

Condensation reaction of 3-(methacryloxypropyl)-trimethoxysilane and diisobutylsilanediol in non-hydrolytic sol-gel process

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Abstract The condensation reaction of 3-methacryloxypropyl-trimethoxysilane (MPTS) and diisobutylsilanediol (DIBSD) in a non-hydrolytic sol-gel process was investigated in terms of the reaction time and the catalyst amount for fabrication of inorganic-organic hybrid materials. The degree of condensation, which was characterized by ^{29}Si NMR, ^1H NMR and Abbe refractometry, increases with increased the reaction time and greater catalyst amount. However, a large catalyst amount breaks the methacryl group during the condensation reaction. Thus, the reaction time and the catalyst amount were optimized to synthesize the condensed methacryl oligosiloxanes.

Keywords Hybrid materials · Condensation reaction · Non-hydrolytic sol-gel · NMR

Introduction

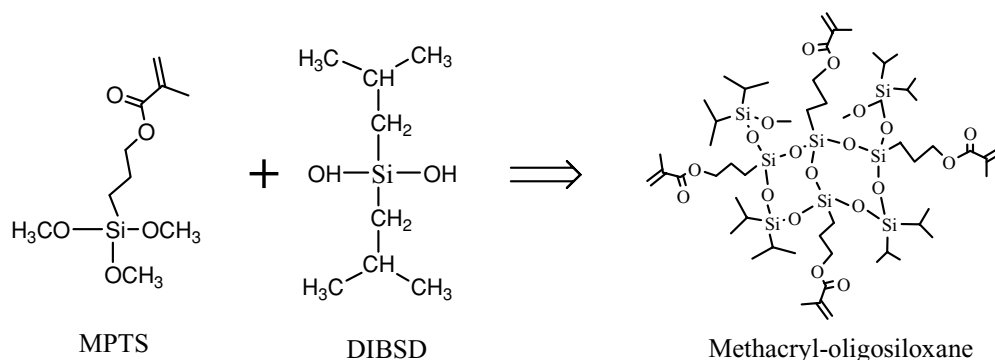
Sol-gel derived inorganic-organic hybrid materials have attracted considerable attention in recent years because of the variety of potential applications provided by the synergistic combination of inorganic oxides with organic compounds [1, 2]. Generally, homogeneously dispersed inorganic-organic

hybrid materials are synthesized by a hydrolytic sol-gel process involving the hydrolysis and condensation reactions of alkoxide (or other) precursors in a solvent system while precluding the common problem of premature phase separation. However, the hydrolysis and condensation reaction in the hydrolytic route suffer from problems associated with the use of water and the need for a compatible solvent. The non-hydrolytic sol-gel process is recognized as a useful route to overcome problems in the traditional hydrolytic sol-gel process. Employing the non-hydrolytic sol-gel process has the potential to avoid the use of solvents, which have various drawbacks, can be avoided. In addition, residual silanol groups in the product resulting from the different mechanistic course of the reaction can be reduced or eliminated with the hydrolytic sol-gel route [3–5]. Accompanying the advantages of the non-hydrolytic sol-gel process, various hybrid materials can be designed by suitable selection of starting precursors, as the properties of the hybrid material mainly rely on the starting precursor. Among the hybrid materials that can be produced through diverse combinations of precursors, those derived from the condensation of organo-alkoxysilane and organosilandiol have been reported under the name of ORMOCER or HYBRIMER [6–8]. Most of these hybrid materials are methacryl-oligosiloxane hybrid materials synthesized by the condensation of 3-methacryloxypropyl-trimethoxysilane (MPTS) and diphenylsilanediol (DPSD). It has been reported that methacryl-oligosiloxane hybrid materials can be used in electronic and optical applications [9].

While the condensation reaction is important to form a desirable molecular structure in the hybrid material, it is not yet fully understood. In addition, the use of commercially available diphenylsilanediol (DPSD) in the synthesis of methacryl-oligosiloxane hybrid materials produces high refractive indices and dielectric constants of the materials

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Scheme 1 Notations of the molecular structure of methacryl oligosiloxanes in ^{29}Si NMR spectra

due to the existence of the phenyl group in the DPSD. In the present study, a new type of methacryl oligosiloxanes hybrid material with lower refractive indices and dielectric constants is prepared using our synthesized diisobutylsilanediol (DIBSD) instead of DPSD. Specifically, the methacryl oligosiloxanes hybrid materials are formed by the condensation reaction of the methoxy groups of the MPTS and the diol groups of the DIBSD, as illustrated in Scheme 1.

