様式第２号（第５条，第１１条関係）

「課程博士用」

学 位 論 文 の 要 旨

専　　攻	機能創成科学　　専攻	ふりがな 氏　　名	ありさら　らっちゃ Arissara　Ratcha
学位論文題目	Preparation and Application of Fluoroalkyl End-Capped Vinyltrimethoxysilane Oligomeric Silica/Butadiene Copolymers Nanocomposites (フルオロアルキル基含有ビニルトリメトキシシランオリゴマー/シリカ/ブタジエンコポリマーナノコンポジット類の調製と応用)		

[Introduction]

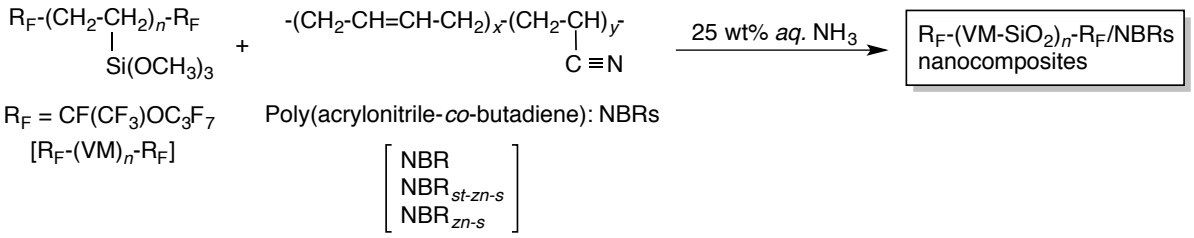
It is well-known that two fluoroalkyl end-capped vinyltrimethoxysilane oligomers [R_F-$(VM)_n$-R_F] can exhibit the unique properties such as good dispersibility and stability in organic media including water, high surface modification ability, and the ability to form nanometer size-controlled self-assembled molecular aggregates[1)], compared with that of the traditional monomeric fluoroalkyl end-capped silane coupling agents[2)]. The R_F-$(VM)_n$-R_F oligomer-coated silica nanoparticles [R_F-$(VM\text{-}SiO_2)_n$-R_F] can be also prepared by the sol-gel reaction of the corresponding fluorinated oligomer [R_F-$(VM)_n$-R_F] under alkaline conditions.[3)] Especially, the modified glass surface treated with these R_F-$(VM\text{-}SiO_2)_n$-R_F oligomeric nanoparticles can exhibit completely superhydrophobic characteristic (water contact angle values: 180°).[3)] In addition, low molecular weight aromatic compounds such as 1,1'-bi(2-naphthol) [BINOL] can be effectively encapsulated into these fluorinated silica nanoparticle cores to give the R_F-$(VM\text{-}SiO_2)_n$-R_F oligomeric nanocomposites - encapsulated BINOL. Interestingly, the R_F-$(VM\text{-}SiO_2)_n$-R_F/BINOL nanocomposites can exhibit a nonflammable characteristic in the fluorinated nanocomposite cores even after calcination at 800 °C under atmospheric conditions.[4)] From the developmental viewpoint of novel fluorinated functional materials, it is of particular interest to explore the encapsulation of not only low molecular weight aromatic compounds but also traditional organic polymers, especially rubbers into the R_F-$(VM\text{-}SiO_2)_n$-R_F oligomeric nanoparticle cores. In this work, the preparation and thermal stability of fluoroalkyl end-capped vinyltrimethoxysilane oligomeric silica/butadiene copolymers such as poly(acrylonitrile-*co*-butadiene) and poly(styrene-*co*-butadiene) nanocomposites are described including applications to the surface modification and the separation of oil and water.

[Experimental, Results and Discussion]

[I] Preparation and Thermal Stability of Fluoroalkyl End-Capped Vinyltrimethoxysilane Oligomeric Silica/Poly(acrylonitrile-*co*-butadiene) Nanocomposites - Application to the Separation of Oil and Water[5)]

Fluoroalkyl end-capped vinyltrimethoxysilane oligomeric silica/poly(acrylonitrile-*co*-butadiene) nanocomposites [R_F-$(VM\text{-}SiO_2)_n$-R_F/NBRs] were prepared by the sol-gel reactions of the corresponding

oligomer [R_F-(VM)$_n$-R_F] in the presence of NBRs under alkaline conditions as shown in Scheme 1. Not only the NBR but also the NBR containing stearic acid, zinc oxide and sulfur [$NBR_{st\text{-}zn\text{-}s}$] and NBR containing zinc oxide and sulfur [$NBR_{zn\text{-}s}$] were also prepared under similar conditions.



