



## Synthesis and characterization of sol–gel derived highly condensed fluorinated methacryl silica and silica–zirconia hybrid materials

Dong Jun Kang<sup>a,\*</sup>, Byeong-Soo Bae<sup>b</sup>

<sup>a</sup>Advanced Materials and Application Research Laboratory, Korea Electrotechnology Research Institute, 28-1 Sungju-dong Changwon, Gyeongsangnam-do 641-120, Republic of Korea

<sup>b</sup>Laboratory of Optical Materials and Coating, Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, 373-1 Guseong-dong, Yuseong-gu, Daejeon 305-701, Republic of Korea

### ARTICLE INFO

#### Article history:

Received 25 March 2008  
Received in revised form 9 July 2008  
Available online 27 August 2008

#### PACS:

81.20.Fw  
81.70.-q  
82.33.Ln

#### Keywords:

Diffraction and scattering measurements  
Neutron diffraction/scattering  
Optical properties  
FTIR measurements  
Sol–gel, aerogel and solution chemistry  
Organic–inorganic hybrids

### ABSTRACT

Sol–gel reaction of 3-trimethoxysilylpropyl methacrylate (MPTS), heptadecafluorodecyltrimethoxysilane (PFAS), and zirconium *n*-propoxide (ZPO) chelated with methacrylic acid (MAA) was investigated depending on the catalyst concentration, the reaction time and the zirconium alkoxide addition for the fabrication of highly condensed fluorinated methacryl silica and silica–zirconia hybrid material (MF and MFZ hybrimer). Controlling the catalyst concentration and the reaction time has been found to be important parameters for the strengthening of the silica networks in MF hybrimer. The addition of zirconium alkoxide enhanced the condensation degree in short reaction time, which could efficiently fabricate the highly condensed MFZ hybrimer. In particular, their molecular sizes have been found to be highly dependent on the extent of sol–gel reaction and were experimentally calculated.

© 2008 Elsevier B.V. All rights reserved.

### 1. Introduction

Sol–gel derived inorganic–organic hybrid materials (hybrimers) have attracted much attention in recent years as candidates for optical and electro-optical applications because of the various potentials provided by synergistic combination of inorganic oxide with organic compounds [1–7]. Generally, homogeneously dispersed hybrimers were synthesized by the hydrolytic sol–gel process involving the hydrolysis and condensation reaction of alkoxide (or other) precursors in a solvent system without the common problem of premature phase separation. In particular, the fluorinated methacryl silica and silica–zirconia hybrid material (MF and MFZ hybrimers) exhibits the high optical performance such as good coating quality, a low absorption, high transparency and a good photo-patternability. Thus, these hybrimers are good candidates for the application to micro-optical elements such as microlenses, microlens arrays, and optical waveguides [8–10]. However, the hydrolysis and the condensation reactions in the

hydrolytic route have suffered from problems such as the existence of reactive hydroxyl and the solution instability due to the continuous reaction, which were associated with the use of water and the need for a compatible solvent. To achieve the objective of the hybrimers for many practical applications, the condensation of alkoxide precursors should be fully competed without remaining alkoxy or hydroxyl radicals. However, since the full condensation is not realizable, the synthesis parameters should be optimized to make the condensation as high as possible. Specially, the condensation reaction in the fluorinated methacryl hybrimers is not liable to be realized due to the hydrophobicity and steric hindrance of the long perfluoroalkyl chain. Thus, for better performance in optical application of fluorinated methacryl hybrimers, optimization of the sol–gel reaction is required for the fabrication of highly condensed and reliable MF and MFZ hybrimers with very little solvent.

In the present study, we thus seek for main synthesis factors of sol–gel process, including a catalyst concentration, a reaction time, a solvent evaporation and the zirconium alkoxide addition, to fabricate highly condensed and reliable MF and MFZ hybrimers with little solvent. In particular, we investigate the effect of these different synthesis factors on the structure change, the condensation

\* Corresponding author. Tel.: +82 55 280 1614; fax: +82 55 280 1590.  
E-mail address: [kangdj@keri.re.kr](mailto:kangdj@keri.re.kr) (D.J. Kang).

degree, and the molecular size of the condensed siloxane in the hybrimers.

