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# Organic–inorganic hybrid materials designed by controlled radical polymerization and mediated using commercial dual functional organophosphorous coupling agents†

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Hybrid materials that are composed of a polymeric material interfaced with an inorganic, metal oxide material have been a rapidly expanding research area in the last few decades. However, interfacial regions remain an important area of focus, and as such hybrid materials do not always possess a very robust or stable interface. Tailor-made interfacial molecules have been successfully reported but material scientists wishing to develop composite interfacial materials would favorably use commercial solutions. Our study shows how we can leverage a commercially available organophosphonic acid group that is coupled with a 2-bromo isobutyrate initiator for surface initiated atom transfer radical polymerization (SI-ATRP) for use as a strong interfacial molecule. We illustrate this mechanism with both nanoparticles of titania and flat titania substrates used as the grafting support and polymerization anchoring points. We demonstrate that the size of the organophosphonic acid initiator, specifically the carbon spacer between the reactive groups, controls the stability of the molecule. The actual covalent linkage between the phosphonic acid group and the titania surface while also leaving the ATRP initiating group able to start the polymerization, is confirmed via <sup>31</sup>P solid state NMR spectroscopy, liquid <sup>1</sup>H NMR spectroscopy XPS, DLS and SEM.

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## Introduction

The use of many surface modification techniques is explored in order to help integrate one object with another through various means. In most cases, these particles or surfaces are modified to change their material properties or structure to integrate a new material into a system, and subsequently create a new composite/hybrid material. The exploration of organic–inorganic hybrid systems is of particular interest. A lot of work has been placed into the development of such systems for the sole purpose of achieving improved properties or structural characteristics for a vast spectrum of applications.<sup>1–3</sup>

Various methods of creating these hybrid organic–inorganic composites involve many surface interactions ranging from weak interactions such as physical adsorption,<sup>4–6</sup> to covalent

bonds from catechols,<sup>7</sup> silanes,<sup>8</sup> phosphonates,<sup>9</sup> or thiols.<sup>10,11</sup> Of course, it is very important to understand the nature of the substrate material when considering what type of functional group can be used to bond to any specific surface.

Phosphonate groups are promising grafting groups because, unlike silanes, they do not stand homopolymerization. However, it has been previously shown that the Si–O–P bond is very sensitive to hydrolysis.<sup>12,13</sup> Mutin *et al.* showed that when a grafting reaction of phosphonic acids onto silica is performed in aqueous media, very few Si–O–P species could be detected. In contrast, this reaction can be observed in higher yields when using organic media. In contrast, this trend is not followed when observed with the Ti–O–P bond. The binding and anchoring of the phosphonate group to the titania surface can be observed with the use of aqueous media, yielding a good method of controlled targeted coating on different surfaces. This raises the notion that phosphonate anchoring groups can be used to effectively pattern non-siliceous metal oxides like titania when using an aqueous media, ensuring that no other surfaces, such as glass, would be affected.

While anchoring groups serve a purpose of providing a good coating to a specific surface, they can also be designed to be a good interfacial region between two different matrices, especially if one matrix can grow from the other. In the case of surface

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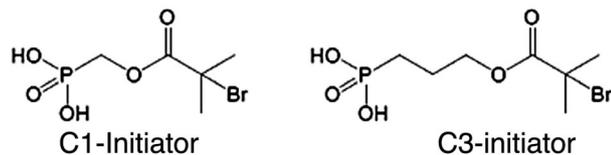


Fig. 1 Structure of organophosphorous initiator molecules used. C1 and C3 names are derived from the hydrocarbon spacer between the ester and phosphonic acid groups.

initiated atom transfer radical polymerization (or SI-ATRP), it is possible to grow a uniform layer of polymer starting from a flat surface substrate. This special controlled radical polymerization (or CRP) technique has been widely used to form coatings and other protective polymer shells for various applications.<sup>14–18</sup> Similar initiator molecules were used, both with a nitroxide mediated radical polymerization,<sup>19–21</sup> or with ATRP initiators.<sup>21–23</sup> Specifically, titania particles have been shown to be coated with amine terminated silane based anchoring groups,<sup>24–26</sup> which can be modified afterwards with typical ATRP initiators. However, this is a rather complex process, and a direct method with both anchoring group and initiator is often more desirable commercially.

