

Preparation of cross-linked fluoroalkyl end-capped cooligomeric nanoparticles-encapsulated fullerenes

A typical procedure for the preparation of cross-linked fluoroalkyl end-capped cooligomeric nanoparticles-encapsulated fullerene by the use of α,ω -bis(perfluoro-1-methyl-2-oxapentylated) isocyanatoethyl methacrylate 2-butanone oxime adduct - 1-hydroxy-5-adamantylacrylate cooligomers [R_F -(IEM-BO) $_x$ -(Ad-HAc) $_y$ - R_F ; R_F = CF(CF₃)OC₃F₇; $x : y = 23 : 77$; Mn = 8460] is as follows: To an *N,N*-dimethylformamide [DMF] (20 ml) solution of R_F -(IEM-BO) $_x$ -(Ad-HAc) $_y$ - R_F cooligomer (1.0 g), which was prepared by the cooligomerization of the corresponding monomers and fluoroalkanoyl peroxide according to our previously reported method^[1], was added C₆₀ (0.5 mg). The mixture was stirred at 130 °C for 1 hr. After the solvent was evaporated off under reduced pressure, the crude products were reprecipitated from methanol-acetone to give cross-linked fluoroalkyl end-capped cooligomeric nanoparticles-encapsulated fullerenes [cross-linked R_F -(IEM) $_x$ -(Ad-HAc) $_y$ - R_F /C₆₀; R_F = CF(CF₃)OC₃F₇] (0.57 g). This nanoparticle exhibited the following FT-IR spectra characteristic: IR(cm⁻¹) 3395 (OH), 1732 (C=O), 1308 (CF₃), 1257(CF₂). Other R_F -(IEM) $_x$ -(Ad-HAc) $_y$ - R_F nanoparticles-encapsulated fullerene were prepared under similar conditions. Cross-linked R_F -(IEM) $_x$ -(Ad-HAc) $_y$ - R_F nanoparticles were also prepared according to our previously reported method^[1]; however, this nanoparticle exhibited a similar FT-IR spectra characteristic as

that of $R_F-(IEM)_x-(Ad-HAc)_y-R_F$ nanoparticles-encapsulated fullerene. These results are as follows:

Run	$R_F-(IEM-BO)_x-(Ad-HAc)_y-R_F$ ^{a)} (mmol)	C_{60} (mg)	Product Yield ^{b)} (%)
1	0.12	0.5	63
2	0.12	1	49
3	0.12	5	47
4	0.12	10	45
5	0.12	30	70
6	0.12	60	61

a) $R_F = CF(CF_3)OC_3F_7$

b) Yield based on $R_F-(IEM-BO)_x-(Ad-HAc)_y-R_F$ and C_{60}

Preparation of cross-linked fluoroalkyl end-capped cooligomeric nanoparticles-encapsulated fullerenes by the use of fluoroalkyl end-capped isocyanato cooligomers

A typical procedure for the preparation of cross-linked fluoroalkyl end-capped cooligomeric nanoparticles-encapsulated fullerene by the use of fluoroalkyl end-capped isocyanato cooligomers is as follows:

Perfluoro-2-methyl-3-oxahexanoyl peroxide (2.4 mmol) in 1 : 1 mixed solvents (AK-225) of 1,1-dichloro-2,2,3,3,3-pentafluoropropane and 1,3-dichloro-1,2,2,3,3-pentafluoropropane (15 g) was added to a mixture of isocyanatoethyl acrylate [IEA] (11.9 mmol), *N*-(1,1-dimethyl-3-oxobutyl)acrylamide [DOBAA] (8.7 mmol) and AK-225 (200 g). The solution was stirred at 45 °C for 1 hr under nitrogen, and to this solution was added a homogeneous toluene solution

containing fluoroalkyl end-capped DOBAA oligomer/C₆₀ nanocomposites, which were prepared by stirring well a toluene solution (5.0 ml) of fluoroalkyl end-capped DOBAA homooligomer [R_F-(DOBAA)_n-R_F; R_F = CF(CF₃)OC₃F₇; Mn = 12100 (20 mg)]^[2] and fullerene (20 mg) with a magnetic stirring bar at room temperature for 2 days. Then, water (50 ml) was added to the solution thus obtained, and this solution was stirred at 45 °C for 4 hr under nitrogen. After the removal of solvent, the obtained crude products were washed well with AK-225, which exhibits a good solubility for IEA, DOBAA and R_F-(DOBAA)_n-R_F homooligomer, to afford directly cross-linked fluoroalkyl end-capped cooligomeric nanoparticles-encapsulated fullerene [cross-linked R_F-(IEA)_x-(DOBAA)_y-R_F/C₆₀; R_F = CF(CF₃)OC₃F₇] (1.63 g). This nanoparticle exhibited the following FT-IR spectra characteristic: IR(cm⁻¹) 1716, 1651, 1551 (C=O, C=ONH), 1310 (CF₃), 1242 (CF₂). Other R_F-(IEM)_x-(DOBAA)_y-R_F nanoparticles-encapsulated fullerene were prepared under similar conditions. Cross-linked R_F-(IEM)_x-(DOBAA)_y-R_F nanoparticles were also prepared under similar conditions; however, this nanoparticle exhibited a similar FT-IR spectra characteristic as that of R_F-(IEM)_x-(Ad-HAc)_y-R_F nanoparticles-encapsulated fullerene. These results are as follows:

Run	(R _F COO) ₂ ^{a)} (mmol)	IEA (mmol)	DOBAA (mmol)	C ₆₀ ^{b)} (mg)	Nanoparticles Yield ^{c)} (%)
7	2.4	11.9	8.7	20	36
8	4.8	23.8	17.4	300	63
9	2.4	11.9	8.7	250	24

a) R_F = CF(CF₃)OC₃F₇

b) R_F-(DOBAA)_n-R_F homooligomer [R_F = CF(CF₃)OC₃F₇, Mn = 12100: 20 mg) was used in each case

c) Yield based on R_F-(IEM-BO)_x-(Ad-HAc)_y-R_F and C₆₀

[1] Mugisawa, M.; Ueno, K.; Hamazaki, K.; Sawada, H. *Macromol. Rapid Commun.* **2007**, *28*, 733 ~ 739.

[2] Fluoroalkyl end-capped DOBAA homooligomer was prepared according to our previously reported method: Sawada, H.; Yoshino, Y.; Kurachi, M.; Kawase, T.; Takishita, K.; Tanedani, *Polymer* **2000**, *41*, 397 ~ 400.