In order to obtain a stable and reliable methacryl oligosiloxanes hybrid material, the condensation reaction must be optimized so as to obtain condensed oligosiloxanes. In this study, variation of the methacryl oligosiloxane molecular structure derived from the condensation reaction was investigated in relation to reaction time and catalyst amount. The optimized conditions for the most condensed methacryl oligosiloxanes were thereupon identified.

Experiments

Synthesis of methacryl oligosiloxanes

Diisobutylsilanediol (DIBSD, $(\text{C}_4\text{H}_9)_2\text{Si}(\text{OH})_2$) and 3-methacryloxypropyl trimethoxysilane (MPTS, $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CO}_2(\text{CH}_2)_3-\text{Si}(\text{OCH}_3)_3$, Aldrich) were used as starting precursor molecules without further purification. A catalyst of barium hydroxide monohydrate ($\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$, Aldrich) was used to promote the hetero-functional condensation reaction between the precursors. DIBSD and MPTS with equal molar ratio in catalyst were mixed without solvent in 100 ml round bottom flasks equipped with a magnetic stirrer. The solution was heated at 80°C with a reflux condenser for accelerating the reaction velocity. Reaction time was measured with reflux condenser in a heated flask. Afterwards the evaporation and vacuum heating were quickly conducted in order to extract the volatile element (here methanol), which is the by-product of the hetero-condensation reaction be-

tween the diol and methoxy groups in the non-hydrolytic sol-gel process. The resin was cooled to room temperature and filtered through a $0.45\ \mu\text{m}$ -size filter to remove the insoluble barium salt of the catalyst.

Characterization

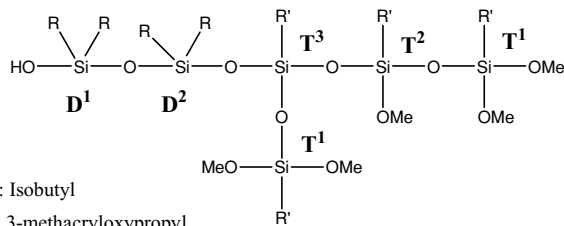
Nuclear Magnetic Resonance (NMR) spectra were recorded using a Bruker AMX FT at 500 MHz for ^1H and 99.36 MHz for ^{29}Si . The sample for NMR measurement was prepared from 30 vol% resin sample in Aceton- d_6 (containing v/v 0.1% Tetramethylsilane (TMS), Aldrich). Tetramethylsilane (TMS) was used as an internal reference. An appropriate quantity of the sample solution was injected via syringe into a NMR glass tube and the samples were shaken briefly without allowing the solution to warm significantly. The sample was then transferred immediately to the NMR spectrometer probe which had already been equilibrated at the desired temperature. Pulse delays were set at $10\ \mu\text{s}$ for ^1H and $12\ \mu\text{s}$ for ^{29}Si and relaxation times were set at 1.00 s for ^1H and 30.0 s for ^{29}Si . FT-IR spectra of the resins were recorded on a JASCO FT-IR 460plus spectrophotometer and at least 50 scans were averaged for each spectrum, and the resolution was $\pm 0.4\ \text{cm}^{-1}$. The refractive indices of the resin were measured using an Abbe refractometer (Bellingham Stanley Ltd 60/ED) at 589.6 nm.

Results and discussion

Effect of reaction time

As the condensation reaction of the methoxy groups of MPTS and the diol groups of DIBSD proceeds, methacryl oligosiloxanes are successively formed during the reaction. The methacryl oligosiloxanes result from a hetero-condensation reaction producing methanol as a by-product and are composed of siloxane bonds and photopolymerizable methacryl groups.