Other groups have developed such grafting molecules with a phosphorus-based anchoring group combined with a 2-bromo isobutyrate ATRP initiator group.<sup>22,27</sup> However, such options refer to “in-house” syntheses and result in a rather low yield of ~30%, which would restrict these studies to the laboratory demonstration scale. Commercially available products, such as those shown in Fig. 1 prove to be a viable alternative to the tedious synthesis method, and as such, the missing link to the actual development of hybrid or nanocomposite materials. However, these molecules have not been fully tested against reaction yield and stability, which is an important first step for their future use.

In our study, we aim to discriminate between the commercially available dual functional organophosphoric acid, displayed in Fig. 1, which one can actually achieve a well-anchored bond to titania interfaces, while still promoting the formation of a polymer layer *via* atom transfer radical polymerization. We describe parameters that are mandatory for the molecular stability of these molecules along the reaction, with the aim of paving the path to future studies using this method in material science, especially in membrane science.

## Experimental

### Materials

Two types of titanium oxide particles were used, including a nanopowder (average size 21 nm) from Sigma Aldrich (> 99.7% anatase, CAS 1317-70-0), and a 40 nm aqueous slurry of anatase (Aerodisp W740X) kindly provided by Evonik. In the following, TiO<sub>2</sub> particles from Sigma were named P21, and those from Evonik, E40. Polyethylene glycol (PEG4000, Sigma Aldrich) was used for the synthesis of the flat titania substrates. CuCl (> 90% purity, Sigma Aldrich), CuBr<sub>2</sub> (Sigma Aldrich), and *N,N*-dimethyl formamide (DMF, Sigma Aldrich) were used as

received. 1,1,4,7,10,10-Hexamethyl tetraethyltriamine (HMTETA, Sigma Aldrich) was also obtained and used as received. Propyl phosphonic acid-2-bromo-2-methyl propanoate (Br-C(CH<sub>3</sub>)<sub>2</sub>(CO)-O(C<sub>3</sub>H<sub>6</sub>)PO<sub>3</sub>H<sub>2</sub>) from Specific Polymers (France) was used as a combined grafting molecule and polymerization initiator (also referred to as C3-initiator). A slightly modified version of the initiator, methyl phosphonic acid-2-bromo-2-methyl propanoate (Br-C(CH<sub>3</sub>)<sub>2</sub>(CO)O(CH<sub>2</sub>)PO<sub>3</sub>H<sub>2</sub>, which will be referred to as C1-initiator) was also provided by Specific Polymers. Polyethylene glycol methyl ether methacrylate (PEGMEMA-475) (Sigma) was chosen as the macromonomer and used as received and stored at 4 °C until use. 18 MΩ ultrapure DI water was used. Ethanol was obtained and used after ultrafiltration using a 0.45 μm filter.

### Grafting of titania particles

Both P21 and E40 nanoparticles were subjected to a similar process. In a typical reaction with P21, 0.1 g of P21 was dispersed using a Powergen 125 homogenizer (Fischer Scientific) into 15 mL of ethanol containing 0.245 g of the C3-initiator grafting molecule and subsequently were dispersed in. The suspension was homogenized for 3 minutes, before being heated at 85 °C for 2 hours in a thermostatted bath. The mixture was then centrifuged at 1000 rpm for 5 minutes and the supernatant was removed. Grafting was achieved by heating the collected powder in an oven for 4 hours at 155 °C. The particles were washed from ungrafted molecules by re-dispersing them by vortex stirring in 40 mL water. The mixture was left for several minutes, and then centrifuged at 5000 rpm for 10 minutes. The subsequent supernatant was also removed and the remaining powder was dried overnight.

