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 × 10⁻⁶ s⁻¹ at 300 K is the fastest process for the first reaction step, thus generating diphenylethoxyxilanol (DPE) and 3-methacryloxypropylmethoxysilanol (MEDO) as products. However, we determine that this reaction pathway could be modified by the presence of the H₂O released from a catalyst such as Ba(OH)₂·H₂O. Next, switching between the DPM hydroxyl and the MEDO methoxy is followed to generate diphenyldimethoxysilane (DPDM) and 3-methacryloxypropylmethoxysiloxane (MEMDO). However, condensation between a MEMDO hydroxyl and a DPD methoxy is found to be most favorable for the third reaction step, which generates the DPD–MEMDO dimer and CH₃OH molecule as products. In a similar fashion, a DPD methoxy of the DPD–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 × 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.

1. 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 to produce siloxane (−SiO−Si−) bridges, and the second step involves cross linking between organic side chains of the inorganic structures in a 3D network by UV light. However, depending on the nature of the interface between organic and inorganic elements in hybrid materials, they are classified into two different groups. One group has their organic and inorganic components linked through van der Waals or hydrogen bonding, and the other group has its network formed through covalent or ionic bonding.

Buestrich et al. and Houbertz et al. synthesized a hybrid material from the sol–gel reactions using diphenylsilanediol (DPD) and 3-methacryloxypropyltrimethoxysilane (MEMO) precursors. A combination of DPD, having OH groups for non-hydrolytic processes, with MEMO, enabling the resulting materials to be patterned by UV, provides a good precursor system. Their IR study shows that there is no SiO−H stretching mode (3600−3200 cm⁻¹) in their synthesized hybrid material that results in low scattering losses (0.3 dB/cm at 1320 nm and 0.6 dB/cm at 1550 nm). It has also shown good adhesion on a silicon substrate and a relatively low processing temperature of 150 °C. However, detailed thermodynamic and kinetic parameters for intermediate nanostructures likely to be produced from the reactions using DPD and MEMO precursors are not reported. Also, there still remains considerable ambiguity as to whether the final products from the sol–gel reaction could be on the nanometer scale.

Here, we use a first-principles calculation and small-angle neutron scattering (SANS) methods to determine the mechanisms and intermediate nanostructures for the sol–gel processes using DPD and MEMO precursors. First, we investigate condensation reactions between two DPDs, between one

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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 diphenyloxethane-1,3-diols (DPM) and 3-methacycloxypropylmethoxysilanol (MEDO) as products. Then, the catalytic effects by the \( \text{H}_2\text{O} \) released from a catalyst such as \( \text{Ba(OH)}_2 \cdot \text{H}_2\text{O} \) 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 diphenyloxethane-1,3-diols (DPDM) and 3-methacycloxypropylmethoxysilanol (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 B3LYP\(^{20}\) and KMLYP\(^{21}\) density functional theories and using the QCISD\(^{22}\) 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 barriers\(^{21,33,34}\) than other DFT methods.

The electronic wave function is expanded using the 6-31G valence double-\(\zeta\)+ basis set and the 6-311+G(d,p) valence diffuse triple-\(\zeta\) plus polarization\(^{35}\) basis set. In this study, the full optimizations of all 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/6-311+G(d,p) 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 sp\(^3\)-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-methacycloxypropyl 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–OCH\(_3\) fragments of the MEMO are active groups that form a siloxane bridge (–Si–O–Si–), thereby releasing H\(_2\)O or CH\(_3\)OH as a byproduct.

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 \( k^{\text{TST}} \) of the canonical rate equation\(^{39}\) is determined by

\[
k^{\text{TST}} = \Gamma(T) \frac{k_B T}{h} \frac{Q_A}{Q_B} \exp\left(-\frac{\Delta E_0}{k_B T}\right)
\]

where \( \Gamma(T) \) is the thermal tunneling coefficient,\(^{21}\) \( k_B \) is the Boltzmann constant, \( h \) is the Planck 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-workers\(^{7}\) 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 CH\(_3\)OH should also be generated as a byproduct. Then, CH\(_3\)OH 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 \( 1.81 \times 10^{-10} \)}
This reaction rate is found to be much smaller than 6.80 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 silicon 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–OCH₃ bond begins to form on the DPD side, whereas the MEMO Si–OCH₃ bond length of 2.10 Å indicates a considerable amount of the bond being broken.

