

PREPARATION AND APPLICATIONS OF FLUOROALKYL END-CAPPED OLIGOMERS/BINAPHTHOL/SILICA NANOCOMPOSITES

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Introduction

Fluoroalkyl end-capped oligomers are attractive functional materials, because they exhibit various unique properties such as high solubility, surface active properties, biological activities, and nanometer size-controlled self-assembled molecular aggregates which cannot be achieved by the corresponding non-fluorinated and randomly fluoroalkylated polymers.[1] In these fluoroalkyl end-capped oligomers, fluoroalkyl end-capped trimethoxyvinylsilane oligomers are in particular interest due to exhibiting higher surface active characteristics compared to the traditional fluoroalkylated silane coupling agents [$R_F-CH_2CH_2Si(OR)_3$; R_F = fluoroalkyl groups].[2] From the developmental viewpoint of new fluorinated polymeric functional materials, it is of particular interest to explore new fluoroalkyl end-capped vinyltrimethoxysilane oligomer nanocomposites which could exhibit improved properties superior to those of the parent fluorinated oligomers. In fact, we have very recently found that the hydrolysis of fluoroalkyl end-capped vinyltrimethoxysilane oligomer under alkaline conditions can afford the corresponding nanometer size-controlled fluorinated vinyltrimethoxysilane oligomer/silica composites.[3] We have also found that the modified glass surface treated with these fluorinated nanocomposites can exhibit a completely super-hydrophobic characteristic (a water contact angle: 180°) with a non-wetting property against water droplet.[3] During our comprehensive studies on the preparation and properties of fluoroalkyl end-capped vinyltrimethoxysilane oligomer/silica nanocomposites, we have prepared fluoroalkyl end-capped vinyltrimethoxysilane oligomer/1,1'-2-bi-naphthol (BINOL)/silica nanocomposite [$R_F-(VM-SiO_2)_n-R_F/BINOL$] by the hydrolysis of the corresponding oligomer in the presence of BINOL under alkaline conditions. $R_F-(VM-SiO_2)_n-R_F/BINOL$ nanocomposite thus obtained were found to afford a clear weight loss at $800^\circ C$, which corresponds to the content of fluoroalkyl end-capped oligomer in the composite. However, unexpectedly, we have discovered that $R_F-(VM-SiO_2)_n-R_F/BINOL$ nanocomposite can exhibit no weight loss characteristic corresponding to the presence of BINOL in the composite at $800^\circ C$ under atmospheric conditions. These findings will be described herein.

Experimental

Materials

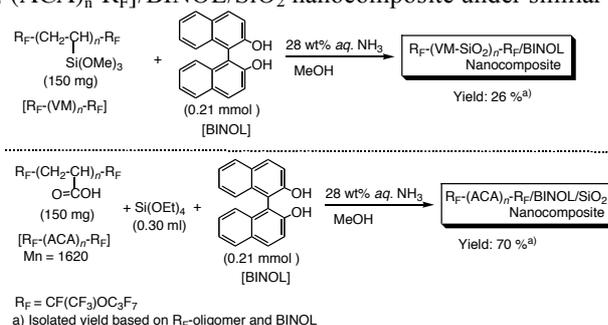
Fluoroalkyl end-capped vinyltrimethoxysilane oligomer was prepared by reaction of fluoroalkanoyl peroxide with the corresponding monomer according to our previously reported method.[2-a]

Preparation of $R_F-(VM-SiO_2)_n-R_F/BINOL$ nanocomposite

A typical procedure for the preparation of $R_F-(VM-SiO_2)_n-R_F/BINOL$ nanocomposite is as follows: To methanol solution (12.5 ml) containing fluoroalkyl end-capped vinyltrimethoxysilane oligomer [150 mg; $R_F-[CH_2CHSi(OMe)_3]_n-R_F$; $R_F-(VM)_n-R_F$; $R_F = CF(CF_3)OC_3F_7$; $n = 2 \sim 3$] and BINOL (0.21 mmol), was added 28 % aqueous ammonia solution (2.4 ml). The mixture was stirred with a magnetic stirring bar at room temperature for 1 day. After centrifugal separation of this solution, the obtained products were well washed with methanol in several times, and dried in vacuo to afford the expected white powdery product (78 mg). Fluoroalkyl end-capped acrylic acid oligomer/BINOL/silica nanocomposite was prepared under similar conditions (see Scheme 1).