### Grafting of titania surfaces

The titania flat substrates were prepared first *via* a mixture of 90% w/w P21 and 10% w/w PEG4000 compressed at 200 psi for 10 minutes. The flat substrate (1 cm diameter) was then sintered at 800 °C for 1 hour, with a ramp-up at 5 °C min<sup>-1</sup> from room temperature. After the titania supports cooled down, they were grafted in a similar manner to the titania particles. In a typical experiment, the C3-initiator (0.24 g) was mixed with ethanol (15 mL) and sonicated for 5 minutes or until all the initiator particles were dispersed. The flat substrates were then heated with the C3-initiator-ethanol mixture at 85 °C for 2 hours. The titania substrate was then removed, rinsed with DI water quickly, and then heated at 155 °C for 4 hours before cooling down. A final rinse with water and ethanol was performed to remove any unbound initiators at this point.

### Preparation of the macromonomer solution

A 0.3 M aqueous solution of the macromonomer stock solution was prepared by gently dispersing 7.15 g PEGMEMA into 45 mL DI water. The resulting mixture was slowly rocked back and forth for one minute to mix, and the resulting mixture was then stored at 4 °C until required for use, at which point was subjected to a 3-cycle freeze-pump-thaw degassing cycle before use.

## Preparation of the catalyst

Following the work prepared by Grajales *et al.*,<sup>28</sup> 30 mL of *N,N*-dimethylformamide (DMF) was degassed using a three-cycle freeze–pump–thaw cycle. Copper I chloride (0.06 g) was added into a vial inside a glovebox, along with copper II bromide (0.04 g) and the degassed DMF was added into the vial and stirred for 3 hours. The degassed HMTETA ligand (490  $\mu$ L) was then added to the vial and was left stirring for another 4 hours. The remaining mixture was then stored in the glove box until use.

## Polymerization

The polymerization mixture was prepared by taking a 9:1 volume ratio between the degassed macromonomer solution to the oxygen free catalyst (final volume of 10 mL, with a macromonomer concentration of 0.27 M). This was achieved using a glass neck that was able to mix both volumes together. The mixture was stirred for several minutes before use.

As previously mentioned, there were several different initiators used for this reaction. In each case, the reaction was attempted using the P21, E40 or flat titania substrates that were grafted with the attached C3-initiator.

## Procedure and equipment

The structure of the initiator molecules before reaction was checked using <sup>1</sup>H NMR spectroscopy (Bruker AVANCE, 400 MHz) and compared to the reference spectra provided by Specific Polymers. In each case, about 10 mg of the initiator was mixed with 450  $\mu$ L of CDCl<sub>3</sub> (or deuterated chloroform) to be measured.

Solid-state <sup>31</sup>P NMR spectra were also recorded (Bruker AVANCE), at a 10 000 Hz frequency, to confirm that the phosphonate groups are actually bound to the surface of the titania. Samples were prepared through taking portions of the C3-initiator grafted titania (P21, E40 or titania flat supports) and performing their analysis in the powdered form.

Dynamic light scattering (DLS) (Vasco Particle Size Analyzer, Cordouan Technologies, France) helped us to follow the growth of polymer-titania hybrid particles over polymerization time by extracting the hydrodynamic diameter calculated from the measured diffusion coefficient. Each timed measurement sample was taken from the reaction flask with the polymerization reaction in progress. A 0.2 mL volume of the reacting nanoparticle suspension with the growing polymer was taken at varying times and diluted/dispersed immediately into 15 mL of filtered ethanol. Each sample was then sonicated for 30 minutes and subsequently measured using the DLS system, with 6 runs of 2–3 minutes each, to ensure the statistical accuracy and reproducibility of the data.

XPS (ThermoFisher Scientific K-ALPHA) was used for surface analysis using a monochromatized AlK $\alpha$  source ( $h\nu = 1486.6$  eV) and a 200 micron spot size. A pressure of 10<sup>-7</sup> Pa was maintained in the chamber during analysis. The full spectra (0–1350 eV) were obtained with a constant pass energy of 200 eV and high resolution spectra at a constant pass energy of 40 eV. Charge neutralization was required for all insulating powders pressed onto indium foil. High-resolution spectra were quantified using the Scofield library

loaded into the AVANTAGE software provided by ThermoFisher Scientific.

Scanning electron microscopy images were taken (Leo FESEM 1530 operating at 5 kV) to complete the study. Two series of concentrations were used in the study – both 0 M (control) and 0.27 M. In both cases, samples of the flat titania substrates were polymerized for 5 minutes, 15 minutes and 30 minutes. The subsequent samples were then prepared for imaging by vacuum drying overnight and gold coated *via* sputtering before imaging.

