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Molecular Building Block Approaches to Ceramic Materials: Tripolyphosphate Cement

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Cement chemistry[2] offers an attractive route to new inorganic composite materials using the molecular building block approach,[3] since the mild processing conditions involved are likely to minimize degradation of the precursor molecules' structural integrity. We report here the successful implementation of a molecular building block approach to the synthesis of cement composite materials through the preparation of a magnesia tripolyphosphate cement. This material, in contrast to magnesia orthophosphate cements,[4] is a high-strength material[5] that differs from magnesia orthophosphate cements not only in terms of its physical properties but also in terms of its processibility and chemical composition.

Magnesia tripolyphosphate cement pastes were prepared by adding MgO powder (Martin Marietta MgO 10CR) to a saturated aqueous solution of $(NH_4)_3H_2P_3O_{10}$ [2.44 g of $(NH_4)_3H_2P_3O_{10}$/g of H_2O] in the proportion of 0.15 g of H_2O/g of MgO, stirring for 1 min, and hand pressing into a mold for 3 min. For purposes of comparison, magnesia orthophosphate cement pastes were prepared as described by Sugama and Kukacka[6] by adding MgO powder to water plus $(NH_4)_2HPO_4$ [0.66 g of $(NH_4)_2HPO_4$/g of H_2O] in the proportion of 0.28 g of H_2O/g of MgO, stirring vigorously for 30 s, transferring to a mold, and vibrating the mold for 1 min to remove air bubbles. In contrast to the magnesia orthophosphate cement paste, which set after about 4 min and required only about 18 h to reach maximum compressive strength, the magnesia tripolyphosphate cement acquired a puttylike consistency after about 10 min, became rigid after about 30 h, and required about 8 days to reach maximum compressive strength. Samples prepared in 1-in. long × 0.5-in. diameter cylindrical molds showed very different mechanical properties, with the hardened magnesia orthophosphate cement paste displaying the expected[6] compressive strength of 22.6 MPa (3270 psi) and the triphosphate past attaining a much higher value, 91.0 MPa (13 200 psi).

The chemical compositions of hardened magnesia orthophosphate and magnesia tripolyphosphate cement pastes are quite different according to X-ray powder diffraction and ^{31}P MAS NMR studies.[7] In agreement with most other studies,[4] the magnesia orthophosphate paste contained only unreacted MgO and crystalline $Mg(NH_4)PO_4\cdot 6H_2O$, struvite. The magnesia tripolyphosphate cement, however, showed only traces of struvite in addition to unreacted MgO. The major products of the exothermic MgO plus aqueous $(NH_4)_3H_2P_3O_{10}$ reaction were amorphous phosphates whose identity was dependent upon processing conditions. ^{31}P MAS NMR spectra of samples prepared in small batches under conditions of good heat transfer showed two resonances, a strong δ −6.5 resonance in the polyphosphate end group region plus a weaker δ −18.5 resonance in the polyphosphate middle-group region, the pattern expected for intact tripolyphosphate ions (see Figure 1A). Samples prepared in 1-in. long × 0.5-in. diameter cylindrical molds, conditions of relatively poor heat transfer, displayed more complex spectra of the type shown in Figure 1B. A strong polyphosphate end-group resonance was still observed, but the polyphosphate middle-group resonance had become very weak, and a sharp struvite resonance plus a second orthophosphate resonance appeared. After these cylindrical samples were heated to 100 °C for 1 h, their ^{31}P MAS NMR spectra were dominated by a strong polyphosphate end-group resonance having shoulders in the orthophosphate and polyphosphate middle-group regions (see Figure 1C). The series of spectra shown in Figure 1 thus showed that hardened magnesia tripolyphosphate cement pastes retain the tripolyphosphate precursor structure under ambient-temperature processing conditions. When the temperature of the cement paste was allowed to rise above ambient temperature, however, the tripolyphosphate structure was degraded, and pyrophosphates $P_2O_7^{4-}$ were the principal reaction products. There is precedent for this type of behavior in the other tripolyphosphate systems. Crystalline sodium tripolyphosphate hexahydrate, for example, degrades to pyrophosphates, even at ambient temperature.[8]

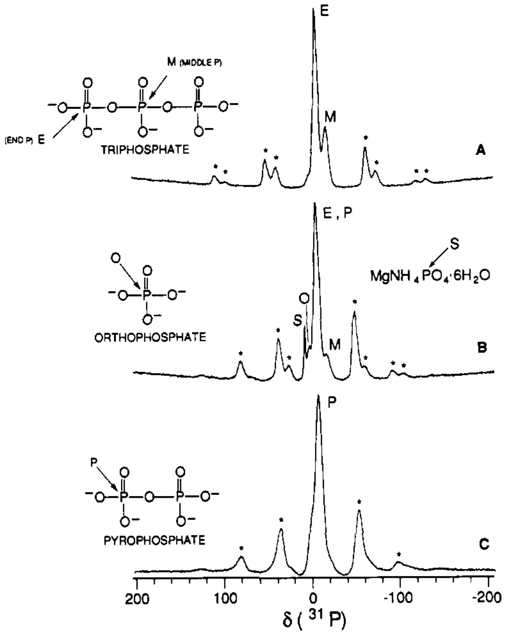

Figure 1. ^{31}P MAS NMR spectra of hardened magnesia tripolyphosphate cement pastes: (A) sample prepared in a small batch under conditions of good heat transfer; (B) sample prepared in a 1-in. long × 0.5-in. diameter cylindrical mold; (C) cylindrical sample of the type just described, after maintaining at 100 °C for 1 h. Spinning sidebands are labeled with asterisks. Chemical shift values referenced to 85% H_3PO_4.