Table 1 Assignment of chemical shift of silane species with bond state in ²⁹Si NMR spectra



Species	Chemical Shift (ppm)
D ⁰ (C ₄ H ₉) ₂ Si(OCH ₃) ₂	- 5.1224
D ⁰ (C ₄ H ₉) ₂ Si(OH) ₂	- 8.4011
D ¹	- 10 ~ - 16
D ²	- 20 ~ - 25
T ⁰	-41.907
T ¹	- 49 ~ - 51
T ²	- 57 ~ - 61
T ³	- 65 ~ - 69

In order to elucidate the effect of reaction time on the condensation reaction, ²⁹Si NMR spectroscopy was used to detect siloxane bonds in the methacryl oligosiloxanes hybrid materials. ²⁹Si NMR spectroscopy yields information on the connectivity of the siloxane bonds, which can confirm the formation of methacryl oligosiloxanes. The notations of different siloxane bonds and the assignments of their chemical shifts in the ²⁹Si NMR spectroscopy are shown in Table 1 [6]. Di-functional and tri-functional silicon sites are labeled with the conventional *Dⁿ* and *T^m* notation, respectively, and the superscript *n* denotes the number of siloxane bonds [11]. Figure 1 represents the ²⁹Si NMR spectra of methacryl oligosiloxanes yielded from the condensation reaction depending on the reaction time. Significant changes appear in the ²⁹Si NMR spectra with increased reaction time. In the initial stage of the condensation reaction (30 min), a small amount of starting precursor (*T⁰*) of MPTS remains while the starting precursor (*D⁰*) of DIBSD cannot be detected, because DIBSD is more reactive than MPTS, which has greater hydrostatic volume than DIBSD. This indicates that the condensation reaction is rapidly made in the early stage of reaction. With increased reaction time, transformation of the molecular structure was observed with decreasing *D¹*, *T¹* and increasing *D²*, *T²*, *T³* by means of ²⁹Si NMR spectra. Finally, the molecular structure in methacryl oligosiloxanes is mainly composed of dimers, trimers, and tetramers as a result of the condensation reaction. The degree of condensation is determined by calculation of the integration of the ²⁹Si NMR peaks at fixed chemical shift regions, as previously reported [12].

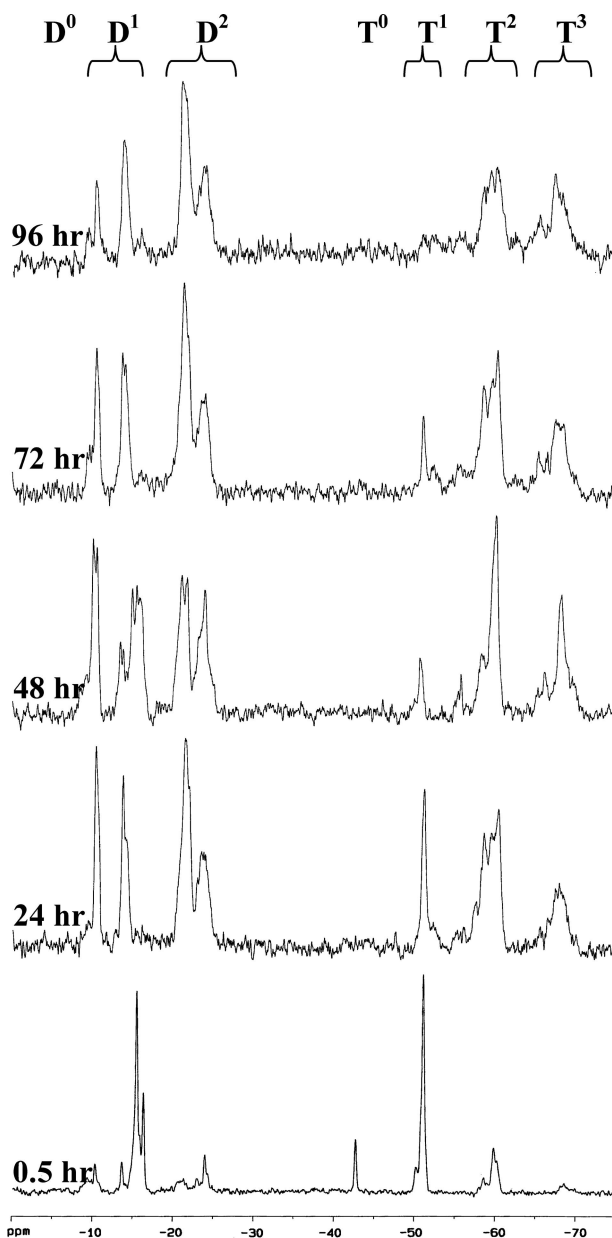


Fig. 1 ²⁹Si NMR spectra corresponding to the progression of condensation reaction as a function of reaction time (catalyst amount of 0.00125 mol/Si)

