Mechanism and Nanosize Products of the Sol–Gel Reaction Using Diphenylsilanediol and 3-Methacryloxypropyltrimethoxysilane as Precursors

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We use a first-principles calculation and small-angle neutron scattering (SANS) to investigate the mechanism and the nanosize products of the sol–gel reaction with diphenylsilanediol (DPD) and 3-methacryloxypropyltrimethoxysilane (MEMO) precursors in synthesizing a hybrid waveguide material. It is predicted that switching between a DPD hydroxyl and a MEMO methoxy with a reaction rate of $6.8 \times 10^{-6}$ s$^{-1}$ at 300 K is the fastest process for the first reaction step, thus generating diphenyldimethoxysilanol (DPM) and 3-methacryloxypropyl(dimethoxysilanol (MEDO) as products. However, we determine that this reaction pathway could be modified by the presence of the $H_2O$ released from a catalyst such as Ba(OH)$_2$·$H_2O$. Next, switching between the DPM hydroxyl and the MEDO methoxy is followed to generate diphenyldimethoxysilane (DPDM) and 3-methacryloxypropylmethoxysilane (MEMDO). However, condensation between a MEMDO hydroxyl and a DPDM methoxy is found to be most favorable for the third reaction step, which generates the DPDM–MEMDO dimer and $CH_3OH$ molecule as products. In a similar fashion, a DPDM methoxy of the DPDM–MEMDO dimer can condense with a MEMDO hydroxyl of the second DPDM–MEMDO dimer to increase the chain, but its reaction rate of $2.8 \times 10^{-11}$ s$^{-1}$ is predicted to be about 5 times smaller than that between a DPDM methoxy and a MEMDO hydroxyl. This implies that the reaction rate for the larger nanostructures becomes smaller. Additionally, our SANS measurements determine that the final products from our sol–gel reaction are on the nanometer scale, at sizes from 1.76 to 2.36 nm.

I. Introduction

There is great interest in designing the ideal waveguide materials for optical applications. Conventional waveguides are made of inorganic glasses and organic polymers. However, there still remain considerable challenges to reducing optical losses and giving them good adhesion on various substrates, high thermal stability, and low processing temperatures. Recently, hybrid materials with both organic and inorganic components have been proposed as good candidates for satisfying the ideal properties and processing conditions simultaneously. In addition, the synthesis of the hybrid materials with nanometer-scale sizes is also important in making fine nanostructures and in getting homogeneous properties within a waveguide.

Both hydrolytic and non-hydrolytic processes have been proposed to produce the hybrid materials. However, hybrid materials synthesized by hydrolytic processes have more optical losses than those synthesized by non-hydrolytic processes. This is because hydrolytic processes generally generate more undesired hydroxyls that are sensitive to vibrational excitations. The non-hydrolytic synthesis of hybrid materials consists of a two-step process. In the first step, the precursors are linked using the ideal properties and processing conditions simultaneously. In addition, the synthesis of the hybrid materials with nanometer-scale sizes is also important in making fine nanostructures and in getting homogeneous properties within a waveguide.

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DPD and one MEMO, and between two MEMOs. Also, the switching reaction between one DPD hydroxyl and one MEMO methoxy is explored, which generates diphenylmethoxysilanol (DPM) and 3-methacryloxypropylmethoxysilanol (MEDO) as products. Then, the catalytic effects by the H2O released from a catalyst such as Ba(OH)2⋅H2O are additionally investigated because they could play an important role in reducing the reaction barrier as reported in the previous studies.23–25 Moreover, the reactions by DPM and MEDO molecules are explored. Next, we investigate the reactions by the diphenyldimethoxysilane (DPDM) and 3-methacryloxypropylmethoxysilanol diol (MEMDO) molecules as well as the reactions by the dimer (DPDM−MEMDO) molecules. Last, the sizes of the final products are determined on the basis of experimental SANS measurements and theoretical predictions.

These results are reported and discussed in section III. Section II provides some details about the calculations, and section IV summarizes our results.

II. Computational Details

All calculations are performed using the self-consistent B3LYP20 and KMLYP21 density functional theories and using the QCISD22 level of theory. The B3LYP was shown to predict accurate geometries and thermochemical data compared to other generalized gradient approximations (GGAs)26–30 and local density approximations (LDAs),31,32 whereas KMLYP was proven to be more accurate in predicting transition-state barriers31,33,34 than other DFT methods.