## Results and discussion

### Method

The grafting/initiation dual function of the molecules was tested by probing the effective binding of the phosphonic acid onto the different titania surfaces, and the ability of the initiator group to induce the polymerization of the macromonomer. Besides analyses using local probes like XPS or NMR spectroscopy, the reaction was validated using both particles and flat surface structures, by confirming by DLS or SEM that the polymer was growing from the titania surface.

### Stability of organophosphorous coupling agents

Liquid <sup>1</sup>H NMR spectroscopy was used to validate the structure and characterize the stability of the initiators. The <sup>1</sup>H NMR spectrum was monitored for the C1-initiator (Fig. S1 in the ESI<sup>†</sup>) and C3-initiator (Fig. S2 in the ESI<sup>†</sup>) over a period of time. It appeared that the storage mode, as initially recommended by the provider, did not prevent the C1-initiator from being destabilized, as shown in Fig. 2 and in Table 1 (<sup>1</sup>H NMR spectra integration values for the C1-initiator, as received and after a three-month storage at room temperature).

These <sup>1</sup>H NMR spectra demonstrate that the stability of the C1-initiator is fairly poor (Fig. 2 & Table 1), with its degradation resulting in the appearance of two new peaks formed by the hydrolysis of the ester group (note the peak formation 'd' and 'e'). It is hypothesized that the single carbon spacer between the ester group and the phosphonic acid group results in an easily hydrolyzable bond. We concluded from this study that the C3-initiator, tested in parallel without noticeable evolution after a three month

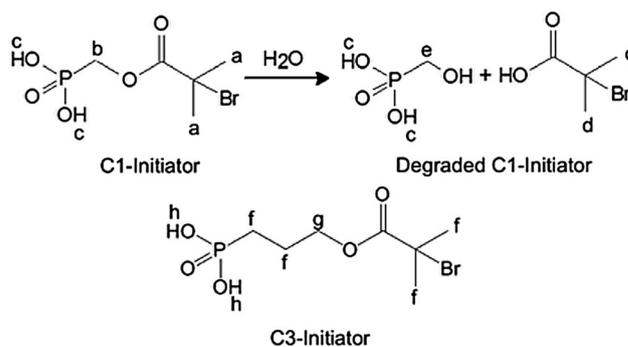


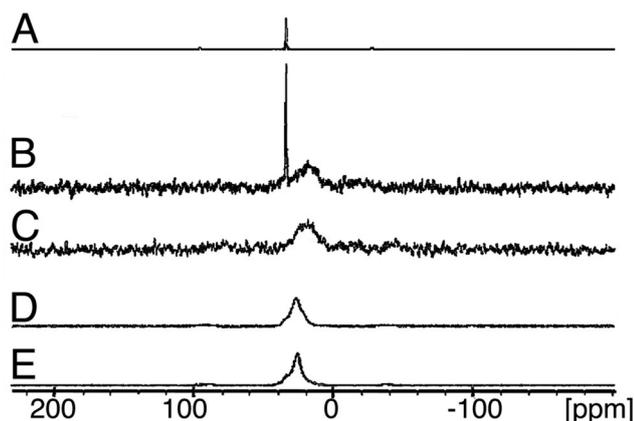
Fig. 2 Organophosphorous initiator: C1-initiator, degraded C1-initiator and C3-initiator with their associated <sup>1</sup>H NMR spectrum labeling.

