

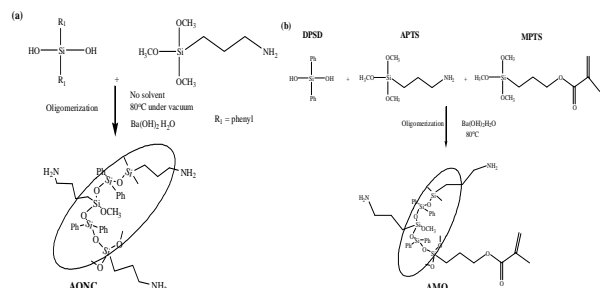
# Fabrication of Imide Hybrid Nanocomposites Using Amine Modified Oligosiloxanes Nanoclusters

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## INTRODUCTION

Fabrication of inorganic-organic hybrid nanocomposites (IOHN) using well-defined nanoclusters has attracted much attention over the last decade due to their potential use in varied applications such as smart coatings, insulation layers in electronics, host materials in rare-earth complexes and organic dye.<sup>1-4</sup> The IOHN prepared from siloxane-based nanoclusters such as polyhedral oligomeric silsesquioxanes (POSS) or metal-oxo-clusters containing siloxanes possess more precisely controlled nanostructures and more reproducible properties compared to conventional IOHN made from inorganic and organic components mixed at the nano-scale level. In particular, POSS derived from the hydrolytic condensation of trifunctional organosilicon monomers offer many advantages for the construction of IOHN. However, their synthesis and functionalization via the introduction of functional organic groups, such as methacrylates, epoxides and amines requires complicated chemical modifications.<sup>5</sup> A simple technique for the synthesis of well-defined, siloxane-based nanoclusters is sought for a straightforward and reproducible method to fabricate IOHN.



**Figure 1.** Reaction scheme of synthesis of AONC (a) and Methacryl modified AONC (b).

In particular, aminopropyl and aminophenyl have very promising properties for roles as binding sites for DNA, microcrystals, diamond surfaces and photo-functional organic molecules.<sup>1,6</sup> Also, they can be easily changed into amide or imide bonds, resulting in IOHN with high thermal stability and mechanical strength.

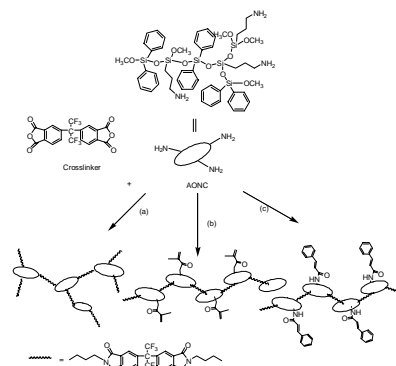
Amine modified oligosiloxanes nanoclusters (AONC) are useful and effective nanoclusters with amine functionality to fabricate IOHN. The AONC have many advantages over POSS, because novel properties can be easily tailored. Their sizes and physical properties can be controlled readily by altering the composition of the reaction mixture. They have attractive optical properties such as a high optical transparency of over 90 % in the visible range and a refractive index that may be modulated easily.

The additional property of AONC can be easily obtained by simple chemical modification. Figure 2b described how to modify AONC by methacryl group as a photosensitive moiety.

We report here the synthesis of amine modified oligosiloxane nanoclusters (AONC) and methacryl modified AONC as described in Figure 1. Additionally, we report the fabrication of photo-functional hybrid nanocomposites derived from AONC, methacryl modified AONC and vinyl cinnamate modified AONC (Figure 2).

Three different photo-functional hybrid nanocomposites were fabricated by using AONC, derivatives of AONC and dianhydrides. (1) colorless Imide hybrid nanocomposites, (2) photo-patternable imide

hybrid nanocomposites and (3) photo-reactive hybrid nanocomposites for photo-alignment of liquid crystals (LCs).



**Figure 2.** Reaction schemes for fabrication of photo-functional imide hybrid nanocomposites. (a) Colorless imide hybrid nanocomposites, (b) photo-patternable imide hybrid nanocomposites and (c) Photo-reactive hybrid nanocomposites for photo-alignments of LCs

## EXPERIMENTALS

### Materials

3-Aminopropyltrimethoxysilane (APTS), diphenylsilanediol (DPSD), 3-methacryloxypropyltrimethoxysilane (MPTS), 1,2,3,4-cyclobutanetetracarboxylic dianhydride (CBDA), 2,2-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6-FDA), cinnamoyl chloride, triethylamine and barium hydroxide monohydrate were used without further purification. 5-(2,5-dioxotetrahydrofuryl)-3-methylcyclohexene-1,2-dicarboxylic anhydride (DODCA) was purified by recrystallization from acetic anhydride and dried at 150°C before use. 1-Methyl-2-pyrrolidinone (NMP) and tetrahydrofuran (THF) were purified by the usual manner and stored under nitrogen atmosphere. Other reagents and solvents were used as received.