The electronic wave function is expanded using the 6-31G valence double-ζ35 basis set and the 6-311+G(d,p) valence diffuse triple-ζ plus polarization35 basis set. In this study, the full optimizations of all available geometry parameters for reactants, transition states, and products are performed at the B3LYP/6-31G level of theory, and then the enthalpies of reactions and transition-state barriers are obtained using the KMLYP/6-31G single-point energies determined at the B3LYP geometries. All calculations are performed with Gaussian 03.36

We use DPD and MEMO precursors to make siloxane bridges. DPD consists of one silicon atom, two hydroxyls, and two phenyl groups. The valence orbitals for the silicon atom are sp3-hybridized, and they bond to two phenyl and two hydroxyl fragments as shown in Figure 1a. Our predicted DPD Si−OH bond length of 1.64 Å is found to be in close agreement with the experimental values of 1.63−1.64 Å.37,38 In addition, the DPD Si−phenyl bond length of 1.89 Å is calculated to be consistent with the QCISD value of 1.90 Å. The MEMO molecule has one 3-methacryloxypropyl group and three methoxy groups around the silicon atom as described in Figure 1b. In all possible sol−gel processes using the DPD and MEMO precursor system, the Si−OH fragments of the DPD and the Si−OCH3 fragments of the MEMO are active groups that form a siloxane bridge (−Si−O−Si−), thereby releasing H2O or CH3OH as a byproduct.

Figure 1. Reactants and the catalyst: (a) DPD (diphenylsilanediol) and (b) MEMO (3-methacryloxypropyltrimethoxysilane) and (c) Ba(OH)2⋅H2O.

III. Results and Discussion

A. Reaction Mechanism and Resulting Nanostructures.

By computing the partition functions for the reactants and the transition state, the reaction rate kTST of the canonical rate equation39 is determined by

\[
k_{TST} = \Gamma(T) \frac{k_B T}{h} \frac{Q_{TS}}{Q_A Q_B} \exp\left(-\frac{\Delta E_0}{k_B T}\right)
\]

where \(\Gamma(T)\) is the thermal tunneling coefficient, \(k_B\) is the Boltzmann constant, \(h\) is the Plank constant, \(Q_{TS}\) is the partition function for the transition state, \(Q_A\) and \(Q_B\) are the partition functions for reactants A and B, and \(\Delta E_0\) is the barrier height. We determine the sequence of the reactions by comparing the calculated reaction rates.

There are three plausible cases for condensation in the first step of the sequence, which include reactions between (1) two DPDs, (2) one DPD and one MEMO, and (3) two MEMOs. The first case begins by the initial attack of one DPD hydroxyl on another DPD hydroxyl and then proceeds through the four-centered transition state as shown in Figure 2a. The predicted barrier is 14.9 kcal/mol. Additionally, we find that the 14.9 kcal/mol barrier is also consistent with the 14.4 kcal/mol barrier determined for the KMLYP/6-31G geometries and the 13.9 kcal/mol barrier determined for the KMLYP/6-311+G(d,p) geometries. These results indicate that the KMLYP/6-311+G(d,p)//B3LYP/6-31G energies are proper for an accurate prediction of the transition-state barriers. The second condensation case can occur through two different reaction pathways. The first type is the attack of a DPD hydroxyl on a MEMO methoxy (Figure 2b), whereas the second one is the attack of a MEMO methoxy on a DPD hydroxyl (Figure 2c). However, the first type having the smaller barrier of 15.1 kcal/mol is found to be more favorable. Figure 2d describes the condensation reaction between two MEMOs, but its barrier of 69.3 kcal/mol is predicted to be relatively high compared to those of the two other cases. Recently, Buestrich and co-workers5 proposed one plausible reaction mechanism for the sol−gel reaction under the DPD and MEMO precursor system. According to their mechanism, first one DPD hydroxyl should condense with one MEMO methoxy to form the DPD−MEMO product having one siloxane bridge, and CH3OH should also be generated as a byproduct. Then, the CH3OH would condense with the DPD side in the DPD−MEMO to substitute its hydroxyl with the methoxy group. In this respect, the DPD side could remove its hydroxyl group. However, there could be an alternative pathway to remove hydroxyl groups in the DPD. If switching between a DPD hydroxyl and a MEMO methoxy could consecutively take place twice, then the DPD could remove its two hydroxyl groups. Moreover, our calculations indicate that switching between a DPD hydroxyl and a MEMO methoxy is most likely to occur in the first reaction step because the switching reaction is predicted to have a rate of \(6.80 \times 10^{-6} \text{ s}^{-1}\) at 300 K, which is much larger than the rates of \(3.77 \times 10^{-9}\) and \(1.81 \times 10^{-10}\)
The reaction rate is found to be much smaller than $6.80 \times 10^{-11}$ s$^{-1}$ for condensations, respectively, between two DPDs and between one DPD and one MEMO. For the switching reaction, the concerted attacks of a DPD hydroxyl on a MEMO methoxy and of a MEMO methoxy on a DPD silicon are determined to generate DPM (DPD hydroxyl substituted with one methoxy) and MEDO (MEMO methoxy substituted with one hydroxyl) as products. For the transition state, the DPD Si–OH bond (1.95 Å) is significantly broken while a MEMO Si–OH bond is being formed as shown in Figure 2e. Simultaneously, the Si–OCH$_3$ bond begins to form on the DPD side, whereas the MEMO Si–OH bond length of 2.10 Å indicates a considerable amount of the bond being broken.