## 2. Experimental section

### 2.1. Chemicals

In our experiments, the highly condensed MF and MFZ hybrimers were synthesized using 3-trimethoxysilylpropyl methacrylate (MPTS, Aldrich) and heptadecafluorodecyltrimethoxysilane (PFAS, Toshiba), zirconium *n*-propoxide (ZPO, Aldrich), and methacrylic acid (MAA, Aldrich) as starting precursors.

### 2.2. Synthesis of MF and MFZ hybrimers

For the fabrication of MF hybrimers, MPTS and PFAS in a 3:1 molar ratio were mixed with 1.5 equivalents of water in the presence of hydrochloric acid (HCl), which acted as a catalyst for sol-gel reaction. The hydrochloric acids with the concentration ranges of from 0.01 N to 0.1 N were respectively used for investigation of the effect of catalyst concentration on sol-gel reaction. The respective mixed solutions were reacted for the different reaction times of from 1 day to 30 days, which is for the investigation of the effect of reaction time on sol-gel reaction. The obtained MF hybrimers after respective sol-gel reactions were totally transparent, and any residual products such as alcohols were removed at 50 °C with a vacuum evaporator.

For the fabrication of MFZ hybrimers, MPTS and PFAS in a 3:1 molar ratio were first hydrolyzed with 0.75 equivalents of water in the presence of 0.01 N HCl as a catalyst. For obtaining MFZ solution in a 3:1:0.7 molar ratio, ZPO was reacted with MAA in a molar ratio of 1:1 to avoid undesired precipitation of ZrO<sub>2</sub> particles by chelating complex formation in N<sub>2</sub> atmosphere. After that, the chelated ZPO solution was added to the pre-hydrolyzed MPTS and PFAS solution in a 3:1 molar ratio and stirred for 1 h to advance hydrolysis and condensation. The mixed solution was reacted with additional water for 20 h to complete the hydrolysis and condensation. Total amount of water was 1.5 equivalents of total alkoxides in the solution. The obtained MFZ solution in a 3:1:0.7 molar ratio was totally transparent. After 20 h stirring for full sol-gel reaction, any residual products such as alcohols were removed at 50 °C with an evaporator.

### 2.3. Characterization by infrared spectroscopy and <sup>29</sup>Si nuclear magnetic resonance spectroscopy

Subsequently, the transparent MF and MFZ hybrimers fabricated through the different conditions were filtered through a 0.45 μm filter to remove impurities and bubbles. Then, the effects of different synthesis conditions on the structural changes and evolutions in the respective MF and MFZ hybrimers were examined through Fourier transform-infrared (FT-IR) spectroscopy (JASCO, FT-IR 460plus) and <sup>29</sup>Si NMR spectroscopy. <sup>29</sup>Si NMR spectra were recorded using a Bruker FT 500 MHz instrument from a sample consisting of 30 vol.% of the MF and MFZ resin in chloroform-*d*. Chromium(III) acetylacetonate as a relaxation agent of silicon was added at a concentration of 30 mg/l. Pulse delays were 30 s, the sample temperature was 300 K, and TMS was used as a reference.

### 2.4. Characterization by small angle neutron scattering and thermogravimetric analysis

The molecular sizes depending on the extent of sol-gel reaction in MF and MFZ hybrimers were measured using small angle neutron scattering (SANS, HANARO at KAERI in Korea). The measured

condition of SANS were as follows: dilution with CD<sub>3</sub>COCD<sub>3</sub> (Acetone-*d*<sub>6</sub>, Aldrich) in 2 mm quartz cell; 5.08 Å monochromatized neutron beam; 2 and 3 m sample-to-detector distance to cover a *Q* range from 0.01 to 0.4 Å<sup>-1</sup>. *Q* is the magnitude of a scattering vector and  $Q = (4\pi/\lambda)\sin(\theta/2)$ , where  $\lambda$  is the neutron wavelength and  $\theta$  is the scattering angle. The scattering was isotropic; therefore, the primary two-dimensional spectra were circularly averaged. All the correcting procedures were done with an IGOR program. In addition, thermal properties of inorganic residuals in the respective MF and MFZ hybrimers were examined through the measurement of the thermal decomposition by thermogravimetric analysis (TGA).

