8. 'H NMR and IR spectra for all of the reactant and products were compared with those in literature.
10. After the ion exchange reactions with NaX and NaY (obtained from Aldrich Chemical Company), exchange levels of the zeolites as measured by inductively coupled plasma atomic emission spectrometer or inductively coupled plasma mass spectrometer are as follows: LiX=84.5%, KX=89.5%, RbX=70.7%, CsX=67.4%, LiY=65.7%, KY=98.3%, RbY=99.1%, CsY=94.9%.

Synthesis of Machinable Optical Monolith of Forsterite-PMMA Organic-Inorganic Nanocomposite through a New Synthetic Strategy

Jin Kang, Seon Hui Park, Hye Young Kwon, Dong Gon Park*, Sung Soo Kim†, Ho-Jin in Kweon‡, Sang Sung Nam§

Department of Chemistry, Sookmyung Women’s University, Seoul 140-742, Korea
§Samsung Display Co. ltd, Suwon 442-390, Korea
†Korea Research Institute of Chemical Technology, Taejon 305-600, Korea

Received December 27, 1997

Many experimenters were attracted by the sol-gel method, because it could be a good synthetic tool for preparing their sample in an exotic morphology such as thin film, preformed monolith, uniformly sized particles, or highly porous monolith. Therefore, in some sense, the method should be considered to have very high processability. But, considering the usefulness of the final products in a practical application, a weak point of the method should also be dealt. The problem is that the mechanical properties of the sample prepared by the method are very poor. During the drying process, shrinkage occurs in an unacceptably large extent. If hastily dried, the sample develops cracks. The monolith experiences warping which render the method useless in preparing a sample in exact dimension. From the reason, the maximum dimension acceptable is ~1 mm thick for a monolith, and ~1 µm for a thin film. Most of all, the sol-gel product has very poor mechanical strength, and is not machinable at all. Without an additional heat treatment, the product disintegrates in polar solvents, and readily breaks by small stress.

These problems had been tackled by various ways. Drying Control Chemical Agents (DCCA) were used to get a crack-free monolith. Solvent was removed in its critical dimension. From the reason, the maximum dimension acceptable is ~1 mm thick for a thin film. Most of all, the sol-gel product has very poor mechanical strength, and is not machinable at all. Without an additional heat treatment, the product disintegrates in polar solvents, and readily breaks by small stress.

These problems had been tackled by various ways. Drying Control Chemical Agents (DCCA) were used to get a crack-free monolith. Solvent was removed in its critical dimension. From the reason, the maximum dimension acceptable is ~1 mm thick for a thin film. Most of all, the sol-gel product has very poor mechanical strength, and is not machinable at all. Without an additional heat treatment, the product disintegrates in polar solvents, and readily breaks by small stress.

To whom correspondence should be addressed.
ified CERamic). In the case the inorganic moiety was silica, it was being called ORMOSIL (ORGanically MODified SILica). Unlike in the conventional sol-gel process, the thickness of the film could build up to several μm. The mechanical strength was largely improved that some were actually commercialized as a protective or antireflective films on lenses or as contact lenses.

Usual synthetic strategy to the composite was to secure chemical bonding between inorganic and organic moieties, by modifying the sol-gel reactants by exchanging one or two alkoxy ligands with other organic ligands whose unsaturated bonds could be polymerized via organic polymerization. The composite could also be prepared by physical blending without such chemical bonding between those two moieties. Some prepared such composite by introducing organic monomers into the pores of the dried gel (silica aerogel) and in-situ polymerizing the monomers. Still, most of the problems described for the sol-gel method should be dealt while the aerogel monolith was prepared. Novak and coworkers synthesized the composite by infiltrating organic monomers into the network structure of aerogel. It was observed that organic polymers with no H-bonding functional group, such as PMMA, leached out from the network during hypercritical treatment, and the composite could not be made with PMMA.

We report newly devised synthetic strategy to prepare a monolith of organic-inorganic composite made from forsterite (Mg2SiO4) and poly(methyl methacrylate) (PMMA) via modified sol-gel route. Previously, none was reported on the preparation of the composite between forsterite and PMMA. Main goal of the study was to get monolithic lenses with acceptable mechanical and optical properties, and into it intentionally to put a dopant with an optical activity. By introducing inorganic moieties into organic polymer, we tried to alter the environment around the dopant.

