was loaded with carbon dioxide at 25 °C and the pressure was raised up to 3000 psi. The w/c microemulsions were prepared after continuous stirring of 30 min. An adequate amount of titanium tetraisopropoxide(TTIP) was slowly added to the cell at rate of 5 μL/min, and then the pressure was controlled to 4000 psi. After 24 h of stirring of reaction mixture, CO$_2$ was vented, and the product was collected. The prepared nanoparticles were washed with ethanol, dried at 105 °C for 1 day, and calcined at 500 °C for 3h.

Measurements

The size of microemulsions and TiO$_2$ particles in CO$_2$ were measured with dynamic light scattering (DLS) connected to the high pressure view cell reactor. A stainless steel light scattering cell with Fe$_3$O$_4$ surface (black oxide, Austex) was equipped with a pair of parallel flat circular sapphire windows. The light source was a He-Ne laser with a wavelength of 632.8 nm, and the scattered light was detected utilizing an optical fiber (NSG America, single mode, specified wavelength of 630 nm) with an avalanche photodiode (Brookhaven). The data were analyzed by using a digital autocorrelator (Brookhaven, model BI-9000AT) with 522 real time channels and the non-negative least squares (NNLS) program.

The major phase of the particles was analyzed by X-ray diffraction (Rigaku D/MAXIIC)

using Cu Kαradiation. Crystallite size of the prepared particles was determined from the broadening of the anatase main peak at $2? = 25.3^{\circ}$ by Schrerrer equation[18].

The particle size and external morphology were observed on scanning electron microscopy (SEM, HITACHM, S-2400) and transmission electron microscopy (TEM, JEOL, JEM-2020) of 200 kV accelerating voltage. The particles calcined at 500 °C were dispersed in ethyl alcohol and then sonicated to separate out individual particles.

Results and Discussion

Particle Formation

For $PDMAEMA_{1.4K}$-b-$PFOMA_{12K}$, a stable single-phase w/c microemulsions were made after stirring the mixture of water and surfactant in CO_2 for 30 min. For $PFPECOO^{-+}NH_4$, only part of the water was emulsified for the higher w_o values based on phase behavior measurements performed with a variable-volume view cell, which is described elsewhere.[14] Thus the experiment was conducted with relatively low w_o since high w_o produces stronger interdroplet interactions for the microemulsion resulting in particle flocculation.[19] Table 1 summarizes the results of particle formation with different w_o values. In the case of W/C microemulsions formed with $PDMAEMA_{1.4K}$-b-$PFOMA_{12K}$ and PEG_{2K}-b-$PDHFOMA_{13K}$, w_o represents the molar ratio of water to each DMAEMA and EO unit in the PDMAEMA block ($[H_2O]$ / $[DMAEMA]$) and PEO block ($[H_2O]$ / $[EO]$), respectively since the water only associates with the polar groups of the polymer. For the hydrolysis of TTIP in the w/c microemulsion stabilized with $PFPECOO^{-+}NH_4$, microemulsions with 0.36 wt% surfactant ($w_o = 5$) and 0.90 wt% ($w_o = 2$) were transparent and lightly yellowish even after the injection of TTIP. When the reactant ratio, R ($[H_2O]/[TTIP]$) and w_o were fixed at 4 and 5 respectively, the surfactant could stabilize particles up to the TTIP concentration of 30 mM, i.e., clear microemulsions with 1.5 wt% surfactant and 0.23 wt% water became orangish-translucent after the precursor was injected. Compared to previous result[7], slow TTIP injection rate seems to play a certain role in the formation of particles, stabilzation, and their flocculation behavior. For polymeric surfactant of $PDMAEMA_{1.4K}$-b-$PFOMA_{12K}$, transparent microemulsions (0.95 wt% surfactant for $w_o = 5$, 2.37 wt% for $w_o = 2$) turned lightly orangish upon the injection of TTIP. With an increased amount of water ($w_o = 10$), the solution became dark orangish, yet translucent, upon the injection of precursor. The precursor concentration was also increased for the latter case to keep R fixed at 4. No precipitation was observed for more than 5 days. The greater stability and reduction in particle aggregation for $PDMAEMA_{1.4K}$-b-$PFOMA_{12K}$ at higher w_o result in part from stronger steric stabilization due to longer PFOMA tails. Furthermore, the greater solvation of PFOMA vs. PFPE by CO_2[8] produces weaker intermicellar interactions.[19]

In contrast, the TiO_2 particles produced by PEG_{2K}-b-$PDHFOMA_{13K}$ were much less stable.