## 3. Results and discussion

### 3.1. Effect of catalyst concentration and reaction time on siloxane structures of MF hybrimers by FT-IR spectroscopy

Firstly, we investigated the effect of the synthesis factors including the catalyst concentration and reaction time on the structural changes by FT-IR spectroscopy. Fig. 1 shows FT-IR spectra of the structural evolutions of MF hybrimers depending on the concentration of HCl catalyst in 1 day reaction. The two bands at 1110 and 1065 cm<sup>-1</sup> in Fig. 1 represent the Si-O-Si asymmetric stretching mode [11–13] and are observed in two different catalyzed hybrimers. As the catalyst concentration increases from 0.01 N to 0.1 N HCl, the Si-O-Si band at 1110 and 1065 cm<sup>-1</sup> increase a little, indicating that the hydrolysis and condensation may be dependent on the catalyst concentration employed in the sol-gel synthesis. Besides the Si-O-Si bands, the other bands at 1200 cm<sup>-1</sup> (C-F stretching mode of the perfluoroalkyl chains) [14], 1165 cm<sup>-1</sup> (-CH<sub>3</sub> rock of Si-OCH<sub>3</sub>) [12,13], 1150 cm<sup>-1</sup> (C-H bending mode in the perfluoroalkyl chains) [14], and 1025 cm<sup>-1</sup> (C-O(H) in MeOH) [15] in Fig. 1 are observed in the ranges of 1200–1000 cm<sup>-1</sup>. We also investigated the effect of reaction time on the structural changes of the hybrimers. Fig. 2 shows FT-IR spectra of the structural evolutions of MF hybrimers depending on the reaction times in the respective HCl catalyst concentrations ((a) 0.01 N HCl, and (b) 0.1 N HCl). In case of 0.01 N HCl, the Si-O-Si band at 1065 cm<sup>-1</sup> increases largely. However, the Si-O-Si band at 1110 cm<sup>-1</sup> and the -CH<sub>3</sub> rock of Si-OCH<sub>3</sub> at 1165 cm<sup>-1</sup> does not almost change. In case of 0.1 N HCl, the Si-O-Si band at 1110 cm<sup>-1</sup>, together with the increased Si-O-Si band at 1065 cm<sup>-1</sup>, also increases significantly with the reduction of the -CH<sub>3</sub> rock of

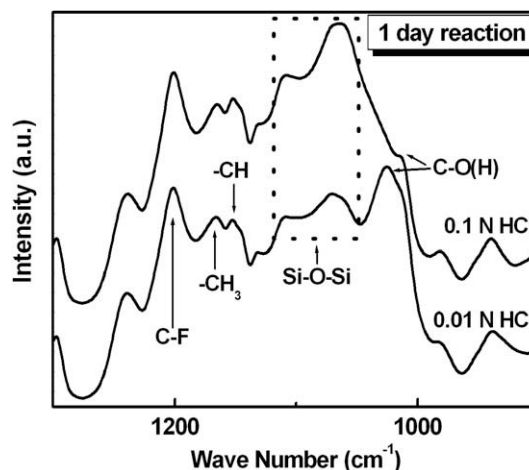
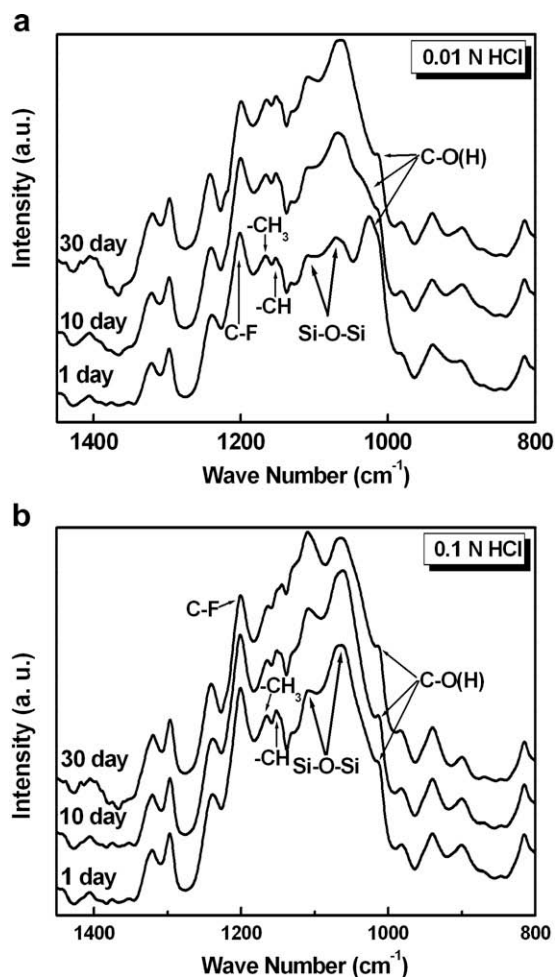


Fig. 1. FT-IR spectra of the structural evolutions of MF hybrimers depending on the concentration of HCl catalyst in 1 day reaction.

