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Journal of Non-Crystalline Solids 354 (2008) 2017–2022

JOURNAL OF
NON-CRYSTALLINE SOLIDS

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Photo-initiation of intermolecular bonding and oxide deposition in Ti-based alkoxide solutions

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Received 19 October 2007
Available online 28 January 2008

Abstract

Photoexposure of a water-stable, Ti-alkoxide, $(OC_6H_6N)_2Ti(OC_6H_2(CH_2N(CH_3)_2)_3\text{-}2,4,6)_2$, dissolved in a water/pyridine solution yielded an insoluble, solid phase, present in the form of suspended particles and a deposited material on the vertical side-wall of the solution container. Raman analysis of these photoproducts confirmed the UV-initiation of hydrolysis and condensation reactions in the alkoxide reagent. The excitation wavelength dependence of the photostructural effects observed provides insight into the mechanisms contributing to these photoinduced phenomena. The results are extended to enable the photopatterned deposition of physical relief structures directly from solution in this system.

PACS: 81.20.Fw; 81.15.z; 82.50.Hp

Keywords: Films and coatings; Laser–matter interactions; Polymers and organics; Organic–inorganic hybrids; Sol–gels (xerogels)

1. Introduction

Manipulation of nanostructure development at the early stages of material formation can provide an important means to control multi-length-scale structure and ensuing properties in solution-synthesized inorganic and molecular hybrid materials. Molecular-linking reactions in metal alkoxides (e.g. hydrolysis and condensation in sol–gel processes) have long been a focus in this context. Control of reaction rates, and associated structural evolution, in these complex reaction mixtures has been typically achieved via molecular (ligand) design and the management of chemical, thermal, or optical environmental conditions [1–5]. In general, these strategies have relied on chemical catalysis of these reaction processes to establish the primary intermolecular bond topology early in nanostructure formation.

Studies involving photoinitiated reaction pathways have included the use of extrinsic, photoactivated catalysts (photoacid generators) [6] to modify reaction kinetics and the resulting nanostructure in conventional homoleptic alkoxide systems, and the use of partially substituted metal alkoxides [4,5]. In the latter case, after primary network topology has been established via conventional reaction kinetics, selective optical disruption of the modified ligand group completes the formation of bridging bonds to the metal-oxide network. This approach has been used to pattern a variety of multifunctional metal-oxide systems via subsequent selective chemical etching of unirradiated regions of the material [7].

The present work reports evidence for the photo-initiation of hydrolysis and condensation reactions at the onset of oxide formation during solution synthesis in a novel, water-stable titanium alkoxide, $(OPy)_2Ti(TAP)_2$ where $OPy = OC_6H_6N$ and $TAP = OC_6H_2(CH_2N(CH_3)_2)_3\text{-}2,4,6$. The bidentate nature of OPy, the steric bulk of TAP, and the amino functionality of the TAP ligand combine to

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doi:10.1016/j.jnoncrysol.2007.12.001

effectively limit conventional hydrolysis of the alkoxide while maintaining solubility in aqueous media. UV-irradiation, resonant with electronic transitions in the ligand groups and the surrounding solvent, was used to catalyze the formation of intermolecular bonds, yielding Ti–O–Ti bridging structures. With proper tuning of the excitation wavelength, the development of a suspended particulate phase in solution was accompanied by the deposition of material on glass surfaces in direct contact with the solution in the area illuminated by the excitation beam. The approach thus also offers a unique opportunity to produce patterned, physical relief structures directly from solution without the need for post-fabrication patterning and etching of a previously deposited, homogeneous film.

2. Experiment

The heteroleptic, mononuclear $(OPy)_2Ti(TAP)_2$ (Fig. 1) was synthesized from the *iso*-propoxide derivative via alcoholysis exchange based upon procedures and techniques described previously [8]. The previously established validity of the alcoholysis exchange process on the OPy_2Ti moiety [8] coupled with solution-NMR (proton) results that confirm the presence of the OPy and TAP moieties, support the successful formation of the monomeric $(OPy)_2Ti(TAP)_2$ complex. The $(OPy)_2Ti(TAP)_2$ as-synthesized material exists as an oil, precluding a full structural determination from solid-state X-ray diffraction analysis.

The inhibition of hydrolysis at ligand sites even when the molecule is dispersed in water is attributed to steric constraints imposed by the bidentate pyridine carbinoxide (OPy) and monodentate tri-amino-phenoxide (TAP) groups. It is believed that the amino groups present on the TAP ligand further facilitate water solubilization through H-bonding with the water. The inert character of the molecule to conventional hydrolysis chemistry enables an evaluation of photoexcitation as a means to influence the evolution of intermolecular bond formation. Previous investigations of photoexcitation effects in transition-metal, heteroleptic alkoxide solutions and solid-state systems indicate that resonant excitation of ligand moieties can result in the destabilization of these ligands and the initiation of hydrolysis and condensation reactions at these sites [2,5,9].