Scheme 1. Preparation of the R_F-(VM-SiO_2)$_n$-R_F/NBRs nanocomposites

Figure 1 shows the thermogravimetric analyses (TGA) curves of the R_F-(VM-SiO_2)$_n$-R_F/NBR, /$NBR_{st\text{-}zn\text{-}s}$ and /$NBR_{zn\text{-}s}$ nanocomposites containing nitrile moieties after calcination at 800 °C. Interestingly, the R_F-(VM-SiO_2)$_n$-R_F/NBR nanocomposites can afford no weight loss behavior even after calcination at 800 °C through the formation of imine units during the calcination process, although the R_F-(VM-SiO_2)$_n$-R_F/$NBR_{st\text{-}zn\text{-}s}$ and /$NBR_{zn\text{-}s}$ nanocomposites afforded a usual weight loss characteristics. Furthermore, the modified glass surface treated with the R_F-(VM-SiO_2)$_n$-R_F/$NBR_{zn\text{-}s}$ nanocomposites can provide the superoleophilic/ superhydrophobic characteristic on the modified surface. These composites, which were prepared through the cross-linking reaction at 150 °C for 30 min, were effective for separation of not only the mixture of oil and water but also the water-in-oil emulsion by using the composites as a packing materials for column chromatography.

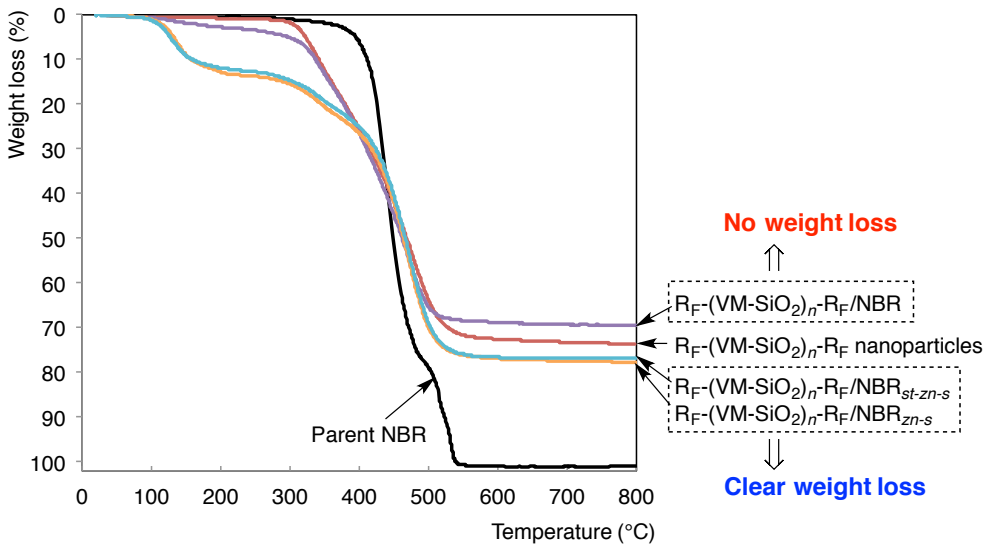
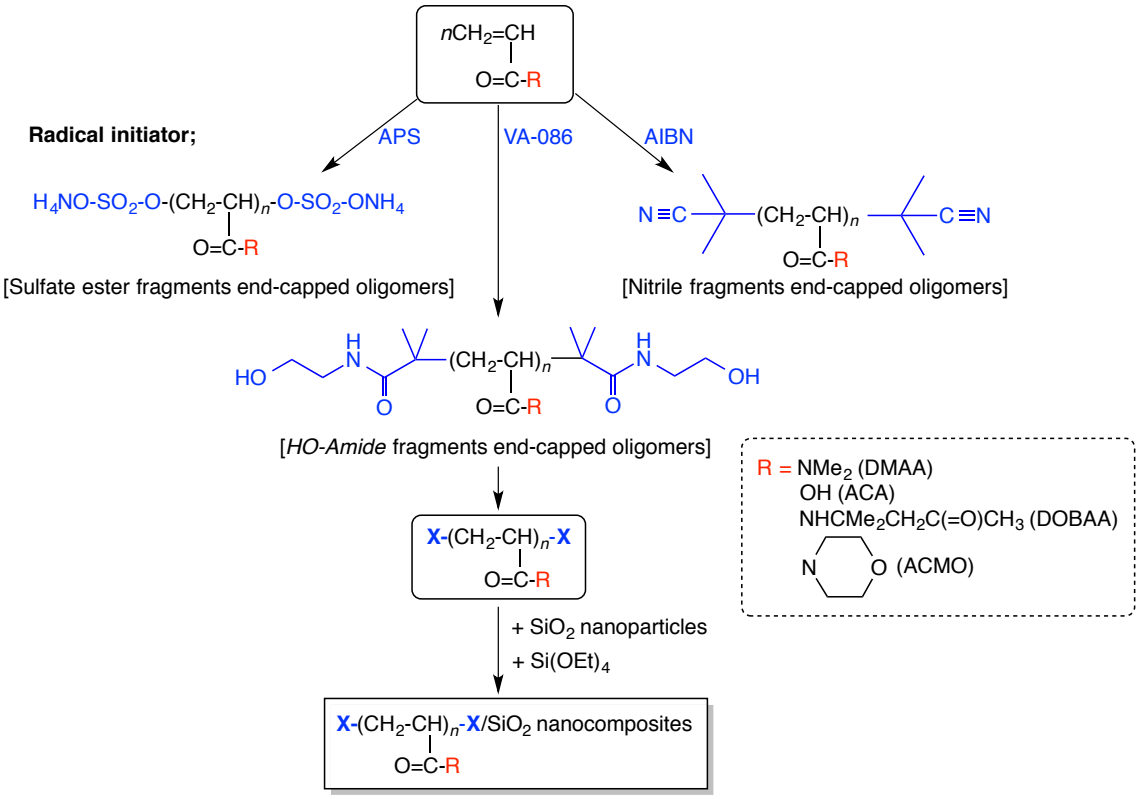