We also explore the reactions by the byproducts of H$_2$O and CH$_3$OH molecules resulting from condensations between two molecules of DPD and MEMO. There exist four types of these reactions. The first type is condensation between one DPD hydroxyl and one CH$_3$OH (Figure 3a), generating H$_2$O and DPM as products with a barrier of 19.8 kcal/mol. The condensation reaction between the MEMO methoxy and the H$_2$O as shown in Figure 3b is the second type, and it is determined to produce CH$_3$OH and MEDO with a barrier of 19.0 kcal/mol. However, its endothermic enthalpy of 0.6 kcal/mol indicates that it is thermodynamically unfavorable to occur. Figure 4 describes the products from the reactions of CH$_3$OH or H$_2$O with the terminal C=–C and C=O bonds in the MEMO, but it is found that the barriers of 35.3 to 91.4 kcal/mol by CH$_3$OH (the third type) and the barriers of 40.4 to 141.7 kcal/mol by H$_2$O (the fourth type) are considerably high as compared to those for the first and second types. The largest reaction rate of $6.45 \times 10^{-12}$ s$^{-1}$ is obtained from the first type among these four types. However, this reaction rate is found to be much smaller than $6.80 \times 10^{-6}$ s$^{-1}$ for the switching reaction between one DPD hydroxyl and one MEMO methoxy. In this respect, the most plausible products from the first reaction step are considered to be DPM and MEDO molecules resulting from the fastest switching process.

There are 10 possible cases for condensation in the second reaction step, which includes the reactions between two DPM hydroxyls, between one DPM hydroxyl and one MEMO methoxy, between two DPM methoxys, between one DPM hydroxyl and one MEDO hydroxyl, between one DPM methoxy and one MEMO hydroxyl, between one DPM hydroxyl and one MEDO methoxy, between one MEMO hydroxyl and one MEDO methoxy, and between two MEDO methoxys. All calculated transition barriers and enthalpies are summarized in Table 1. Among these reactions, the attack of a DPM hydroxyl on a MEDO methoxy, whose transition state structure is shown in Figure 5a, is found to have the largest rate of $1.12 \times 10^{-8}$ s$^{-1}$. However, the switching reaction between a DPM hydroxyl and a MEDO methoxy, generating DPDM and MEMDO as products, is determined to have a much larger rate of $4.61 \times 10^{-7}$ s$^{-1}$ than those for condensation. In this respect, the switching reaction is determined to be the fastest process in the second reaction step. The transition state for the switching reaction involves several simultaneous bond breakings and formations: (1) a DPM Si–OH bond being broken with an elongated bond length of 1.82 Å, (2) a Si–OH bond of 1.84 Å formed between a DPM hydroxyl and a MEDO silicon, (3) a Si–OCH$_3$ bond being broken with the elongated 1.94 Å on the MEDO side, and (4) a Si–OCH$_3$ of 2.03 Å formed on the DPM side as shown in Figure 5b.