We also explore the reactions by the byproducts of H₂O and CH₃OH 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 CH₃OH (Figure 3a), generating H₂O and DPM as products with a barrier of 19.8 kcal/mol. The condensation reaction between the MEMO methoxy and the H₂O as shown in Figure 2 is the second type, and it is determined to produce CH₃OH 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 CH₃OH or H₂O 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 CH₃OH (the third type) and the barriers of 40.4 to 141.7 kcal/mol by H₂O (the fourth type) are considerably high as compared to those for the first and second types. The largest reaction rate of 6.45 × 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 × 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 MEMO hydroxyl, between one DPM hydroxyl and one MEMO methoxy, between one DPM methoxy and one MEMO hydroxyl, between one DPM methoxy and one MEMO methoxy, between two MEDO hydroxyls, between one MEDO 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 × 10⁻⁸ s⁻¹. However, the switching reaction between a DPM hydroxyl and a MEMO methoxy, generating DPD and MEMO as products, is determined to have a much larger rate of 4.61 × 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–OCH₃ bond being broken with the elongated 1.94 Å on the MEDO side, and (4) a Si–OCH₃ 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 × 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 × 10⁻¹¹ s⁻¹ than that for the case between a DPDM methoxy and a...
noted that H₂O participates in this reaction as a catalyst donating one hydrogen atom to form a Si–O bond. Simultaneously, a MEMO methoxy transfers to the DPD to replace the DPD hydroxyl group. It is to be noted that H₂O 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 H₂O included in the catalyst can significantly reduce the condensation rate between two DPDs. Before making a transition-state structure, H₂O 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 H₂O and the oxygen atom of a DPD hydroxyl, between one H atom of another DPD hydroxyl and the oxygen atom of the H₂O 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 H₂O 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 H₂O to the O atom of a Si–OCH₃ group in MEMO, (2) Si–OCH₃ bond dissociation, (3) one H atom transfer from the DPD hydroxyl to the H₂O, 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 H₂O 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 H₂O attaches the MEMO silicon atom to form a Si–OH bond in the MEMO while one H₂O 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
Mechanism/Nanosize Products of Sol–Gel Reaction