Synthetic scheme was schematically shown in Figure 1. The polymerization was carried out first in the inorganic component by usual sol-gel reaction (hydrolysis and condensation). Then, the polymerization in the organic component was carried out by radical polymerization of methyl methacrylate (MMA). The forsterite (Mg2SiO4) gel network, the inorganic moiety of the composite was synthesized by the H2O2-assisted sol-gel method. This forsterite gel was an alcohols whose pores in the inorganic network of the gel were filled with a mixture of methanol, ethanol, and water. The key step in this synthetic strategy was to exchange alcohol solvent in the pores of the alcohols with MMA, thereby preparing an “organogel” which included MMA in its pores, instead of alcohol. The solvent exchange was carried out by centrifugally washing the forsterite alcohols several times with undiluted MMA, thereby gradually raising the MMA content relative to the alcohol. After being aged for 1-2 weeks, the inorganic moieties of the alcohols was separated from solvent by centrifuge. The supernatant was discarded. The inorganic moiety was redissolved in MMA, and the same collection was repeated several times. Inorganic loss through the supernatant was negligible. Therefore, solvent composition could easily be selected by adjusting the number of centrifugation and relative amount of MMA addition. Final composition of the solvent in the “organogel” of this study was calculated to be >99% MMA with a trace of alcohol. Then the MMA infiltrated into the inorganic gel network was in-situ polymerized by radical polymerization by incubating the “organogel” in 45 °C oven. By this manner, all that problematic drying steps were skipped. A solid block of the forsterite-PMMA composite prepared was further cut into a desired shape and polished if necessary.

In order to see the pore characteristics of the inorganic gel network, the alcohol solvent was removed in its critical state in order to minimize a variation in the inorganic network structure. By hypercritical drying method, the solvent was extracted at 265 °C and 1000 psi, and an aerogel of forsterite was prepared. The aerogel had very big surface area, exhibiting the BET surface area of 800 m2/g. Figure 2 shows the accumulated pore distribution of the forsterite aerogel, obtained from nitrogen adsorption-desorption isotherm which exhibited the type IV of mesoporous solids, with a hysteresis near to the type H2 which indicated the shape of the pores was near to the ink-bottle. The dimension of the pore was in a mesopore range of 100-500 Å with fairly broad size distribution. Contrary to the highly porous aerogel, the BET surface area of the composite was 5.8 m2/g. The isotherm obtained from the forsterite-PMMA composite was type II which was typically observed for a nonporous solid. The weight fraction of the inorganic moieties assessed by elemental analysis, thermal analysis, and ICP/MS was in a range 4-8%. The theoretical fill calculated from the porosimetry results came out to be about 11 weight %. Considering the structural variation of the network during the hypercritical drying was not significant, we assumed that liquid MMA filled these pores which were occupied previously by alcohol. This observation indicated the pores were completely filled with PMMA which was in-situ polymerized from MMA infiltrated into the pores.

The forsterite-PMMA composite had hybrid mechanical properties. Measurement carried out by a microindenter showed the hardness of the composite was 3.1 Kg/mm2. Comparing the hardness of the sole PMMA was 2.7 Kg/mm2, and that of the aerogel monolith was 32.6 Kg/mm2, the hardness of the composite was near to the property of the organic component. Whereas a block (20 × 4 × 1 mm3) of sole PMMA was unbreakable (Modulus of Rupture up to 200 MPa) during three-point bending test, the composite broke at MOR of around 140 MPa, which indicated the strength of the composite was much weaker than the or-
ganic counterpart. Though, comparing to the weakness of the xerogel monolith of forsterite, the improvement of the mechanical strength by PMMA incorporation was immense. The bending test could not even be performed on a block of the forsterite xerogel because it was too weak. Even if the extent was small, the thermal stability of the composite was also observed to be better than sole PMMA. The melting temperature of the composite observed by thermal analysis was about 30 °C higher than that of the sole PMMA.