DPDM and MEMDO are the products from the switching reaction in the second reaction step. There exist three possible condensation reactions by these molecules. The first one is the attack of a MEMDO hydroxyl on a DPDM methoxy, which is shown in Figure 6a. The transition barrier is 14.0 kcal/mol. Parts b and c of Figure 6 show condensation reactions between two MEMDO hydroxyls and between one MEMDO hydroxyl and one MEMDO methoxy, respectively, with barriers of 18.7 and 19.8 kcal/mol. We find that condensation between one DPDM methoxy and one MEMDO hydroxyl has the largest reaction rate of $1.22 \times 10^{-10}$ s$^{-1}$, thus in the third reaction step the process to produce the DPDM–MEMDO dimer as seen in Figure 7f is considered to be the most probable. The dimer can be also grown by condensation between a methoxy of a dimer DPDM site and a hydroxyl of a dimer MEMDO site, but its reaction is determined to have a smaller rate of $2.76 \times 10^{-11}$ s$^{-1}$ than that for the case between a DPDM methoxy and a

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**Figure 2.** B3LYP/6-31G transition-state geometries for condensations between (a) a DPD hydroxyl on a DPD hydroxyl, (b) a DPD hydroxyl on a MEMO methoxy, (c) a MEMO methoxy on a DPD hydroxyl, and (d) a MEMO methoxy on a MEMO methoxy as well as for the switching reaction between (e) a DPD hydroxyl and a MEMO methoxy. Ph and MCP indicate phenyl and methacryloxypropyl groups, respectively. Bond lengths are in angstroms.

**Figure 3.** B3LYP/6-31G transition-state geometries for condensations between (a) a DPD and a CH$_3$OH and (b) a MEMO and a H$_2$O. Ph and MCP indicate phenyl and methacryloxypropyl groups, respectively. Bond lengths are in angstroms.
MEMDO hydroxyl. Meanwhile, this rate is found to be slightly larger than the $1.17 \times 10^{-11}$ s$^{-1}$ for condensation between a hydroxyl of a dimer MEMDO site and a methoxy of a dimer MEMDO site. Here, it should be noted that the reaction rate on the larger nanostructures become smaller. This might be due to the increased geometry hindrance. Additionally, our SANS (small-scattering neutron scattering) measurements determine that the final products from the sol–gel reaction are mostly on the nanometer scale at sizes from 1.76 to 2.36 nm, which compare to the value of 2.01 nm determined on the elongated product by three dimers. The experimental size of the products is determined from the $R_g$ (radius of gyration) of the products measured by SANS (small-angle neutron scattering). The products of the reaction between DPD (50 mol %) and MEMO (50 mol %) are solvated in 10 wt % acetone-$d_6$ to obtain accurate SANS results. Under this condition, $R_g$ of the products is 0.68 nm. When the structure of the particle is spherical, the radius of the particle is $R = \sqrt[3]{3R_g}$, whereas the length of the rodlike particle is $L = \sqrt{12R_g}$. Consequently, the experimentally predicted size of the products is in the range of 1.76–2.36 nm.

B. Effects of H$_2$O on the Sol–Gel Reaction. H$_2$O can be released from the catalyst. The enthalpy of H$_2$O dissociation from the catalyst of Ba(OH)$_2$:H$_2$O is calculated to be endothermic by 3.8 kcal/mol, whereas those from Sr(OH)$_2$:H$_2$O and Ca(OH)$_2$:H$_2$O are endothermic by 3.2 and 2.5 kcal/mol, respectively. Figure 8a describes a concerted H$_2$O attack on hydroxyl fragments of two DPDs by forming a six-centered structure that involves one H atom transfer from the H$_2$O to the DPD hydroxyl, bond dissociation of a Si–O bond to generate one H$_2$O molecule, one H atom transfer from the DPD OH to the attacking H$_2$O, and formation of a Si–O–Si bond. It is to be noted that H$_2$O participates in this reaction as a catalyst donating one hydrogen atom to the DPD hydroxyl and accepting one hydrogen atom from the other DPD hydroxyl simultaneously. The predicted barrier for this reaction is 16.9 kcal/mol with respect to an intermediate water complex formed from two DPD molecules, and this reaction is determined to be exothermic by 3.3 kcal/mol. Consequently, its predicted barrier and exothermic enthalpy indicate that the presence of H$_2$O included in the catalyst can significantly reduce the condensation rate between two DPDs. Before making a transition-state structure, H$_2$O and two DPD molecules form a water-mediated structure with a high exothermic enthalpy of 20.0 kcal/mol due to three hydrogen bonds between one hydrogen atom of the H$_2$O and the oxygen atom of a DPD hydroxyl, between one H atom of another DPD hydroxyl and the oxygen atom of the H$_2$O molecule, and between the hydrogen atom of one DPD and the oxygen atom of another DPD.