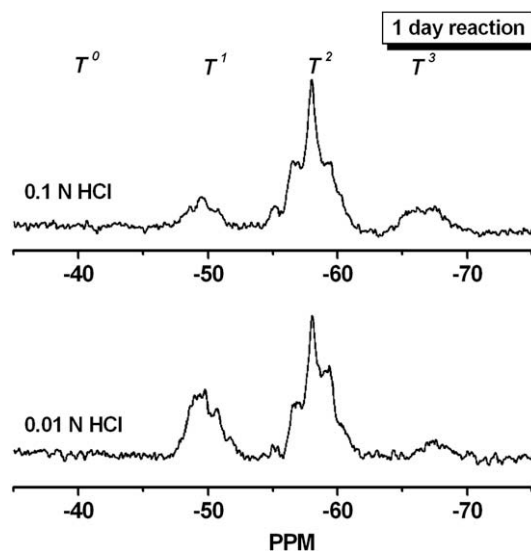


**Fig. 2.** FT-IR spectra of the structural evolutions of MF hybriders depending on the reaction times in the respective HCl catalyst concentrations ((a) 0.01 N HCl, and (b) 0.1 N HCl).

Si-OCH<sub>3</sub> at 1165 cm<sup>-1</sup> as the reaction time increases. Thus, the increase of the catalyst concentration and the reaction time may improve the hydrolysis and polycondensation of the alkoxide. Some more conclusive experiments are still necessary, however, to clarify the relation with the structure of the hybridmer depending on the synthesis factors.

### 3.2. Effect of catalyst concentration and reaction time on siloxane structures of MF hybriders by <sup>29</sup>Si NMR spectroscopy

<sup>29</sup>Si NMR was used to confirm the condensation degree and formation structure of siloxane bond in MF hybriders reacted with the respective catalyst concentrations and reaction times. Fig. 3 shows <sup>29</sup>Si NMR spectra of siloxane structures depending on the concentration of HCl catalyst in 1 day reacted MF hybriders. The notations of Si atoms in NMR spectroscopy are as follows: T<sup>n</sup> represents Si from MPTS and PFAS, respectively. The superscript, *n*, denotes the number of siloxane bonds of the Si atom. The chemical shifts of Si in the <sup>29</sup>Si NMR spectroscopy according to its bond states are shown in Table 1 [16,17]. As shown in Fig. 3, there is no T<sup>0</sup> peak, which indicates that the hydrolysis and condensation reaction between the two precursor molecules proceeds favorably, and that the MF hybriders have been successfully synthesized. As the HCl catalyst concentration increases from 0.01 N to 0.1 N, T<sup>2</sup> and T<sup>3</sup> peaks increase with the reduction of T<sup>1</sup> peaks. In the 1 day reacted MF hybriders, T<sup>2</sup> peak is the main peak and T<sup>3</sup> peaks



**Fig. 3.** <sup>29</sup>Si NMR spectra of siloxane structures depending on the concentration of HCl catalyst in 1 day reacted MF hybriders.

**Table 1**

Chemical shifts of silicon in the liquid <sup>29</sup>Si NMR spectroscopy according to its bond states

Species T <sup>n</sup>	Chemical shifts (ppm)
T <sup>0</sup>	-41
T <sup>1</sup>	-49 to 51
T <sup>2</sup>	-57 to 61
T <sup>3</sup>	-65 to 69

T<sup>n</sup> = RSi(OMe)<sub>3-n</sub>(OH)<sub>m</sub>(OSi)<sub>n</sub>, where R = -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O(CO)C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>(CF<sub>2</sub>)<sub>7</sub>CF<sub>3</sub>.

were relatively are small, which indicated the siloxane networks are relatively weak.