The results just described demonstrate that the molecular building block approach is a viable route to novel

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cement composite materials under conditions of careful temperature control. According to mercury intrusion porosimetry data currently being analyzed, the superior mechanical properties observed for the magnesia tripolyphosphate cement are not molecular in origin, but instead have their origin in lower porosity arising from a lower water-to-solids ratio (g of water/g of MgO) determined by the superior solubility of the triphosphate precursor. If longer polyphosphate chains are employed, however, it is possible that molecular structure may play a role in determining bulk properties, and we are currently investigating this possibility.

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Second Harmonic Generation of Poled 4-[*N*-Methyl-*N*-(4′-nitrophenyl)aminomethyl]styrene Polymer Film

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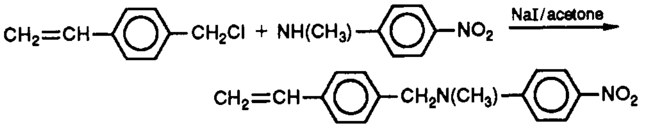
Since *p*-nitroaniline (pNA) was found to have relatively high hyperpolarizability[1] for one aromatic ring chromophores with a short maximum absorption wavelength of ca. 375 nm and a cutoff wavelength of ca. 480 nm, several polymers having pNA units were prepared to obtain high second-order nonlinearity, i.e., second harmonic generation (SHG). Marks et al.[2,3] and Eich et al.[4] introduced pNA units into polystyrene or poly(allylamine) through polymer reactions. However, it is usually difficult to obtain a high functionalization level or high chromophore concentration through polymer reactions. Most polymers previously reported[5,6] have long spacer units, which facilitate the orientation of the chromophore unit by electrical poling. But the long spacer units are also considered to increase the relaxation of the orientation when the electric field is removed, leading to a decrease of SHG characteristics. Therefore, the polymerization of a chromophore-linked polymerizable group with a short spacer is expected to provide a polymer with a suppressed relaxation of the orientation as well as with a high chromophore concentration per unit volume.

To obtain this, we synthesized a new styrene derivative, MNPAMS, 4-[(*N*-methyl-*N*-(4′-nitrophenyl)amino)methyl]styrene, a pNA unit linked by only one methylene carbon, and examined the polymerization behavior. The optical properties of the polymer were also studied.

MNPAMS was obtained by the reaction of *p*-chloromethylstyrene with *N*-methyl-*p*-nitroaniline in acetone in the presence of sodium iodide (yield 71%):



The crude MNPAMS was purified by recrystallization in ethanol to obtain a yellow prismlike crystal (mp 121 °C).

Polymerization of MNPAMS was carried out in a glass ampule in a nitrogen atmosphere. Table I shows the results of polymerization. We obtained polymers with radical and anionic initiators but not a cationic catalyst. With a radical initiator a polymer prepared in a polar solvent, such as dimethylformamide (DMF) or dimethylacetamide (DMAc), had a higher molecular weight than one prepared in benzene. The polymers prepared were soluble in polar solvents such as DMF, DMAc, and dimethyl sulfoxide and insoluble in less polar solvents such as benzene, tetrahydrofuran, and chloroform.

A thin polymer film was cast on ITO coated glass from a DMAc solution of polymer 3 (Table I) by using a spin coater. The film had a maximum absorption of 393 and a cutoff wavelength of 480 nm. These values are almost equal to those of pNA. The short cutoff wavelength indicates the possibility of using this polymer for frequency doubling in waveguide devices of IR lasers such as neodymium–YAG and some semiconductor lasers and for some electrooptical modulators and switches. The refractive indices n were measured by the m-line method,[7] as shown in Table II. The refractive index of this film at 532 nm could not be measured using an optical prism (n = 1.7936 at 532 nm), because the refractive index of the polymer at this wavelength was near or higher than that of the prism. The d coefficients were calculated by using a refractive index of 632.8 nm instead of 532 nm. The film thickness, $l = 0.85 \pm 0.02$ μm, was determined from interference fringes and refractive indices, $l = [2\bar{n}(1/\lambda_1 - 1/\lambda_2)]^{-1}$, where $\bar{n}$ is the average refractive index.

The pNA units in the polymer film were aligned by corona poling, keeping the film at 110 °C (T_g 103 °C) under a dc electric field of 5 kV (ca. 59 MV/cm) for 1 h and then cooling to room temperature. The orientation of the thin

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