Results and Discussion

Fluoroalkyl end-capped vinyltrimethoxysilane oligomer suffered the hydrolysis under alkaline conditions in the presence of 1,1'-2-bi-naphthol (BINOL) to afford $R_F-(VM-SiO_2)_n-R_F/BINOL$ nanocomposite in 26 % isolated yield. Similarly, we have succeeded in preparing fluoroalkyl end-capped acrylic acid oligomer [$R_F-(ACA)_n-R_F$]/BINOL/ SiO_2 nanocomposite under similar



a) Isolated yield based on R_F -oligomer and BINOL

Scheme 1

conditions. These results were shown in Scheme 1.

The obtained $R_F\text{-(VM-SiO}_2)_n\text{-R}_F\text{/BINOL}$ nanocomposite has a good dispersibility in traditional organic solvents such as methanol, ethanol, *i*-propyl alcohol (*i*-PrOH), chloroform, tetrahydrofuran (THF), 1,2-dichloroethane (DE), hexane, dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF) and fluorinated aliphatic solvents (AK-225: 1 : 1 mixed solvents of 1,1-dichloro-2,2,3,3,3-pentafluoropropane and 1,3-dichloro-1,2,2,3,3-pentafluoropropane) except for water. On the other hand, $R_F\text{-(ACA)}_n\text{-R}_F\text{/BINOL/SiO}_2$ nanocomposites were found to exhibit higher dispersibility not only in water but also in these organic solvents. Dynamic light-scattering (DLS) measurements at 25 °C show that the size of $R_F\text{-(VM-SiO}_2)_n\text{-R}_F\text{/BINOL}$ nanocomposite and $R_F\text{-(ACA)}_n\text{-R}_F\text{/BINOL/SiO}_2$ nanocomposite in methanol were 840 ± 210 nm and 188 ± 45.0 nm, respectively.

Thermal stability of fluorinated nanocomposites in Scheme 1 was studied by the use of thermogravimetric analyses (TGA), in which the weight loss of these nanocomposites was measured by raising the temperature around 800 °C (the heating rate: 10 °C/min) in air atmosphere, and the results were shown in Figs. 1 and 2.

The parent BINOL decomposed completely around 300 °C (see Fig. 1 (A)-c)), and the weight of parent $R_F\text{-(ACA)}_n\text{-R}_F$ oligomer markedly dropped around 250 °C and decomposed gradually, reaching 0% around 540 °C (data not shown). A similar tendency was observed in $R_F\text{-(ACA)}_n\text{-R}_F\text{/SiO}_2$ nanocomposite, and a constant value for its weight loss was observed above 540 °C, indicating that this nanocomposite could possess silica gel nanoparticles (see Fig. 1 (A)-a)). $R_F\text{-(ACA)}_n\text{-R}_F\text{/BINOL/SiO}_2$ nanocomposite (see Fig. 1 (A)-b)) decomposed effectively at 800 °C

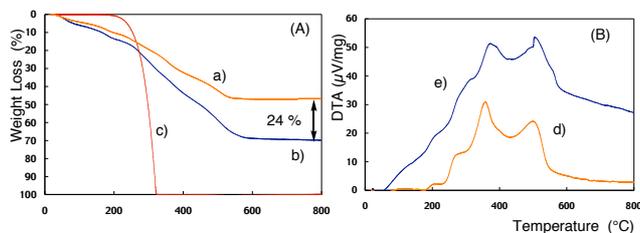


Fig. 1 Thermogravimetric analyses [TGA (A)] and differential thermal analyses [DTA (B)] of $R_F\text{-(ACA)}_n\text{-R}_F\text{/BINOL/SiO}_2$ nanocomposite, $R_F\text{-(ACA)}_n\text{-R}_F\text{/SiO}_2$ nanocomposite and BINOL

- a),d) $R_F\text{-(ACA)}_n\text{-R}_F\text{/SiO}_2$ nanocomposites
b),e) $R_F\text{-(ACA)}_n\text{-R}_F\text{/BINOL/SiO}_2$ nanocomposites
c) parent BINOL