**Table 1** Integration values for C1-initiator taken from  $^1\text{H}$  NMR spectra provided from Specific Polymers and after 3 months storage

Peak	Integration value (original)	Integration value (3 months)
a (1.93 ppm)	6	4.8
d (1.95 ppm)	—	1.1
e (3.8 ppm)	—	0.3
b (4.5 ppm)	2	1.4
c (10–11 ppm)	2.3	2.2

**Table 2** Integration values for C3-initiator taken from  $^1\text{H}$  NMR spectrum – measurements upon receiving C3-initiator and post 3 months

Peak	Integration value (original)	Integration value (3 months)
f (1.93 ppm)	9.8	10.2
g (4.23 ppm)	2.0	2.0
h (8–10 ppm)	2.4	3.1

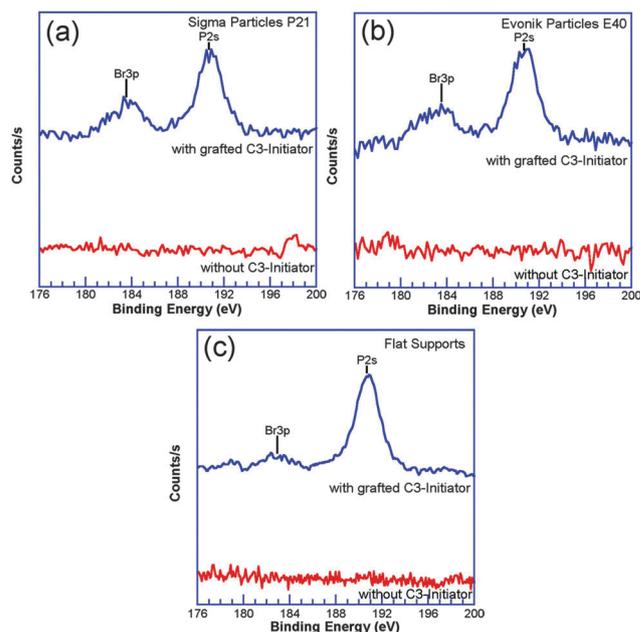
**Fig. 3**  $^{31}\text{P}$  Solid State NMR spectroscopy for (A) C3-initiator, (B) C3-initiator bound to the flat titania substrate (unwashed), (C) the C3-initiator bound to the flat titania substrate (after washing), (D) C3-initiator bound to Evonik titania particles after washing and (E) C3-initiator bound to Sigma titania particles after washing.

storage, was the only organophosphorous coupling agent that remained stable (Table 2), which could be used in this study.

### Organophosphorous coupling agent anchoring onto titania

The actual grafting of the C3-initiator was followed by  $^{31}\text{P}$  NMR spectroscopy performed on the unbound C3-initiator along with the C3-initiator bound to the titanium oxide based surface (with and without washing). The results are presented in Fig. 3.

A narrow peak at around  $\sim 35$  ppm is observed for the unbound initiator (Fig. 3A), which is assigned to the free phosphonic acid group. This peak remains after grafting but before washing (Fig. 3B), along with a broader peak at 18 ppm. This broadening and peak shift is consistent with previous results found with phosphonic acid group binding.<sup>29,30</sup> Upon washing (Fig. 3C), the narrow peak disappears and only the broad peak assigned to the phosphonic group bound to the titania surface remains. This is observed for flat titania substrates (Fig. 3C) and particles (Fig. 3D & E). Confirmation with

**Fig. 4** XPS results for the presence of bromine and phosphorous on: (a) Sigma P21 particles, (b) Evonik E40 particles, and (c) flat titania support.

the use of both Evonik and Sigma particles yielded similar results, but with the exception that the binding ability of the phosphonic acid increased substantially with particles, as the signal intensity was much greater than that performed using the solid flat surface.  $^{31}\text{P}$  NMR spectrum analyses also revealed that this grafting mechanism takes place at room temperature, an important asset for future grafting (see ESI,† Fig. S3 & S4).

XPS allowed us to further characterize the nature of the surface on the powders and flat supports, with a special emphasis on the stability of the bromine group located on the other side of the initiator molecule. Both bromine and phosphorous atoms are clearly identified on the XPS spectra, Fig. 4, which confirm the actual grafting and the stability of the initiator function upon grafting.