$$\frac{D^1 + 2D^2 + T^1 + 2T^2 + 3T^3}{2(D^0 + D^1 + D^2) + 3(T^0 + T^1 + T^2 + T^3)} \times 100 \quad (1)$$

Figure 2 presents the change in the degree of condensation as a function of reaction time. In the first stage of the reaction, the degree of condensation increases rapidly from 53% to 73%, and is almost saturated after 24 h. At 96 h of reaction, the degree of condensation (≈79%) is high enough that has high viscosity (~500 cps). Thus, it is confirmed that siloxane bonds are formed by the condensation reaction to make methacryl oligosiloxanes.

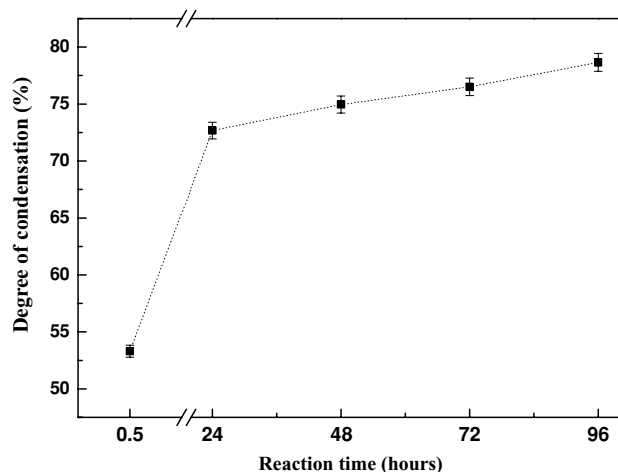


Fig. 2 Degree of condensation as a function of reaction time (catalyst amount of 0.00125 mol/Si)

In order to attain a more detailed understanding of the condensation reaction, the consumption of organic groups in precursors such as the diol groups in DIBSD and the methoxy groups in MPTS during the condensation reaction was examined by means of ^1H NMR spectroscopy. The consumption of the methoxy group of MPTS can confirm the condensation reaction of the precursors since MPTS is less reactive than DIBSD, as discussed above. The ^1H NMR spectra according to the reaction time is represented in Fig. 3. The intensity of the chemical shift of the methoxy group (3.577 ppm) in MPTS continuously decreased with the progression of the condensation reaction depending on the reaction time. At 96 h of reaction, almost all of the methoxy groups are consumed by the condensation reaction. The minimum methoxy group by the condensation reaction detected by the ^1H NMR spectra is in accordance with the maximum connectivity of the siloxane bond by the ^{29}Si NMR spectra.

The densification, which is a decrement of free volume, can also provide information on the condensation reaction. The densification was examined by measurement of the refractive index of methacryl oligosiloxanes hybrid materials, since the increase in the refractive index indicates a reduction of the free volume. In the Lorentz-Lorentz equation, the polarizability during the condensation reaction does not change and the refractive index is directly related with the free volume of the methacryl oligosiloxanes hybrid materials. Figure 4 shows the increase of the refractive index depending on the reaction time. The refractive index increases with the reaction time in the same behavior as the degree of condensation, as shown in Fig. 1. Finally, the refractive index reaches a maximum of 1.4584 at 589.6 nm with 96 h condensation reaction. Therefore, the condensation reaction continues with the reaction time and is almost completed at 96 h condensation reaction.