Then, we investigated the effect of reaction time on the formation structure of siloxane bonds in sol-gel reaction using <sup>29</sup>Si NMR spectroscopy. Fig. 4 shows <sup>29</sup>Si NMR spectra of MF hybriders depending on the HCl catalyst concentration and reaction time ((a) 0.01 N HCl, and (b) 0.1 N HCl). In case of 0.01 N HCl catalyst, T<sup>2</sup> peak is the main peak and increases with the reduction of T<sup>1</sup> peak as the reaction time increases. However, T<sup>3</sup> peaks do not almost increase under 0.01 N HCl catalyst condition. On the other hand, in case of 0.1 N HCl catalyst, T<sup>2</sup> and T<sup>3</sup> peaks are the main peaks and increase with the reduction of T<sup>1</sup> peak as the reaction time increases. Then, T<sup>1</sup> peaks almost are disappeared after 10 day reaction. This indicates the increase of reaction time in 0.1 N HCl condition extraordinary affected the strengthening of siloxane networks. Moreover, the inorganic condensation degree in MF hybriders can be calculated by integration of the individual signals from <sup>29</sup>Si NMR spectra of MF hybriders, according to the different chemical shifts of the hydrolysis and condensation species of the silane components depending on the catalyst concentration and reaction time (Eq. (1)) [18]:

$$\text{Condensation degree (\%)} = \frac{0 * T^0 + 1 * T^1 + 2 * T^2 + 3 * T^3}{3 * \sum_{n=0}^3 T^n}, \quad (1)$$

where T is the Si-species with three hydrolysable silane compounds, *n* in T<sup>n</sup> is the number of siloxane bonds on the Si atom. The respective areas of <sup>29</sup>Si NMR spectra (Figs. 3 and 4) were deconvoluted and calculated by software using inverse gated decoupling functions in <sup>29</sup>Si NMR spectroscopy. Fig. 5 shows the condensation degree of MF hybriders depending on the HCl catalyst concentration and

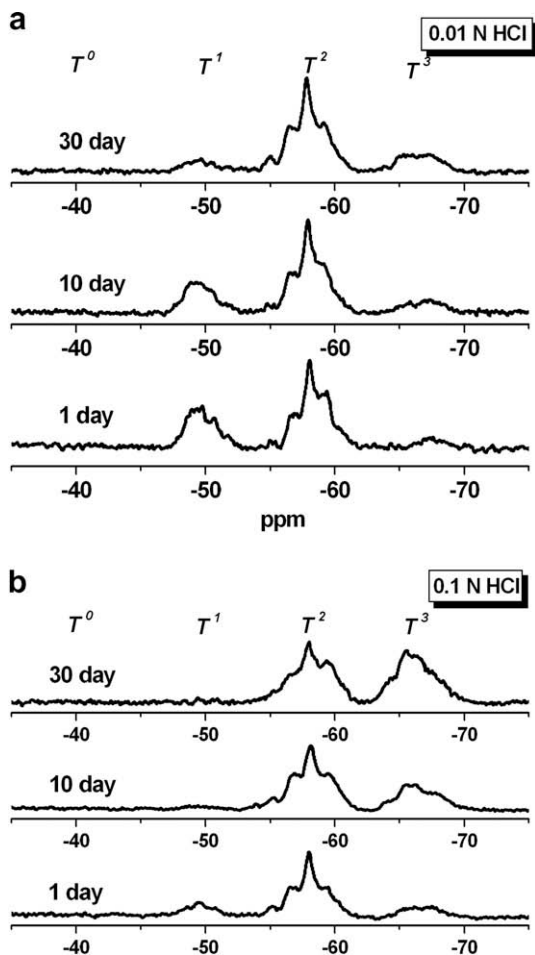


Fig. 4.  $^{29}\text{Si}$  NMR spectra of MF hybridizers depending on the HCl catalyst concentration and reaction time ((a) 0.01 N HCl, and (b) 0.1 N HCl).

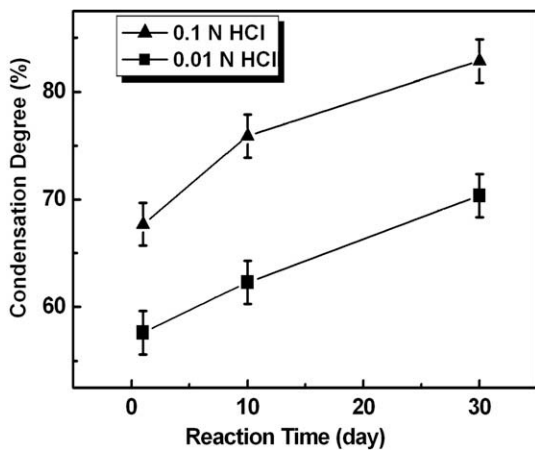


Fig. 5. Condensation degree of MF hybridizers depending on the HCl catalyst concentration and reaction time calculated by  $^{29}\text{Si}$  NMR spectroscopy.