These resulting signals only exist for samples that were bound to the organophosphorous/C3-initiator, and not to the C1-initiator. We quantified the proportion of each component as shown in Table 3. The actual phosphorus to bromine ratio was not the expected 1:1 ratio, which we assigned to the potential degradation under the exposure to sunlight during

**Table 3** XPS atomic percentages obtained for the particles P21 (sigma), E40 (Evonik) and flat titania surfaces

Element (%)	P21-blank <sup>a</sup> (%)	P21 + C3-initiator <sup>a</sup> (%)	E40-blank <sup>a</sup> (%)	E40 + C3-initiator <sup>a</sup> (%)	Flat titania-blank <sup>b</sup> (%)	Flat titania + C3-initiator <sup>b</sup> (%)
Br3p3	—	0.46	—	0.41	—	0.13
P2p	—	3.73	—	3.59	0.22	2.86
C1s	30.44	28.03	21.39	27.37	17.6	22.3
N1s	0.38	0.38	1.04	0.45	0.19	1.8
Ti2p	19.34	17.25	21.64	17.40	23.3	20.1
O1s	47.38	48.79	53.40	49.04	53.8	52.2

<sup>a</sup> Data was obtained *via* averaging of 4 different points on the surface of the particles. <sup>b</sup> Data was obtained *via* one point measurement.

reaction, as it was previously shown to potentially break the P–C bond.<sup>30</sup> However, comparative tests with grafted samples exposed to UV light (see ESI,† Table S1) preliminary appeared to indicate this was not the main cause of bromine loss in our case. We hypothesize that the heating temperature could be a factor in bromine loss, which makes further grafting at room temperature important, but will be subject to future studies.

### Confirming polymeric growth

After this first step of local analysis regarding the occurrence of grafting and molecule stability, dynamic light scattering was used as a means to confirm that the grafted initiator would allow polymer growth on the particle surface. We applied the loading procedure with the C3-initiator to each set of titania particles (both P21 and E40), which were further exposed to a solution of 0.27 M macromonomer (PEGMEMA) to form the polymeric hybrid core-shell structure. The resulting data were collected at varying time intervals. The graphs of the auto-correlation functions are reported in Fig. 5a & c, as per the corresponding hydrodynamic diameters (Fig. 5b & d) calculated from these curves.

All autocorrelation functions could be fitted with a single size cumulant fit, as the proof of a monodisperse suspension of particles all along the polymerization step. The decay of these autocorrelation functions, as a function of time, translates in a

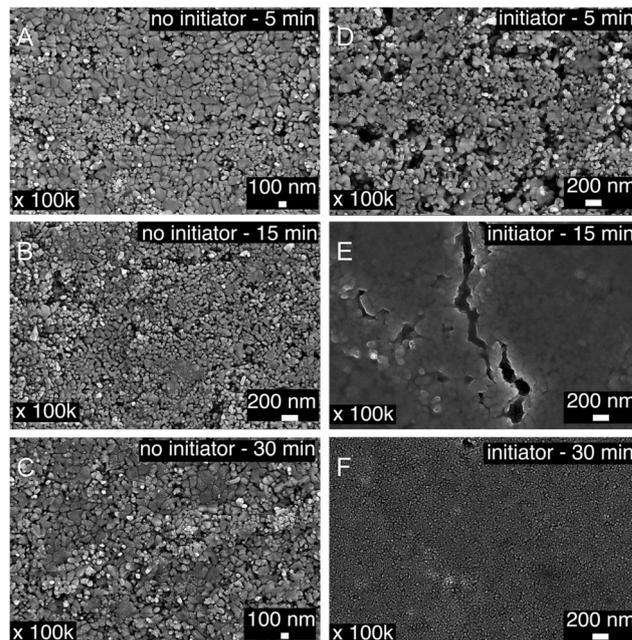


Fig. 6 SEM images obtained for flat titania substrates with bound initiators exposed to different concentrations of macromonomer and time. The substrates exposed to 0 M macromonomer were in A–C for 5 min, 15 min and 30 min, respectively. Images D–F were exposed to 0.27 M macromonomer for 5 min, 15 min and 30 min respectively as well.