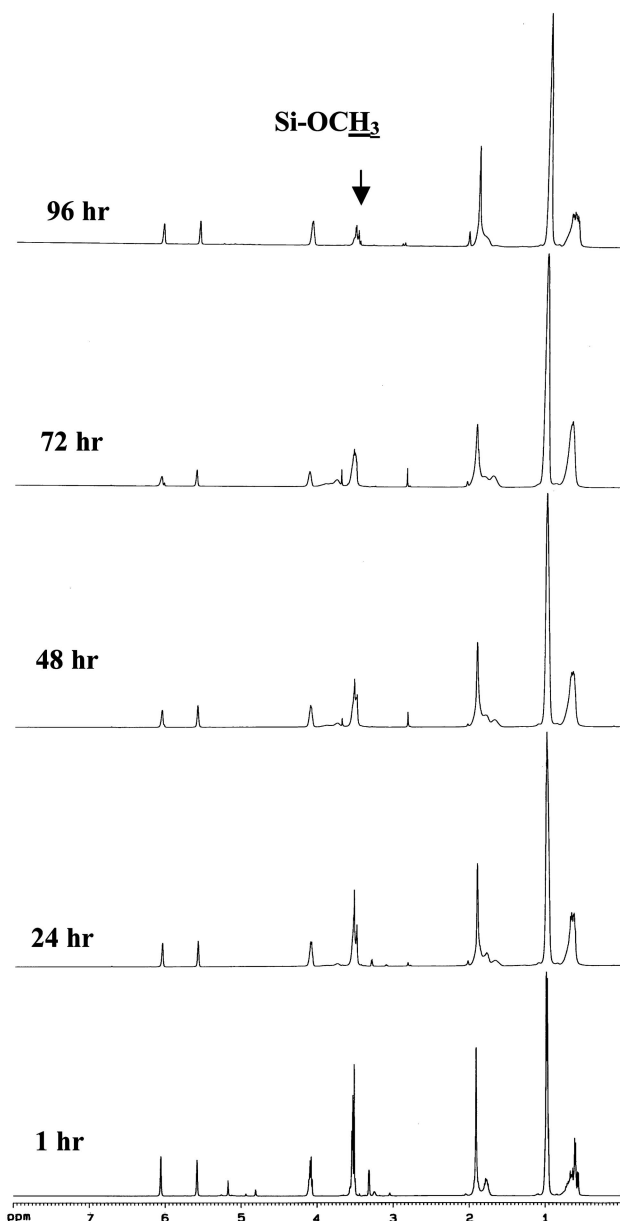


Fig. 3 ^1H NMR spectra indicate the change of chemical shift of methoxy group in methacryl oligosiloxane corresponding to the progression of condensation reaction as a function of reaction time (catalyst amount of 0.00125 mol/Si)

Effect of catalyst amount

The catalyst is an important factor to enhance and control the hetero-condensation reaction of the precursors. However, it must be carefully applied, since it creates an activated chemical environment for the condensation reaction as well as other undesirable reactions. For example, the catalyst can break the organics in the precursors during the condensation reaction. The mechanism of this action of the catalyst is currently under investigation and will be reported in a later paper.

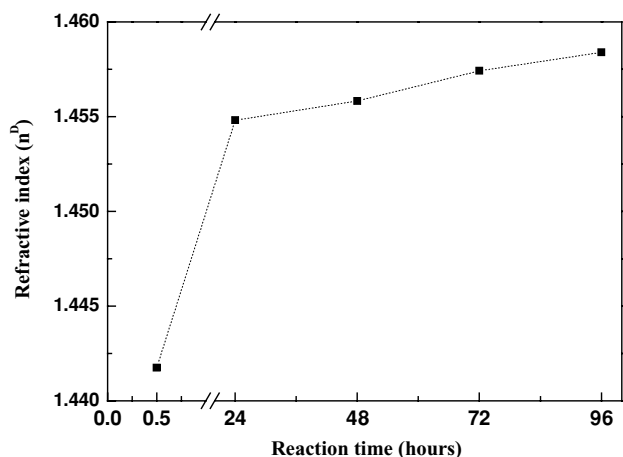


Fig. 4 Change in refractive index of methacryl oligosiloxanes as a function of reaction time (catalyst amount of 0.00125 mol/Si)