reaction time calculated by  $^{29}\text{Si}$  NMR spectroscopy. Condensation degree grows with increasing reaction time up to 30 days for both catalysis concentrations. The condensation degree of 0.1 N HCl condition is much higher than that of 0.01 N HCl condition and reaches to 80% with 30 day reaction. However, longer reaction time is required to make full condensation in MF hybridizer since the condensation degree keeps rising even in the 30 day reaction.

### 3.3. Effect of zirconium alkoxide on siloxane structures of MF hybridizers by $^{29}\text{Si}$ NMR spectroscopy

We doped the zirconium alkoxide, which has the self-catalytic effect on condensation, in MF hybridizers in order to shorten the reaction time for the fabrication of the highly condensed hybridizers. The zirconium alkoxide were chelated with MAA to balance the reaction of other alkoxides. Fig. 6 shows  $^{29}\text{Si}$  NMR spectrum of MFZ hybridizers doped with the chelated zirconium alkoxide. The synthesis condition for MFZ hybridizers was 1 day reaction time and 0.01 N HCl catalyst concentration. Through the addition of zirconium alkoxide to MF hybridizers, the condensation degree (90.7%) and the strength of siloxane network were highly enhanced even in shorter reaction time as shown in  $^{29}\text{Si}$  NMR spectrum of MFZ hybridizer in Fig. 6.

### 3.4. Molecular sizes and shapes of MF and MFZ hybridizers characterized by SANS

Small angle neutron scattering (SANS) technique is very useful for characterizing nano-sized materials to give information about molecular size. Thus, the synthesized MF and MFZ hybridizer resins were characterized using the SANS to relate molecular size of the condensed siloxane with the extent of sol-gel reaction. The SANS can measure experimentally the radius of gyration ( $R_g$ ) and molecular size of the condensed siloxane can be calculated. In the SANS, the scattering intensity ( $I(Q)$ ) is defined (Eq. (2)) by the Guinier law [15].  $R_g$  can be estimated from a linear plot of  $\ln(I(Q))$  against  $Q^2$  in the Guinier region:

$$I(Q) = \rho_0^2 v^2 \exp\left(-\frac{1}{3} Q^2 R_g^2\right). \quad (2)$$

$I(Q)$  is the scattering intensity,  $Q$  is the scattering vector,  $\rho_0$  is the scattering length density of the resin,  $v$  is the molar volume of the resin, and  $R_g$  is the radius of gyration of the condensed siloxane.

Fig. 7 shows the SANS result of MF (30 day, 0.1 N HCl) and MFZ hybridizer resins and the corresponding Guinier plots for the data, respectively. As shown in Fig. 7, the slopes of the Guinier plots negatively increase with the addition of Zr alkoxide, indicating that the molecular size of the resin becomes larger and has the intimate relation with the extent of sol-gel reaction.

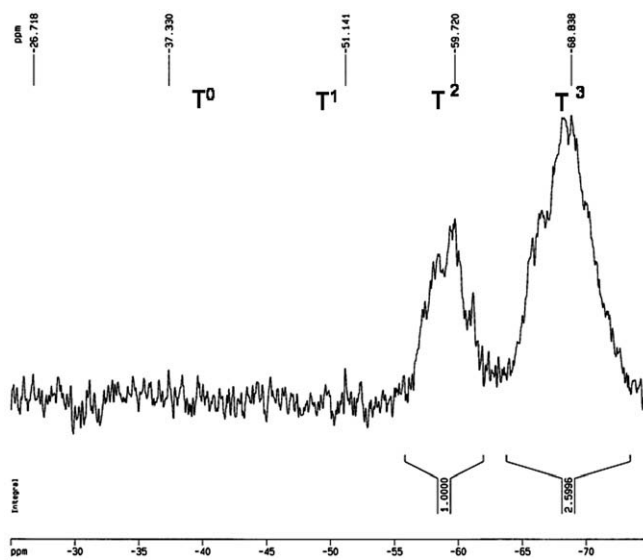
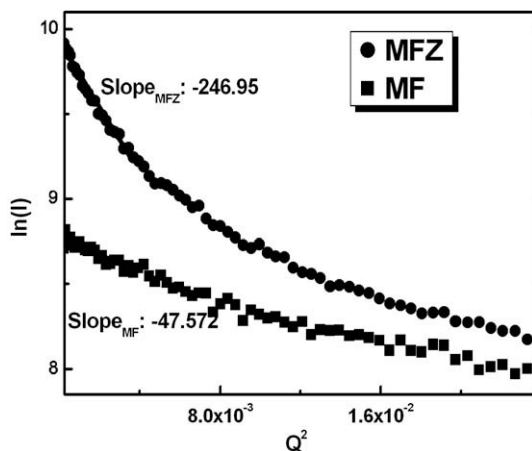