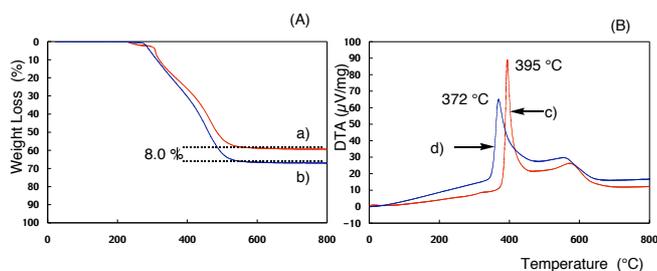


Fig. 2 Thermogravimetric analyses [TGA (A)] and differential thermal analyses [DTA (B)] of $R_F\text{-(VM-SiO}_2)_n\text{-R}_F\text{/BINOL}$ nanocomposite, and $R_F\text{-(VM-SiO}_2)_n\text{-R}_F$ nanocomposite

- a),c) $R_F\text{-(VM-SiO}_2)_n\text{-R}_F\text{/BINOL}$ nanocomposites
b),d) $R_F\text{-(VM-SiO}_2)_n\text{-R}_F$ nanocomposites

to exhibit a higher weight loss behavior, compared to that of $R_F\text{-(ACA)}_n\text{-R}_F\text{/SiO}_2$ nanocomposite, indicating that the content of BINOL in this composite is 24 %.

On the other hand, unexpectedly, we could not observe the effective weight loss of $R_F\text{-(VM-SiO}_2)_n\text{-R}_F\text{/BINOL}$ nanocomposite corresponding to the presence of BINOL at all from room temperature to 800 °C (see Fig. 2-(A)-a)), compared to the corresponding $R_F\text{-(VM-SiO}_2)_n\text{-R}_F$ nanocomposite (see Fig. 2-(A)-b)), although the $R_F\text{-(VM-SiO}_2)_n\text{-R}_F\text{/BINOL}$ nanocomposite contains BINOL which decomposes completely around 300 °C. Thus, the content of BINOL in the composite was estimated to be 8.0 % by TGA measurements.

DTA (differential thermal analyses) for $R_F\text{-(ACA)}_n\text{-R}_F\text{/BINOL/SiO}_2$ nanocomposite in air atmosphere (the heating rate: 10 °C/min) showed that as the temperature reached around 300 °C, exothermic phenomenon occurred, and exothermic peaks appeared around 380 °C and 500 °C, respectively, which may be caused by the decomposition of $R_F\text{-(ACA)}_n\text{-R}_F$ oligomer in the composite (see Fig. 1-(B)-e)). A similar result was obtained in the case of the $R_F\text{-(ACA)}_n\text{-R}_F\text{/SiO}_2$ nanocomposite (see Fig. 1-(B)-d)), indicating that the usual composite reaction of $R_F\text{-(ACA)}_n\text{-R}_F$ oligomer with silica gel (tetraethoxysilane) in the presence of BINOL should proceed smoothly under alkaline conditions. On the other hand, DTA for $R_F\text{-(VM-SiO}_2)_n\text{-R}_F\text{/BINOL}$ nanocomposite was able to exhibit a clear exothermic peak at 395 °C (see Fig. 2-(B)-c)). This exothermic temperature is extremely higher than that (372 °C) of $R_F\text{-(VM-SiO}_2)_n\text{-R}_F$ nanocomposite (see Fig. 2-(B)-d)), indicating that BINOL should be encapsulated quite effectively as a guest molecule into the nanometer size-controlled $R_F\text{-(VM-SiO}_2)_n\text{-R}_F$ nanocomposite matrices through the molecular-level combination, which is due to the intermolecular hydrogen bonding interaction between the hydroxy groups in BINOL and residual silanol groups in the composite matrices.

Conclusion

We have succeeded in preparing $R_F\text{-(VM-SiO}_2)_n\text{-R}_F\text{/BINOL}$ nanocomposite by the hydrolysis of fluoroalkyl end-capped vinyltrimethoxysilane oligomer in the presence of BINOL under alkaline conditions. $R_F\text{-(ACA)}_n\text{-R}_F\text{/BINOL/SiO}_2$ nanocomposite was also prepared under similar conditions. $R_F\text{-(ACA)}_n\text{-R}_F\text{/BINOL/SiO}_2$ nanocomposite exhibited a clear weight loss corresponding to the presence of BINOL in the nanocomposite at 800 °C. In contrast, unexpectedly, $R_F\text{-(VM-SiO}_2)_n\text{-R}_F\text{/BINOL}$ nanocomposite was found to exhibit no weight loss corresponding to the presence of BINOL in the composite at 800 °C.

References

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