Fig. 1. Thermogravimetric analyses (TGA) of parent NBR, the R_F-(VM-SiO_2)$_n$-R_F/NBR, the R_F-(VM-SiO_2)$_n$-R_F/ $NBR_{zn\text{-}s}$, the R_F-(VM-SiO_2)$_n$-R_F/$NBR_{st\text{-}zn\text{-}s}$ nanocomposites and the R_F-(VM-SiO_2)$_n$-R_F nanoparticles Feed ratio of R_F-(VM)$_n$-R_F/NBRs is 100/10 (mg/mg)

[II] Preparation and Thermal Stability of Initiator Fragments End-Capped Oligomers/Silica Nanocomposites[6)]

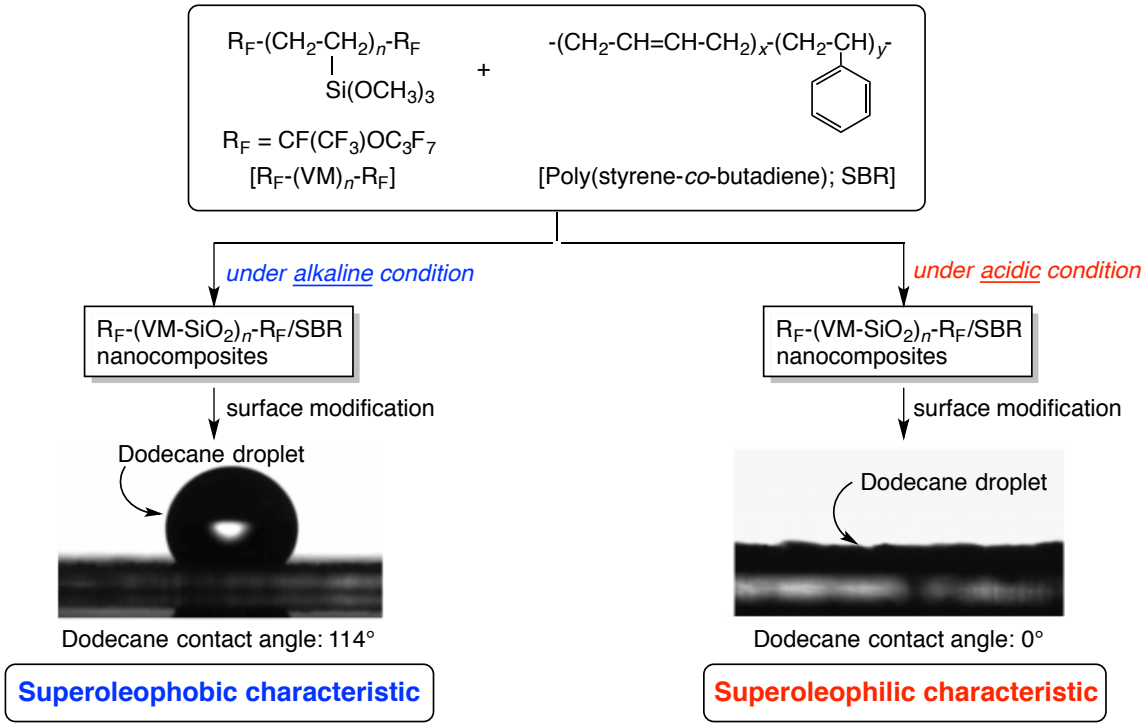
A variety of initiator fragments end-capped oligomers such as *N,N*-dimethylacrylamide (DMAA), acrylic acid (ACA), *N*-(1,1-dimethyl-3-oxobutyl)acrylamide (DOBAA) and acrylomorpholine (ACMO) oligomers were synthesized by the oligomerizations of the corresponding monomers initiated by a variety of radical initiators such as ammonium persulfate (APS), 2,2'-azobis(2-methyl-*N*-(2-hydroxyethyl)propionamide) (VA-086) and azobisisobutyronitrile (AIBN). Furthermore, the obtained initiator fragments end-capped oligomers/silica nanocomposites were prepared by the sol-gel reactions of the corresponding oligomers in the presence of silica nanoparticles and tetraethoxysilane (TEOS) under alkaline condition as shown in Scheme 2. The sulfate ester fragments end-capped oligomers/silica nanocomposites can provide a clear weight loss behavior even after calcination at 800 °C; however, the *HO-Amide* fragments end-capped oligomers/silica nanocomposites and the nitrile fragments end-capped DMAA oligomer/silica nanocomposites can exhibit no weight loss behavior under similar conditions (see Scheme 2). In this way, it was verified that the nitrile units in oligomers are much related to the nonflammable characteristic in the silica gel matrices. Especially, nitrile unit end-capped oligomers including their oligomers/silica nanocomposites were prepared and their thermal stability was also studied in detail in order to clarify the thermal stability related to the nitrile units in the fluorinated oligomer/silica/poly(acrylonitrile-*co*-butadiene) nanocomposites.