### Synthesis of AONC (Figure 1a)

AONC was prepared from APTS and DPSD. 7.17g (4 mmol) of APTS was mixed with 0.02g (0.01 mmol) of barium hydroxide monohydrate at 80°C. 8.65g (4 mmol) of DPSD was added to the mixture continuously over two hours to prevent the self-condensation of DPSD and phase separation. The solution was kept at 80°C for a further two hours to progress the reaction. After that, the methanol, which is a by-product of the condensation reaction, was removed by vacuum heating. The solution was cooled to room temperature and filtered through a 0.45μm-size teflon filter to remove the barium hydroxide monohydrate, leaving the AONC as a clear, viscous liquid.

### Synthesis of colorless imide hybrid nanocomposites (Figure 2b)

Imide hybrid nanocomposites were prepared from AONC and various dianhydrides. For colorless nanocomposites, alicyclic dianhydrides and fluorinated dianhydrides was used. The mole ratio of the amine/anhydride groups was maintained at 1:1 during the mixing of the two substances. We then separately dissolved 13.26 g (4 mmol of NH<sub>2</sub>) of AONC and 8.89 g (2 mmol) of DODCA in NMP. The solid content in solution was 10 wt%. After vigorously stirring the mixture for 12 hours at 0°C, the final solution was spin-coated on silicon substrate or cast on slide glass. The prepared films were dried at 60°C for 3 hours and at 120°C for another 3 hours in air. After curing the films at 300°C for 2 hours in an N<sub>2</sub> atmosphere, we then obtained the final samples

### Synthesis of photo-patternable imide hybrid nanocomposites

To fabricate photo-patternable imide hybrid nanocomposites, methacryl modified AONC were used. Methacryl modified AONC (AMO) were synthesized from APTS, MPTS and DPSD (Figure 1b). Photo-patternable imide hybrid nanocomposites were prepared from AMO and DODCA. The mole ratio of amine/anhydride groups was kept at 1:1. AMO, 21.3g (4 mmol of NH<sub>2</sub>) and DODCA, 8.89g (2 mmol) were dissolved in NMP, separately. The solid content in solution was 10 wt%. They were mixed with vigorous stirring for 12 hours at 0°C. The final solution was spin-coated on silicon substrate or cast on slide glass. The prepared films were prebaked at 90°C for 15 minutes and exposed to

UV radiations under N<sub>2</sub> atmosphere. After the UV exposure (mercury lamp), the films were dried at 90°C for 1 hour and at 120°C for another 3 hours in air. Final sample were obtained after curing at 300°C for 2 hours under N<sub>2</sub> atmosphere.

#### Synthesis of photo-reactive hybrid nanocomposites for photo-alignment of LCs

To fabricate photo-reactive hybrid nanocomposites for photo-alignment of LCs, vinyl cinnamate groups were modified on surface of AONC. 3.33 g (2 mmol) of cinnamoyl chloride dissolved in anhydrous NMP was added dropwise to an ice-cooled solution of AONC, 19.9 g (6 mmol of NH<sub>2</sub>) and triethylamine (2 mmol) in NMP. The reaction mixture was stirred for 2 hours under N<sub>2</sub> and the precipitates were filtered out. 6-FDA (4 mmol) dissolved in NMP were added to filtered solution and solid content in final solution was 5 wt%. The final solution was spin-coated on slide glass. The films were dried at 120°C for 2 hours. After exposure of linear polarized UV on films, photo-alignment layers were obtained.

#### Characterization

<sup>29</sup>Si NMR, FT-IR, MALDI-TOF, Raman and SANS were used for structure analysis. Photochemical reactions depending on UV dose and optical transparency were measured by UV-vis spectroscopy. Thermal and mechanical properties were investigated using TGA and TMA. Surface topology and photo-patterned shapes were observed by optical microscope and SEM.