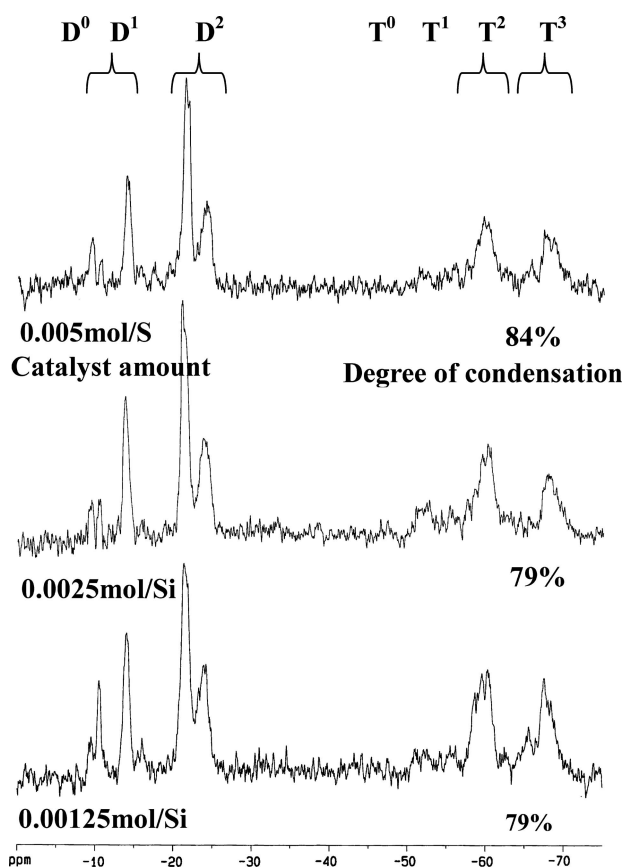


Fig. 5 ²⁹Si NMR spectra corresponding to the progression of condensation reaction as a function of catalyst amount. All reactions were conducted for 96 h

In this study, barium hydroxide monohydrate (Ba(OH)₂(H₂O)) was used for the hetero-condensation reaction. In order to optimize the catalyst amount for adequate condensation reaction without breaking the organics in the precursors, the effect of the catalyst amount on the condensation reaction was first investigated. Figure 5

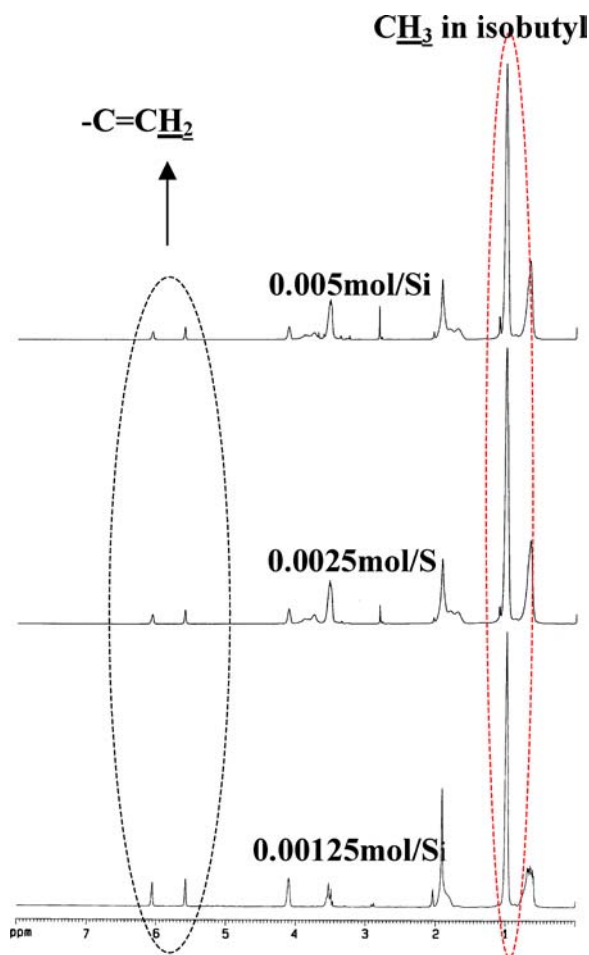


Fig. 6 ¹H NMR spectra indicate change in chemical shift of methoxy group corresponding to the progression of condensation reaction as a function of catalyst amount. All reactions were conducted for 96 h