Samples for UV-exposure and optical spectroscopic study were prepared by dissolution of $(OPy)_2Ti(TAP)_2$ (106 mM) in anhydrous pyridine (1 mL typical specimen size) under standard inert atmosphere (Ar) conditions (referred to here as the ‘stock’ solution). Solution samples containing a 4:1 molar ratio of H_2O to Ti (designated ‘stock (aq)’) were also prepared by appropriate water addition to the 106 mM $(OPy)_2Ti(TAP)_2$ (anhydrous pyridine) stock solution. Both anhydrous (stock) and water-containing (stock (aq)) samples that were not subsequently photo-exposed served as controls during the investigation. All solutions were contained within fused silica cuvettes (1 cm square cross-section) during optical evaluation. Fig. 2 contains the corresponding solution UV–vis absorption spectra. Included in the figure is the pyridine solvent absorption spectrum and a diluted (10.6 mM alkoxide)) stock (aq) solution spectrum. The lower absorbance of the latter spectrum enables the observation of a broadened resonance at 340 nm, corresponding to the metal-to-ligand charge-transfer band in the molecule. In order to characterize intrinsic molecular absorption at photon energies greater than the absorption onset for the pyridine solvent, thin films of precursor material were spin-coat deposited from $(OPy)_2Ti(TAP)_2$ in pyridine (34 mM) at 500 rpm for 30 s onto fused silica substrates suitable for UV–vis

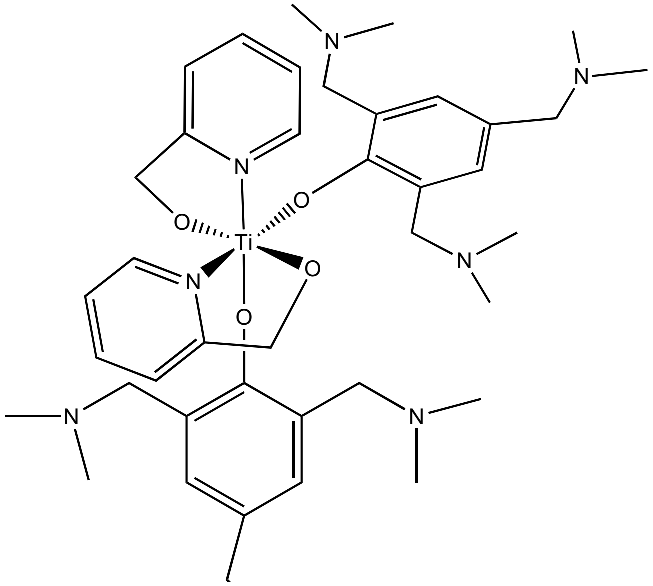

Fig. 1. Molecular structure of $(OC_6H_6N)_2Ti(OC_6H_2(CH_2N(CH_3)_2)_3\text{-}2,4,6)_2$.

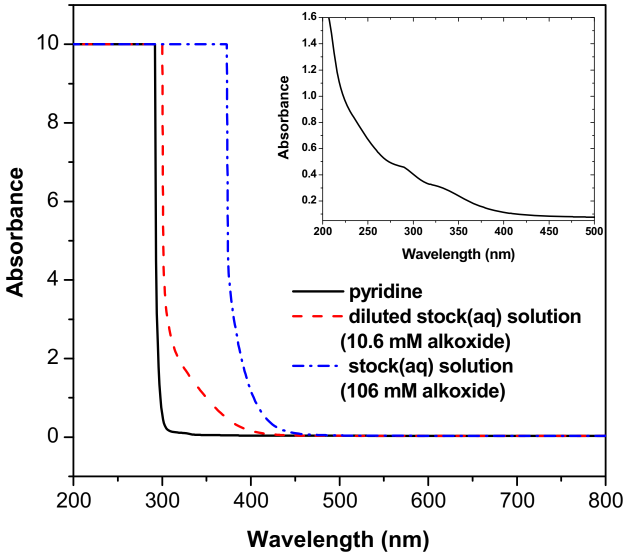

Fig. 2. Representative UV–vis optical absorption spectra from hydrous $(OPy)_2Ti(TAP)_2$ solutions in pyridine. The corresponding absorption spectrum from pyridine is provided for comparison. The inset contains the absorption spectrum from a spin-coated film of $(OPy)_2Ti(TAP)_2$ on fused silica (thickness = 100 nm).