Fig. 6.  $^{29}\text{Si}$  NMR spectrum of MFZ hybridizer doped with the chelated zirconium alkoxide.





**Fig. 7.** Results of SANS experiment of MF and MFZ hybrid resins:  $\ln(I(Q))$  vs  $Q^2$  graphs of MF and MFZ hybrid resins from corresponding Guinier plot for SANS data.

The real molecular size of the condensed siloxane can be estimated from  $R_g$  by Eq. (3) or Eq. (4), depending on their shapes [19]:

$$\text{Spherical shape } R_S = \sqrt{\frac{5}{3}} R_g, \quad (3)$$

$$\text{Thin rod-like shape } R_T = \sqrt{12} R_g. \quad (4)$$

$R_S$  is the radius of the spherical condensed siloxane,  $R_T$  is the length of the thin rod-like condensed siloxane, and  $R_g$  is the radius of gyration.

Assuming the condensed siloxane has a spherical shape, the molecular size is the smallest. On the other hand, assuming the condensed siloxane has a thin-rod structure, the molecular size of is the largest. Thus, it can be expected that the real molecular size of the condensed siloxane is in the range between  $2R_S$  and  $R_T$ . The measured  $R_g$  and the calculated molecular size values of the condensed siloxane for the MF and MFZ hybrid resins are shown in Table 2. As expected in the results of condensation degree measured by  $^{29}\text{Si}$  NMR spectra, addition of Zr alkoxide increase the molecular size of the condensed siloxane from around 3–4 nm to around 7–9 nm. Thus, it is found that the enhancement of siloxane condensation by addition of Zr alkoxide create the larger molecular size of the condensed siloxane.

### 3.5. Thermal stabilities of MF and MFZ hybrid resins by TGA

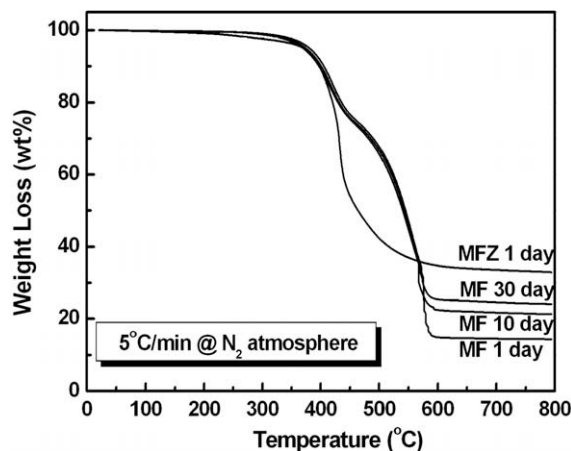
In addition, we investigated the thermal stabilities in MF and MFZ hybrid resins to identify the strength of inorganic networks depending on the reaction time and zirconium alkoxide addition. Fig. 8 shows the dynamic thermogravimetric curves exhibiting the different inorganic residual weight loss of MF and MFZ hybrid resins depending on the reaction time and zirconium alkoxide addition. The HCl catalyst concentration for MF hybrid resins was 0.1 N. Five weight percentage weight loss temperature in MF and MFZ hybrid resins was around 370–390°C. Rapid weight loss does not oc-

**Table 2**

Particle sizes of MF and MFZ hybrid resins calculated from  $R_g$  experimentally obtained from SANS

	$R_g$ (nm)	MSSH (nm)	MSTRH (nm)
MFZ	2.72	~7.03	~9.42
MF	1.19	~3.08	~4.12

MSSH: Molecular size of spherical hybrid; MSTRH: molecular size of thin rod-like hybrid.