presents the ²⁹Si NMR spectra of the samples with different catalyst amounts. The degree of condensation was calculated using Eq. (1), as above, and is given in Fig. 5. The ²⁹Si NMR spectra varied little with variation of the catalyst amount. The degree of condensation increased slightly from 79% to 84% as the catalyst amount was raised from 0.00125 mol/Si to 0.005 mol/Si. Thus, it is found that the catalyst amount has only a minor effect on the condensation reaction. Figure 6 shows the ¹H NMR spectra indicating the change of chemical shift in the tip sites of DIBSD (CH₃) and MPTS (CH₂) depending on the catalyst amount. The peak intensity of CH₃ in DIBSD is maintained regardless of the catalyst amount. On the other hand, the peak intensity of CH₂ in MPTS decreases with increasing the catalyst amount. This indicates that the methacryl group is destroyed during the condensation reaction. C=C and C=O radicals in the methacryl group of the methacryl-oligosiloxanes can be observed in the FT-IR spectroscopy depending on the catalyst amount, as shown in Fig. 7. At a low catalyst amount (0.00125 mol/Si), C=C and C=O radicals are observed.

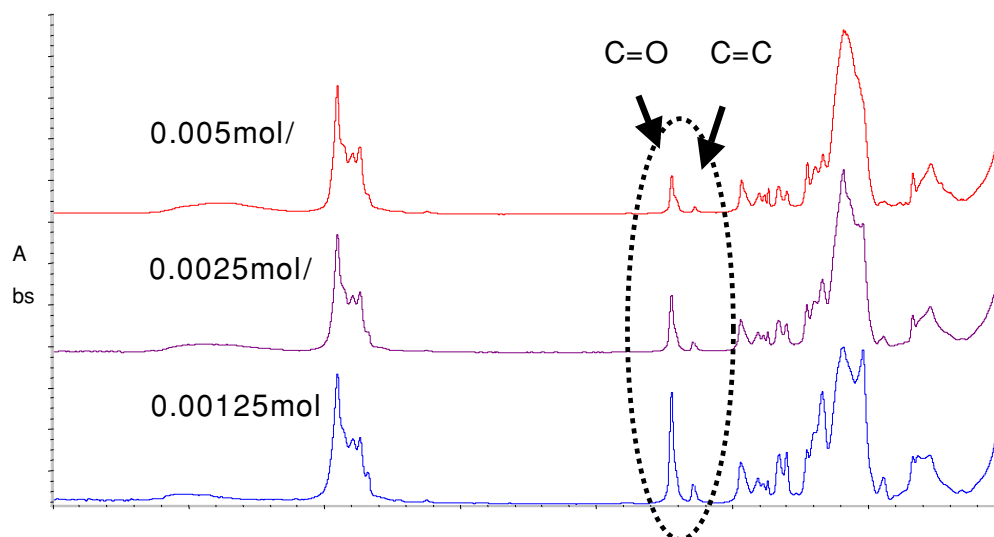


Fig. 7 FT-IR spectra corresponding to the progression of condensation reaction as a function of catalyst amount. The indicated peaks represent the C=O and C=C bonds in the methacryl group of methacryl oligosiloxanes. All reactions were conducted for 96 h

However, they are damaged at the higher catalyst amount (0.0025, 0.005 mol/Si). Thus, the larger catalyst amount breaks the methacryl groups during the condensation reaction, preventing the formation of methacryl oligosiloxanes. Therefore, an adequate concentration of catalyst should be optimized so as to form maximum connectivity of the siloxane bonds while preserving the methacryl groups in the methacryl oligosiloxanes during the condensation reaction.

Conclusion

The condensation reaction of MPTS and DIBSD to synthesize methacryl oligosiloxanes for fabrication of an inorganic-organic hybrid material was investigated in relation to reaction time and the catalyst amount. Using the ^{29}Si NMR and ^1H NMR, it was found that the degree of condensation increases up to 79% with increased reaction time. Thus, a higher refractive index of the methacryl oligosiloxanes is obtained with longer reaction time. On the other hand, the catalyst amount does not have a significant effect on the degree of condensation. Notably, a larger catalyst amount breaks the methacryl group in the methacryl oligosiloxanes during the condensation reaction. Thus, an adequate catalyst amount and longer reaction time are required to synthesize condensed methacryl oligosiloxanes.

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