**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

<table>
<thead>
<tr>
<th>sequence</th>
<th>reaction</th>
<th>barrier</th>
<th>enthalpy</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Condensation Reaction</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Step I</td>
<td>DPD OH + DPD OH → DPD–DPD + H₂O</td>
<td>14.9</td>
<td>−9.1</td>
</tr>
<tr>
<td></td>
<td>DPD OH + MEDO OCH₃ → DPD–MEDO + CH₂OH</td>
<td>15.1</td>
<td>−8.4</td>
</tr>
<tr>
<td></td>
<td>DPD OH + MEDO OCH₃ → DPD–MEDO + CH₂OH⁺</td>
<td>73.1</td>
<td>−8.4</td>
</tr>
<tr>
<td></td>
<td>MEMO OCH₃ + MEMO OCH₃ → MEMO-MEMO + (CH₃)₂O</td>
<td>69.3</td>
<td>−12.7</td>
</tr>
<tr>
<td><strong>Switching Reaction</strong></td>
<td>DPD OH + MEDO OCH₃ → DPM + MEDO</td>
<td>6.9</td>
<td>−0.4</td>
</tr>
<tr>
<td><strong>Condensation Reaction</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Step II</td>
<td>DPM OH + DPM OH → DPM–DPM(I) + H₂O</td>
<td>18.5</td>
<td>−9.7</td>
</tr>
<tr>
<td></td>
<td>DPM OH + DPM OCH₃ → DPM–DPM(II) + CH₂OH⁺</td>
<td>16.3</td>
<td>−8.3</td>
</tr>
<tr>
<td></td>
<td>DPM OH + DPM OCH₃ → DPM–DPM(II) + CH₂OH⁺</td>
<td>68.5</td>
<td>−8.3</td>
</tr>
<tr>
<td></td>
<td>DPM OCH₃ + DPM OH → DPM–DPM(III) + (CH₃)₂O</td>
<td>69.5</td>
<td>−11.9</td>
</tr>
<tr>
<td></td>
<td>DPM OH + MEDO OH → DPM–MEDO(I) + H₂O</td>
<td>15.8</td>
<td>−9.4</td>
</tr>
<tr>
<td></td>
<td>DPM OH + MEDO OH → DPM–MEDO(I) + H₂O⁺</td>
<td>17.7</td>
<td>−9.4</td>
</tr>
<tr>
<td></td>
<td>DPM OCH₃ + MEDO OH → DPM–MEDO(II) + CH₂OH⁺</td>
<td>16.2</td>
<td>−8.0</td>
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<tr>
<td></td>
<td>DPM OCH₃ + MEDO OH → DPM–MEDO(II) + CH₂OH⁺</td>
<td>64.6</td>
<td>−8.0</td>
</tr>
<tr>
<td></td>
<td>DPM OH + MEDO OCH₃ → DPM–MEDO(III) + CH₂OH⁺</td>
<td>12.1</td>
<td>−8.2</td>
</tr>
<tr>
<td></td>
<td>DPM OH + MEDO OCH₃ → DPM–MEDO(III) + CH₂OH⁺</td>
<td>65.6</td>
<td>−8.2</td>
</tr>
<tr>
<td></td>
<td>DPM OCH₃ + MEDO OH → DPM–MEDO(IV) + (CH₃)₂O</td>
<td>59.9</td>
<td>−11.7</td>
</tr>
<tr>
<td></td>
<td>DPM OCH₃ + MEDO OH → DPM–MEDO(IV) + (CH₃)₂O⁺</td>
<td>73.1</td>
<td>−11.7</td>
</tr>
<tr>
<td></td>
<td>MEDO OH + MEDO OH → MEDO-MEDO(I) + H₂O</td>
<td>19.5</td>
<td>−9.0</td>
</tr>
<tr>
<td></td>
<td>MEDO OH + MEDO OH → MEDO-MEDO(I) + H₂O⁺</td>
<td>16.8</td>
<td>−9.3</td>
</tr>
<tr>
<td></td>
<td>MEDO OH + MEDO OH → MEDO-MEDO(II) + CH₂OH⁺</td>
<td>71.8</td>
<td>−9.3</td>
</tr>
<tr>
<td></td>
<td>MEDO OCH₃ + MEDO OCH₃ → MEDO-MEDO(III) + (CH₃)₂O</td>
<td>68.2</td>
<td>−13.0</td>
</tr>
<tr>
<td><strong>Switching Reaction</strong></td>
<td>DPM OH + MEDO OCH₃ → DPD + MEMDO</td>
<td>8.5</td>
<td>−0.6</td>
</tr>
<tr>
<td><strong>Condensation Reaction</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Step III</td>
<td>DPD OCH₃ + MEMDO OH → DPD–MEMDO + CH₂OH</td>
<td>14.0</td>
<td>−7.6</td>
</tr>
<tr>
<td></td>
<td>MEMDO OH + MEMDO OH → MEMDO-MEMDO(I) + H₂O</td>
<td>18.7</td>
<td>−9.1</td>
</tr>
<tr>
<td></td>
<td>MEMDO OH + MEMDO OCH₃ → MEMDO-MEMDO(II) + CH₂OH⁺</td>
<td>19.8</td>
<td>−8.3</td>
</tr>
</tbody>
</table>

* Energies are in units of kcal/mol. a DPD OH attack. b MEMO OCH₃ attack. c DPM OH attack. d DPM OCH₃ attack. e DPM OCH₃ attack. f MEDO OH attack. g MEDO OH attack. h MEDO OCH₃ attack. i DPM OH attack. j DPM OCH₃ attack. k MEDO OCH₃ attack. l MEDO OCH₃ attack. m MEDO OCH₃ attack.