Unlike the xerogel monolith prepared by the sol-gel method, the forsterite-PMMA composite was machinable. The picture in the Figure 3 showed a transparent lens cut out of a cylindrical mould of the forsterite-PMMA composite, which was compared to a xerogel monolith made by carefully drying forsterite alcogel. Large extent of shrinkage (of around 75%) experienced by xerogel was manifested by relatively small size of the monolith (same volume of gel was used for making both composite lens or the monolithic xerogel). Because the content of the composite was high in organic, the mechanical properties resembled those of PMMA. The composite could be cut into a block or any shape of lenses, and its surface could be polished in usual way. Its surface could be preformed into a concave or convex shape by using a mould. By adopting extra monomers on top of the mould, the extent of the shrinkage of the composite during polymerization was almost negligible (cf. the extent of the shrinkage occurred was less than 1%).

The UV-vis spectrum taken from a lens (3 mm thick) of composite was compared to the one obtained from the sole PMMA in the Figure 4. Compared to the air, the transparency in the visible range was about 88%. The transparency which was compared to the sole PMMA was near 98%. Apparently, the shoulder in the ultraviolet region indicated the transparency in the region was actually improved. Considering the high transparency up to the ultraviolet region, it could be conceived that domain of the inorganic moieties should be very small, and considered to be in a nano-range. Most of all, the transparency was not lost by cycles of heating and cooling up to 200 °C. The loss of the transparency by being heated around 200 °C was observed in many ORMOCER samples with high inorganic content, and speculated to be caused by Si-OH sites still remained in the sample. By getting FTIR spectrum from xerogel powder of forsterite which was thoroughly washed with MMA (under inert atmosphere) and dried under vacuum, the possible ligand exchange on the surface of the inorganic network was eliminated. The lack of the chemical bonding between inorganic moiety and PMMA was previously reported. Therefore, without any chemical bonding between the inorganic and organic moieties, phase separation was expected to occur. Therefore, the good optical transparency of the composite suggested that the domain of the inorganic moieties was in a size of nanometer range, which conformed to the formation of nanocomposite. If the size of the domain were larger than 100 nm, the lens should become opaque by phase separation upon being heated.

In summary, a new synthetic strategy of preparing an organic-inorganic composite from 'organogel' was successful.
ly applied on the preparation of a monolithic forsterite-PMMA nanocomposite. The monolithic composite prepared had very good optical transparency, and largely improved mechanical characteristics relative to the inorganic counterpart, and most of all it was machinable. The mechanical property of the composite had hybrid characteristics of those inorganic and organic moieties. Doping of the optically active materials (either ions or macromolecules) into this new forsterite-PMMA nanocomposite is in progress, and some dopants have been successfully incorporated into this host material, which would be dealt in forthcoming report.

Acknowledgment. The support of the Korean Science and Engineering Foundation (K-N96048) is acknowledged with gratitude.

References
18. Gregg, S. J.; Sing, K. S. W. Adsorption, Surface area and Porosity; Academic: London, 1982; p 111.
20. personal communication with Dr. H. K. Kim/Hannam University.

Design and Synthesis of Furoxan Derivatives as Probe for the Nitric Oxide Generation

Kwang-Jin Huang* and Hokyoun Kang

Department of Industrial Chemistry, Hongik University, Jojuiwon, Chungnam 339-800, Korea
Received February 2, 1998

Nitric oxide (NO), known to be the smallest biomolecule up-to-date, is involved in various physiological activities such as vasodilation and tumoricidal and bactericidal activities. More interestingly, it mediates a signal transduction in the brain. Due to these diverse biological activities, the NO precursors have been a main subject of interest in the treatment of NO-related diseases. Furoxan (Furazan N-Oxide) I has been known to release NO by interacting with a thiol compound such as cysteine and glutathione in vivo. We also reported the NO generation from various furoxan derivatives by the electron impacted fragmentation. The biochemical mechanism for NO generation from the furoxan, however, is not explored exactly in the molecular level.

To probe such a biochemical mechanism and to develop a potential NO-precursor for biomedical study, we designed thiol containing furoxan derivatives IIa and IIb expecting the NO generation by the intramolecular sulfide-nitrate interaction. Here, we wish to report a synthetic method of the furoxans IIa and IIb containing protected thiol.

The furoxans IIa and IIb were prepared through dimerization of the corresponding nitrile oxide as a key step.