**Fig. 8.** Dynamic thermogravimetric curves exhibiting the different inorganic residual weight loss of MF and MFZ hybrid resins depending on the reaction time and the addition of chelated zirconium alkoxide.

cur until 400 °C. Importantly, the residual weights in MF and MFZ hybrid resins are proportional to the inorganic condensation degree as shown in Figs. 5 and 6. This supports the effect of the reaction time and the Zr alkoxide addition on strengthening siloxane networks shown in FT-IR and  $^{29}\text{Si}$  NMR spectra.

## 4. Conclusion

Highly condensed fluorinated methacryl hybrid materials (MF and MFZ hybrid resins) were successfully fabricated through the control of the main synthesis factors in sol-gel process, that is, a catalyst concentration, a reaction time, a solvent evaporation, and a Zr alkoxide addition. It was confirmed that increase of the condensation degree with strengthening of siloxane network was made with growing the catalysis concentration as well as reaction time. Specially, it was found the addition of Zr alkoxide shorten the reaction time to obtain highly condensed siloxane by catalyzing the condensation reaction. We successfully measured the molecular size of the condensed siloxane using the SANS and compared those of MF and MFZ hybrid resins. Faster reaction and higher degree of the condensation made by Zr alkoxide (MFZ hybrid resins) produce larger molecular size of the condensed siloxane. The control of the catalyst concentration, the reaction time, the self-catalytic effect of heterometal alkoxides such as Zr and Ti in a sol-gel process is very crucial for strengthening the siloxane structure and increasing the condensation degree of the hybrid resins, which make a role in increasing molecular sizes of hybrid resins.

## References

- [1] A. Vioux, Chem. Mater. 9 (1997) 2292.
- [2] L. Bourget, R.J.P. Corriu, D. Lecercq, P.H. Mutin, A.J. Vioux, J. Non-Cryst. Solids 242 (1998) 81.
- [3] J.N. Hay, D. Porter, H.M. Raval, J. Mater. Chem. 10 (2000) 1811.
- [4] C. Sanchez, B. Lebeau, MRS Bull. 26 (2000) 377.
- [5] R. Buestrich, F. Kahlenberg, M. Popall, P. Dannberg, R. Müller-Fieldler, O. Rösch, J. Sol-Gel Sci. Technol. 20 (2001) 181.
- [6] B.S. Bae, J. Sol-Gel Sci. Technol. 31 (2004) 309.
- [7] B.J. Scott, G. Wirnsberger, G.D. Stucky, Chem. Mater. 13 (2001) 3140.
- [8] D.J. Kang, J.U. Park, B.S. Bae, J. Nishii, K. Kintaka, Opt. Express 11 (2003) 1144.
- [9] D.J. Kang, J.K. Kim, B.S. Bae, Opt. Express 12 (2004) 3947.
- [10] D.J. Kang, P.V. Phong, B.S. Bae, Appl. Phys. Lett. 85 (2004) 4289.
- [11] P. Innocenzi, G. Brusatin, M. Guglielmi, R. Bertani, Chem. Mater. 11 (1999) 1672.
- [12] K. Saravanamuttu, X.M. Du, S.I. Najafi, M.P. Andrews, Can. J. Chem. 76 (1998) 1717.
- [13] D.L. Ou, A.B. Seddon, J. Non-Cryst. Solids 210 (1997) 187.

- [14] R.M. silverstein, G.C. Bassler, T.C. Morrill, in: D. Sawicki (Ed.), *Spectrometric Identification of Organic Compounds*, vol. 130, John Wiley, New York, 1991.
- [15] N. Viart, D. Niznansky, J.L. Rehspringer, *J. Sol–Gel Sci. Technol.* 8 (1997) 183.
- [16] O. Soppera, C. Croutxe-barghorn, *J. Polym. Sci.: Part A: Polym. Chem.* 41 (2003) 716.
- [17] Y.J. Eo, T.H. Lee, S.Y. Kim, J.K. Kang, Y.S. Han, B.S. Bae, *J. Polym. Sci.: Part B: Polym. Phys. Mater. Res.* 43 (2005) 827.
- [18] S. Sepeur, N. Kunze, B. Werner, H. Schmidt, *Thin Solid Films* 216 (1999) 351.
- [19] R.J. Roe, *Methods of X-ray and Neutron Scattering in Polymer Science*, Oxford University, Oxford, 2000. p. 155.