**Figure 5.** B3LYP/6-31G transition-state geometries for (a) condensation between a DPM hydroxyl and a MEDO methoxy and (b) switching between a DPM hydroxyl and a MEDO methoxy. Ph and MCP indicate phenyl and methacryloxypropyl groups, respectively. Bond lengths are in angstroms.

indicates that the final nanostructure could be modified by the presence of H₂O. This is because the H₂O released from the catalyst plays an important role in changing reaction pathways to modify the resulting product.

**C. Vibrational Frequencies.** We compute the frequencies of SiOH and SiOCH₃ fragments in the DPD, MEMO, DPM, and MEMO molecules at the B3LYP/6-31G level of theory using a scaling factor of 0.961. The previous study showed that the scaling factor for B3LYP frequencies to match with experimental values is closer to the scaling factor of unity than for the case with KMLYP. In this respect, we report only the vibrational frequencies obtained through the B3LYP calculations. The predicted frequency for a DPD Si–OH stretching mode is 648 cm⁻¹, whereas the frequency for a DPD Si–O–H stretching mode is in the range of 3623–3621 cm⁻¹, which is consistent with experimental IR peaks of 3600–3200 cm⁻¹.

We also determine the frequencies of 561 and 1044 cm⁻¹, respectively, for MEMO Si–OCH₃ and SiO–CH₃ stretching modes. In addition, a C–H stretching mode of the MEMO SiOCH₃ is found to be in the range of 2921–2911 cm⁻¹. All frequencies in DPD and MEMO are similar to those in DPD and MEMO, which are shown in Table 2.

**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 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·H₂O 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.

**Figure 6.** B3LYP/6-31G transition-state geometries for condensations between (a) a DPDM methoxy and a MEMDO hydroxyl, (b) two MEMDO hydroxyls, and (c) a MEMDO hydroxyl and a MEMDO methoxy. Ph and MCP indicate phenyl and methacryloxypropyl groups, respectively. Bond lengths are in angstroms.

**Figure 7.** Products for condensations between (a) two DPM hydroxyls, (b) a DPM hydroxyl and a DPM methoxy, (c) two DPM methoxys (or two DPD hydroxyls), (d) one DPM hydroxyl and one MEDO hydroxyl, (e) one DPM methoxy and one MEDO methoxy (or one DPD hydroxyl and one MEMO methoxy), (f) one DPM hydroxyl and one MEDO methoxy (or one DPD methoxy and MEMDO hydroxyl), (g) one DPM methoxy and one MEDO hydroxyl (or one DPDM methoxy and MEMDO hydroxyl), (h) two MEDO hydroxyls (or two MEMO methoxys), (i) one MEDO hydroxyl and one MEDO methoxy, (j) two MEDO methoxys (or two MEMDO hydroxyls), and (k) one MEMDO hydroxyl and one MEMDO methoxy.

**Figure 8.** Catalytic effects of H$_2$O on transition states for (a) condensation between two DPDs, (b) condensation between a DPD hydroxyl and a MEMO methoxy, and (c) switching between a DPD hydroxyl and a MEMO methoxy. Ph and MCP indicate the phenyl group and methacryloxypropyl group, respectively. Bond lengths are in angstroms, where the B3LYP/6-31G geometries are used.
rate of $2.76 \times 10^{-11}$ 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

\begin{table}[h]
\centering
\caption{Computed Frequencies of Various Stretching Modes for SiOH and SiOCH$_3$ of DPD, MEMO, DPM, and MEDO at the B3LYP/6-31G Level with a Scaling Factor of 0.961$^a$}
\begin{tabular}{|c|c|c|c|c|c|}
\hline
molecule & Si–OH & Si–O–H & Si–OCH$_3$ & Si–OCH$_3$ & Si–OC–H$_3$ \\
\hline
DPD & 648 & 3623 & 3621 & & \\
MEMO & 561 & 1044 & 2921 & 2913 & 2911 \\
DPM & 695 & 3621 & 712 & 1037 & 2911 \\
MEDO & 647 & 3644 & 570 & 1058 & 2922 \\

\hline
& 1052 & 2912 & 1045 & & \\

\hline
& 3600–3200$^b$ & & & 2840$^b$ & \\
\hline
\end{tabular}
\end{table}

$^a$ Frequencies in units of cm$^{-1}$. $^b$ Experimental values taken from ref. 7.

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References and Notes