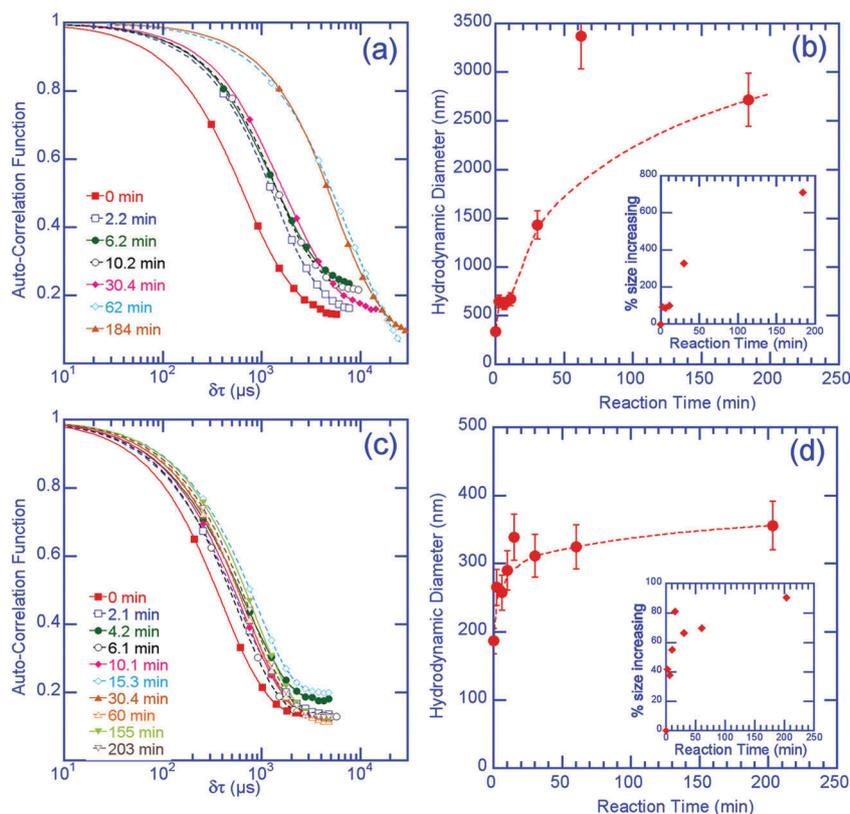


Fig. 5 Dynamic light scattering of growing core-shell hybrid particles of titania taken at different reaction times. The samples shown are (a) log-scale graph of P21, (b) subsequent size of the P21 particles, (c) log-scale graph of E40, and (d) subsequent size of the E40 particles over time.

concomitant increasing hydrodynamic diameter, which is quantified in the size evolution as a function of time. The fast reaction kinetics noted from our results are in line with the rates reported in the literature.<sup>31,32</sup> Thus, there is clear evidence that the grafted initiator particles are able to initiate a homogeneous polymerization on a curved surface to create an integrated hybrid core-shell structure.

This polymerization with the C3-initiator was further confirmed on the flat titania substrates by direct observation using SEM (Fig. 6). The flat titania substrates were loaded with the C3-initiator and were

left to polymerize in either 0 M (used as a reference), or 0.27 M macromonomer solution (with the catalyst). Comparison of the 0.27 M macromonomer sample with the reference (0 M macromonomer) yields striking differences with the 15 minute and 30 minute samples, and shows the formation of a veil that coats the ceramic surface and reduces the surface roughness. This helps to further confirm and solidify that these commercially available organophosphorous initiator molecules are able to bond effectively and initiate an ATRP reaction from a metal oxide surface, regardless of the surface topology.

Among the possible uses for such hybrid structures are the applications linked with liquid or gas separation. Gas separation is a challenge since dense polymers offer high gas selectivity but low permeability and difficulty to scale-up very large surfaces of thin films (several hundreds of square meters at least). On the other hand, porous ceramic membranes are excellent regarding durability and permeability but display low gas selectivity. Combining both high selective polymer thin film and high permeability robust ceramic support is a promising design if the polymer film can be homogeneously coated onto a large surface with no point defect and regular thickness. As growing the polymer film directly from the ceramic support would be the best solution, we conducted exploratory studies with the current system to assess its potential in membrane development. SEM observations (Fig. 7) confirm that a thick polymer carpet can be generated from the ceramic support using our method.