A concentration of 1 wt% surfactant did not completely dissolve in CO_2 presumably due to the

Table 1. Nanosized TiO_2 powders[a] from hydrolysis of TTIP in W/C microemulsions stabilized by different surfactants

	Concentration				Observation after TTIP injection[b]	Size by DLS (nm)	
	[TTIP] (mM)	w_o	Surfactant wt%	Water wt%		Micro-emulsions	Particle
PDMAEMA$_{1.4K}$-b-PFOMA$_{12K}$	7.2	2	2.37	0.055	Yellowish (tp)	6.3, 21.5	7.7, 33.3
		5	0.95	0.055	Yellowish (tp)	6.9, 25.7	9.9, 44.6
	14.4	10	0.95	0.11	Orangish (tp)	Not conducted	
PEO$_{2K}$-*b*-PFOMA$_{13K}$	-	2	1.00	0.11	-	Not conducted	
	7.2	2	0.50	0.055	Dark orangish (tl)	28.1	34.3
	14.4	5	0.40	0.11	Cloudy	Not conducted	
PFPECOO$^-$ $^+$NH$_4$	7.2	2	0.90	0.055	Lightly yellowish (tp)	3.3, 24.3	3.4, 36.2
		5	0.36	0.055	Yellowish (tp)	3.8, 36.6	3.5, 36.2
	30	5	1.50	0.23	Dark orangish (tl)	Not conducted	

[a] R = 4, 4000 psi, 25 °C   [b] tp: transparent, tl: translucent

low temperature, 25 °C. PEO-type surfactants often require higher temperature to form microemulsions in CO_2. Microemulsion with 0.40 wt% surfactant for w_o = 5 took dark orangish tint, and turned cloudy after the precursor was injected. Precipitate was observed in 6 hrs while the upper CO_2 phase remained hazy for more than 5 days. Thus, DLS could not be conducted with w_o = 5. With a reduced amount of water w_o = 2, a clear microemulsion was formed. The solution became dark orangish after the precursor was injected.

Dynamic Light Scattering (DLS)

The sizes of the particles and their distribution have been measured by on-line DLS. The data in Table 1 indicate that two populations of aggregates coexist typically in this reaction condition except for PEG$_{2K}$-*b*-PDHFOMA$_{13K}$. The small micelles were dominant over larger aggregates, which increased slightly upon adding TTIP. The size of microemulsions with PFPECOO$^+$NH$_4$ (w_o = 5) was measured to be 3.8 nm which is comparable to the value in previous report. The radius of water core of w/c microemulsions stabilized by PFPECOO$^+$NH$_4$

([PFPE] = 2.1 wt%, w_o = 11) at 35 ^{o}C was measured to be 2.0 nm by small angle neutron scattering.[10]

For PDMAEMA$_{1.4K}$-b-PFOMA$_{12K}$, the particles were collected after venting CO_2 and redispersed in CO_2 at 4000 psi. The sizes of redispersed particles were well correspond to the particles as prepared. Thus it is evidenced that the surfactant prevents aggregation after hydrolysis and stabilizes particles effectively.

Crystal Structure and Morphology

XRD measurement showed that as prepared particles were amorphous, while the particles calcined at 500 ^{o}C for 3 hrs were in the anatase form as depicted in Figure 2.
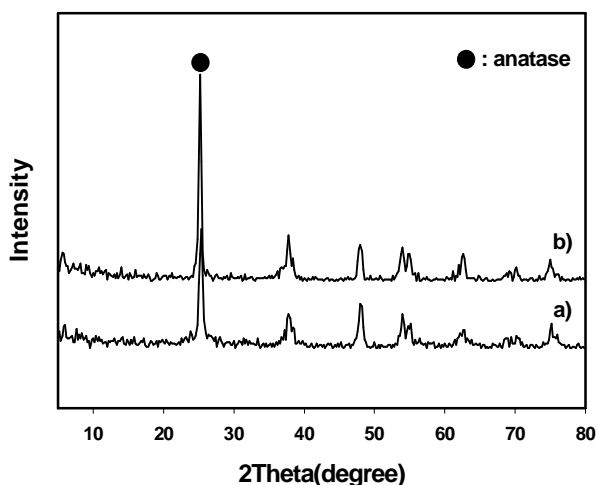