## RESULTS AND DISCUSSION

#### Synthesis of AONC

AONC can be easily prepared in a single step by using the barium hydroxide monohydrate-catalyzed condensation reactions between APTS and DPSD. Barium hydroxide monohydrate is an effective catalyst that can activate a condensation reaction between APTS and DPSD, and it restricts self-condensation of the DPSD. The evidence for restricted self-condensation of DPSD is very few water contents, released from DPSD self-condensation, in the final solution. FT-IR results of AONC show a strong and broad vibrational band (1000–1200 cm<sup>-1</sup>) related to siloxane backbone and small vibration band of NH<sub>2</sub> (~3350 cm<sup>-1</sup>: N-H stretch and 1617: N-H bending).

The <sup>29</sup>Si NMR data confirmed that the siloxane backbones in AONC were well established by condensation reactions. The size of AONC as determined by SANS is below 2 nm. These results represent that AONC were successfully synthesized.

Methacryl modified AONC (AMO) was also prepared by same procedure. The formation of siloxane frames and restricted self-condensation of DPSD were confirmed by <sup>29</sup>Si NMR spectroscopy. Each oligosiloxane did not agglomerated by further condensation reactions. The sizes of AMO determined by small angle neutron scatterings (SANS) were below 2 nm. These results represent that AMO has uniform and confined sizes.

#### Synthesis of colorless imide hybrid nanocomposites

To fabricate imide hybrid nanocomposites, we used a general method of organic polyimide synthesis. The AONC reacted with the DODCA to form an AONC amic acid solution as an intermediate state before forming the imide hybrid nanocomposite. In this step, each AONC was connected to short amide chains. The amic acid groups were then changed into imide groups after thermal imidization. Finally, we fabricated the imide hybrid nanocomposites in which each AONC was cross-linked with short diimide chains.

Thermal properties of imide hybrid nanocomposites were characterized by TGA. Their 5% weight loss temperatures under N<sub>2</sub> were approximately 430 °C. The incorporation of AONC can retard the decomposition at lower temperatures due to the low molecular weight of the short imide segments in the nanocomposites.

Imide hybrid nanocomposites prepared from DODCA and CBDA had excellent transmittance over 90% in the visible range and were entirely colorless. They have UV cutoffs at 295 nm and 270 nm, respectively.

#### Synthesis of photo-patternable imide hybrid nanocomposites (PINs)

To fabricate PINs, AMO was reacted with DOCDA to form AMO/amic acid solution as intermediate state before imide hybrid nanocomposite. In this step, each AMO was connected with short amide

chains. Photo-polymerization of methacryl groups in nanocomposites was conducted at this step, because methacryl groups were decomposed during thermal imidization. After thermal imidization, imide hybrid nanocomposites that each AMO was cross-linked by short diimide chains were fabricated.

PIN consisting of AMO and DOCDA in NMP was chosen for photo-patterning. 2,4,6-Trimethylbenzoyldiphenyl phosphine oxide (TPO) was used as photoinitiator. The PIN film containing TPO showed good photo-patternability.

#### Synthesis of photo-reactive hybrid nanocomposites for photo-alignment of LCs

Photo-reactive imide hybrid nanocomposites were prepared from vinyl cinnamate modified AONC and 6-FDA. Vinyl cinnamate groups on AONC surface were photo-dimerized after polarized UV exposures. These photochemical reactions induced the anisotropic orientation of main chain and side groups. The decreased absorption of cinnamate groups around 280nm represented that photo-dimerization occurred in the hybrid nanocomposites films.

The direction of the LC alignment on prepared photo-alignment layer was perpendicular to the electric vectors of linear polarized UV. The introduction of imide bonds offered high thermal stability and mechanical strength. Good photoalignment of LCs with high photosensitivity was shown in the fabricated films of imide hybrid nanocomposites containing vinyl cinnamates groups and orientations of LCs were stable in high temperature.

## CONCLUSIONS

Various imide hybrid nanocomposites were fabricated by reaction of AONC with dianhydrides. Imide hybrid nanocomposites prepared from AONC and alicyclic dianhydrides had excellent optical transparency in the region of visible light and high thermal stability up to 430 °C. Photo-patternable imide hybrid nanocomposites prepared from AMO and alicyclic dianhydrides had good patternability. The resulting pattern of PIN exhibited a 10 μm resolution, including a high transmittance, above 85% at 400 nm wavelength. Photo-reactive imide hybrid nanocomposites containing vinyl cinnamate groups showed good photoalignment of LCs with high photosensitivity and thermal stability.

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