Fig. 7a shows how the polymer is actually growing from the ceramic support, not only coated onto it. The reliefs observed in Fig. 7b and others result from the high vacuum drying required for SEM observation that reduces the polymer film thickness. Finally, Fig. 7c illustrates how a continuous relatively uniform polymer film can be created on the ceramic support with no interfacial defect. These preliminary tests are promising for the development of our hybrid materials synthesized with the help of commercially available dual functional organophosphorous agents.

## Conclusions

From the information presented, we have found that initiator groups with a phosphonate-anchoring group are highly effective for covering different morphologies of surfaces on titania surfaces. Besides, the function of each component of these organophosphorous initiator molecules is independent of the other, and enables us to potentially use the molecule on any terrain/morphology that yields a metal oxide surface. It is also important to note that the phosphonate group must be separated from the ester group (or any other reactive group) by more than one hydrocarbon spacer to ensure stability of the molecule, and that reactions in the dark might be required for a quantitative reaction.

Polymerization is not affected whether the initiator molecule is bound to the surface or free in solution. This provides us proof that the molecule functions properly without fear of interference from other initiator molecule functional groups or from functional groups

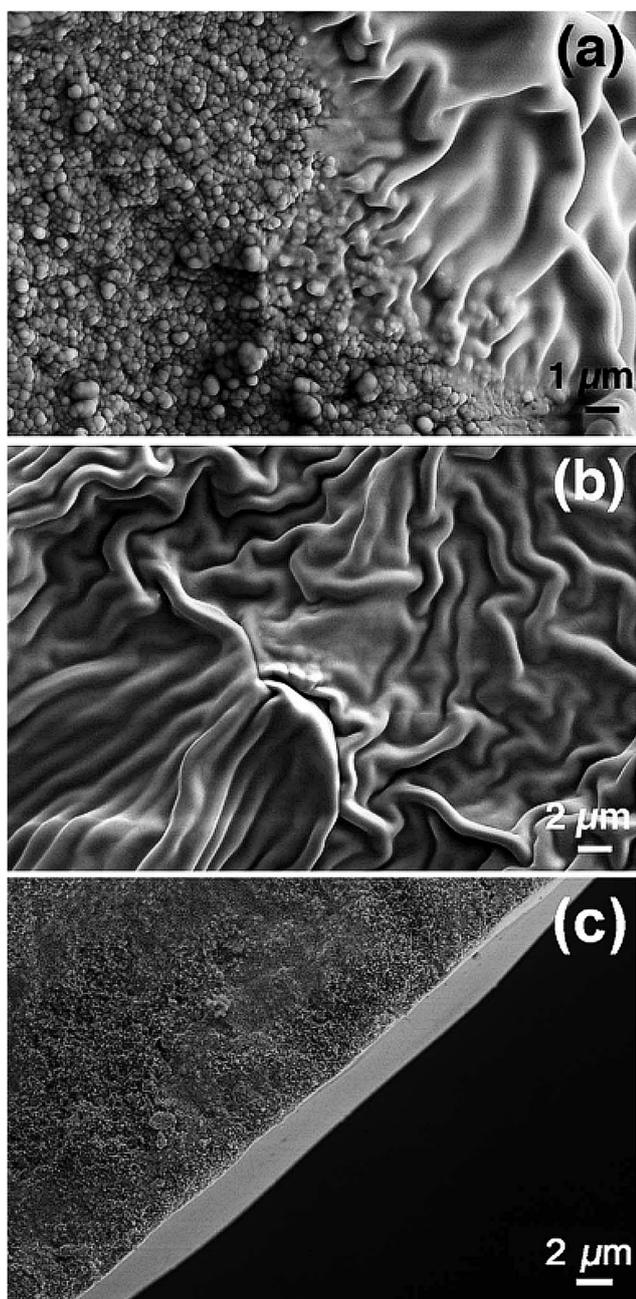


Fig. 7 SEM images obtained with a flat titania substrate grafted and exposed to a 0.27 M solution of macromonomer for 24 hours: (a) ceramic/polymer interface, (b) polymer carpet topography and (c) side view of ceramic/polymer interface.

that exist within the organophosphorous molecule itself. This undoubtedly will help provide an excellent interface towards metal-oxide/polymer materials that have the potential, through the synthesis in a less toxic environment, to offer innovative solutions in many application domains such as membrane-based gas separation.

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