Scheme 2. Synthesis of initiator fragments end-capped oligomers

[III] Wettability Control Between Superoleophobic and Superoleophilic Characteristics on the Modified Superhydrophobic Surfaces Treated with Fluoroalkyl End-Capped Vinyltrimethoxysilane Oligomeric Silica/Poly(styrene-*co*-butadiene) Nanocomposites: Application to the Separation of Oil and Water[7)]

Fluoroalkyl end-capped vinyltrimethoxysilane oligomeric silica/poly(styrene-*co*-butadiene) [R_F-(VM-SiO_2)$_n$-R_F/SBR] nanocomposites have been prepared by the sol-gel reactions under alkaline and acidic conditions as shown in Scheme 3. The modified glass surface treated with these R_F-(VM-SiO_2)$_n$-R_F/SBR nanocomposites, which were prepared under alkaline and acidic conditions, can exhibit the superoleophobic and superoleophilic characteristics, respectively, on their surface. It was demonstrated that these R_F-(VM-SiO_2)$_n$-R_F/SBR nanocomposites possessing the superoleophilic/superhydrophobic characteristic can separate the mixture of oil and water and water-in-oil emulsion effectively.



Scheme 3. Preparation of the R_F-(VM-SiO_2)$_n$-R_F/SBR nanocomposites: Application of these nanocomposites to the surface modification of glass

[References]

1) a) H. Sawada, *Chem. Rev.*, **96**, 1779 - 1808 (1996).
b) H. Sawada, *Polym. J.*, **39**, 637 - 650 (2007).
c) H. Sawada, *Polym. Chem.*, **3**, 46 - 65 (2012).

2) T. Kawase, T. Fujii, M. Minagawa, H. Sawada, T. Matumoto, and M. Nakayama, *J. Adhes. Sci. Technol.*, **10**, 1031 - 1046 (1996).

3) H. Sawada, T. Suzuki, H. Takashima, and K. Takishita, *Colloid Polym. Sci.*, **286**, 1569 - 1574 (2008).

4) H. Sawada, Y. Matsuki, Y. Goto, S. Kodama, M. Sugiya, and Y. Nishiyama, *Bull. Chem. Soc. Jpn.*, **83**, 75 - 81 (2010).

5) A. Ratcha, T. Saito, R. Takahashi, S. Kongparakul, and H. Sawada, *Colloid Polym. Sci.*, **294**, 1529 - 1539 (2016).

6) H. Sawada, M. Kabutomori, A. Ratcha, S. Kongparakul, and M. Nishida, *Colloid Polym. Sci.*, **294**, 1173 - 1186 (2016).

7) A. Ratcha, R. Takahashi, S. Kongparakul, and H. Sawada, *J. Coat. Technol. Res.*, DOI: 10.1007/s1198-017-0003-x.