A concerted attack of the DPD on the MEMO in the presence of the H$_2$O is also described in Figure 8b, where the transition state is a six-centered ring structure. This step consists of several competing reactions. These are (1) one H atom transfer from the H$_2$O to the O atom of a Si–OCH$_3$ group in MEMO, (2) Si–OCH$_3$ bond dissociation, (3) one H atom transfer from the DPD hydroxyl to the H$_2$O, and (4) Si–O–Si bond formation. We obtain a transition-state barrier of 12.5 kcal/mol, and this process is found to be exothermic by 4.9 kcal/mol. The decreased barrier indicates that the presence of the catalyst can increase the condensation rate between one DPD and one MEMO, which is opposite to the case between two DPDs.

The H$_2$O effect on the switching reaction between DPD and MEMO is also explored. The transition state of this reaction is based on a six-centered ring structure as shown Figure 8c. The hydroxyl group of the catalyst H$_2$O attaches the MEMO silicon atom to form a Si–OH bond in the MEMO while one H$_2$O molecule is newly generated by bonding between the remaining H of the attacking water with a DPD hydroxyl. Simultaneously, a MEMO methoxy transfers to the DPD to replace the DPD hydroxyl with the methoxy group. The transition barrier for this case is 30.5 kcal/mol, which is higher than the cases of DPD with DPD and DPD with MEMO. Consequently, this result

Figure 4. Products of H$_2$O or CH$_3$OH with a C=C or C=O of MEMO: (a) a CH$_3$OH with a C=C, (b) a CH$_3$OH with a C=O, (c) a H$_2$O with a C=C, and (d) a H$_2$O with a C=O.
Table 1: KMLYP/6-311+G(d,p)/B3LYP/6-31G Transition-State Barriers and Enthalpies for the Sol–Gel Processes Using DPD and MEMO Precursors

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<th>Barrier (kcal/mol)</th>
<th>Enthalpy (kcal/mol)</th>
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<td>14.9</td>
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<td></td>
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<td>73.1</td>
<td>-8.4</td>
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<td></td>
<td>MEMO OCH₃ + MEMO OCH₃ → MEMO-MEMO + (CH₃)₂O</td>
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Switching Reaction

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<tr>
<td>DPD OH + MEMO OCH₃ → DPM + MEDO</td>
<td>6.9</td>
<td>-0.4</td>
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IV. Summary and Conclusions

Making the hybrid materials from the sol–gel reaction with nanometer-scale sizes is one interesting issue today. This is because the nanosizes of the resulting hybrid materials are useful for making fine nanostructures of optical waveguides and getting homogeneous properties within a waveguide. A first-principles calculation and experimental SANS measurement methods have been used to investigate the mechanism and the nanosize products of the sol–gel reaction using DPD and MEMO precursors. To determine the size of the products resulting from the sol–gel reaction, we have first explored the reaction mechanism by comparing the rates of all possible reactions at each step. It has been found that the switching reaction between a DPD hydroxyl and a MEMO methoxy having a kinetic frequency of 6.80 × 10⁻⁶ s⁻¹ at room temperature, which generates one DPM and one MEDO as products, is the fastest process in the first reaction step. However, it has been determined that the reaction pathway can be modified by the presence of a catalyst such as Ba(OH)₂ because the H₂O released from the catalyst changes the reaction barrier. In the second reaction step, we have also found that the switching...
reaction between the DPM hydroxyl and the MEDO methoxy forming DPDM and MEMDO is the most favorable. This switching has a reaction rate of $4.61 \times 10^{-7}$ s$^{-1}$. Next, the condensation between a methoxy of DPDM and a hydroxyl of MEMDO having a reaction rate of $1.22 \times 10^{-10}$ s$^{-1}$ has been determined to be most favorable in the third reaction step, which generates the DPDM--MEMDO dimer. In a similar fashion, additional growth has been found to occur by condensation between a methoxy of the dimer in the DPDM site and a hydroxyl of the dimer in the MEMDO site, which has a reaction
TABLE 2: Computed Frequencies of Various Stretching Modes for SiOH and SiOCH₃ of DPD, MEMO, DPM, and MEDO at the B3LYP/6-31G Level with a Scaling Factor of 0.961a

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3600–3200b 2840b

Frequencies in units of cm⁻¹. a Experimental values taken from ref 7.

rate of 2.76 × 10⁻¹¹ s⁻¹. In addition, our SANS measurements have shown that the final products for the sol–gel reaction are on the nanometer scale at sizes of 1.76–2.36 nm, which compare to the size of 2.01 nm for the elongated structure by

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**References and Notes**