Figure 2. XRD patterns of nanosized TiO_2 powders prepared by different surfactants: a) PFPECOO$^-$NH$_4$ and b) PDMAEMA$_{1.4K}$-b-PFOMA$_{12K}$, calcination temperature; 500 °C

TEM was used to investigate the exact microstructure of the particles as shown in Figure 3. The uniform 12 nm particles in the TEM photograph of the sample made by PFPECOO$^-$NH$_4$ are highly aggregated, while the particles produced by PDMAEMA$_{1.4K}$-b-PFOMA$_{12K}$ are average size of 9 nm and less aggregated. It is likely that the particles flocculated during the depressurization, but they could not be separated completely in ethanol after calcination. Moreover, the extent of flocculation appears stronger for PFPECOO$^-$NH$_4$ than PDMAEMA$_{1.4K}$-b-PFOMA$_{12K}$. In the case of PEG$_{2K}$-b-PDHFOMA$_{13K}$, highly polydisperse particles are observed. (Figure 3C)   The formation of a big crystallite is possibly related to the fact that the water is likely dispersed throughout the PEO chains rather than in a water pool at the center of the micelle-like structure, which is currently investigated. It is noted that the average diameters of TiO_2 particles after calcination are larger than the core size of microemulsions, especially for PFPECOO$^-$NH$_4$. The increase of size is most likely due to the grain growth during the
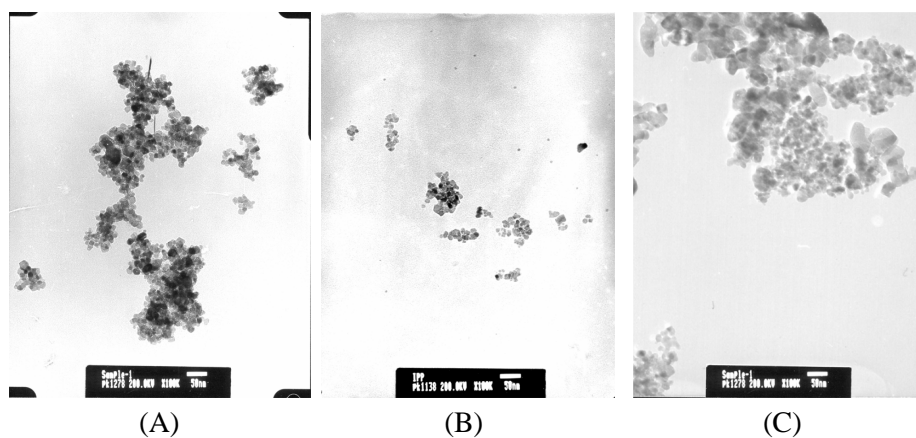
calcination at high temperature.[20]

(A)   (B)   (C)

Figure 3. TEM micrographs of TiO_2 particles obtained by hydrolysis of TTIP in w/c microemulsion stabilized by (A); $PFPECOO^+NH_4$, (B); $PDMAEMA_{1.4K}$-b-$PFOMA_{12K}$, (C); PEG_{2K}-b-$PDHFOMA_{13K}$, calcined at 500 °C for 3 hrs

Conclusion

TiO_2 nanoparticles were produced by the controlled hydrolysis of TTIP in the w/c microemulsions stabilized by low molecular weight and polymeric surfactants. For the hydrolysis of TTIP in the w/c microemulsion ($w_o = 5$) stabilized with $PFPECOO^+NH_4$ and $PDMAEMA_{1.4K}$-b-$PTHFOMA_{12K}$, the particles formed were stable and optically transparent for 24 h. The greater control of particle formation was achieved at higher w_o with $PDMAEMA_{1.4K}$-b-$PTHFOMA_{12K}$ compared with $PFPECOO^+NH_4$. In contrast, the particle aggregations were unstable and highly polydisperse particles were produced by PEO_{2K}-b-$PDHFOMA_{13K}$ at same conditions.

Acknowledgement

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