

Polymer Communication

# Synthesis and surface properties of novel fluoroalkyl end-capped amphiphilic fullerene cooligomers

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## Abstract

New fluoroalkyl end-capped fullerene cooligomers were prepared by the reactions of fluoroalkanoyl peroxides with fullerene and comonomers such as acryloylmorpholine, *N,N*-dimethylacrylamide and acrylic acid. These fluorinated fullerene cooligomers were easily soluble in water and common organic solvents, and were able to reduce the surface tensions of both water and benzene, quite effectively. Additionally, these fullerene cooligomers were found to form a stable monomolecular film at the air–water interface, and the modified polystyrene surface treated with these cooligomers was shown to have a strong hydrophilicity with good oil repellency. © 2001 Elsevier Science Ltd. All rights reserved.

**Keywords:** Fluorinated fullerene cooligomer; Hydrophilicity; Surface activity

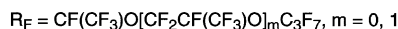
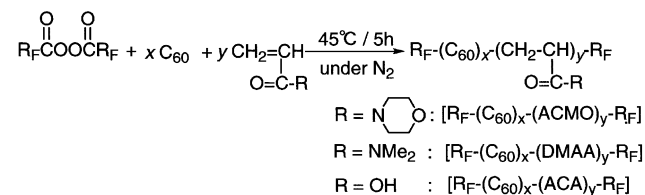
Recently, a great interest has been focused on polymeric fullerene materials due to their potential technological applications in a variety of fields [1–13]. On the other hand, we have already reported on the synthesis and applications of fluoroalkyl end-capped polymers possessing numerous unique properties, such as a high surface active property, the formation of self-assembled molecular aggregates and biological activities which cannot be achieved in the corresponding randomly fluoroalkylated polymers and the perfluoropolymers [14–19]. From such a point of view, it is very interesting to explore novel fluoroalkyl end-capped fullerene polymers. However, studies on the synthesis and properties of these polymeric compounds have been hitherto very limited, but these fluorinated materials have been the subject of considerable research of both fundamental and applied nature. In this communication, we report on the synthesis of novel fluoroalkyl end-capped amphiphilic fullerene ( $C_{60}$ ) cooligomers by the use of fluoroalkanoyl peroxide as a key intermediate, with particular emphasis on the surface properties of these fluorinated fullerene cooligomers.

A typical experiment for the synthesis of fluoroalkyl end-capped  $C_{60}$  cooligomers was as follows (Scheme 1). Perfluoro-2,5-dimethyl-3,6-dioxanonoyl peroxide (3.3 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 (250 g) was added to a chlorobenzene solution (9.4 g) of  $C_{60}$  (0.21 mmol) and acryloylmorpholine (ACMO: 12.0 mmol). The solution was stirred at 45°C for 5 h under nitrogen. The dark brown solution was obtained after removal of the precipitant. After evaporating the solvent under reduced pressure, the crude product obtained was reprecipitated from chloroform-hexane to give a  $\alpha,\omega$ -bis(perfluoro-1,4-dimethyl-2,5-dioxaoctylated)  $C_{60}$ -ACMO cooligomer (2.95 g). This oligomer exhibited the following spectra characteristics: IR ( $cm^{-1}$ ) 1630 (C=O), 1302 ( $CF_3$ ), 1243 ( $CF_2$ ), 1161 ( $-C_{60}-$ ), 1117 ( $-O-$ ), 580 ( $-C_{60}-$ ), 534 ( $-C_{60}-$ );  $^1H$  NMR(DMSO- $d_6$ )  $\delta$  0.97 ~ 1.99 ( $CH_2$ ), 2.27 ~ 2.99 (CH), 3.15 ~ 4.10 ( $CH_2$ );  $^{19}F$  NMR(DMSO- $d_6$ , ext.  $CF_3CO_2H$ )  $\delta$  -4.16 ~ -9.06 (26F), -53.87 (6F), -69.82 (2F); average molar mass ( $M_n$ ) = 6520,  $M_w/M_n$  = 1.34 [determined by gel permeation chromatography (GPC) calibrated with standard polystyrenes by using tetrahydrofuran as eluent].

A variety of fluoroalkyl end-capped  $C_{60}$  cooligomers were obtained 34–62% isolated yields under very mild conditions by the reactions of fluoroalkanoyl peroxides with  $C_{60}$  and comonomers such as ACMO, *N,N*-dimethylacrylamide (DMAA) and acrylic acid (ACA), and the results were shown in Scheme 1 and Table 1.

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Scheme 1.

Hitherto, it is well known that  $\text{C}_{60}$  can easily react with free radicals to produce various adducts as well as the usual radical polymerizable monomers [4]. The concentration of fluoroalkanoyl peroxide used was higher than that of comonomer or  $\text{C}_{60}$  [molar ratio of comonomer (or  $\text{C}_{60}$ )/peroxide = 3.6, 4.5 (or 0.06)], in contrast to the usual case for radical polymerization. Under these conditions, mainly  $\text{C}_{60}$  cooligomers with two fluoroalkylated end-groups would be obtained via primary radical termination or radical chain transfer to the peroxide, as well as by our previously reported method for the synthesis of acrylic acid oligomers having two fluoroalkylated end-groups in one oligomeric molecule  $[\text{R}_F-(\text{CH}_2\text{CHCOOH})_n-\text{R}_F]$ :  $\text{R}_F$  = fluoroalkyl group [20,21].

The  $\text{C}_{60}$  content in these fluorinated cooligomers is estimated by the IR spectra and the UV absorption (see Fig. 1). As shown in Fig. 1, UV-Vis spectra (Fig. 1) of fluorinated  $\text{C}_{60}$  cooligomer  $[\text{R}_F-(\text{C}_{60})_x-(\text{ACMO})_y-\text{R}_F]$ :  $\text{R}_F = \text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$  showed a weak absorption band at a 324 nm in chloroform, in contrast with a 329 nm in chloroform of the parent  $\text{C}_{60}$ . From the UV-Vis data, the cooligomerization ratio of  $\text{C}_{60}$  in this cooligomer was estimated to be about 1%. Interestingly, fluorinated  $\text{C}_{60}$  cooligomers in Table 1 were found to be easily soluble not only in water but also in common organic solvents such as methanol, ethanol, tetrahydrofuran, ethyl acetate, a fluorinated solvent (1:1 mixed solvents of 1,1-dichloro-2,2,3,3,3-pentafluoropropane and 1,3-dichloro-1,2,2,3,3-pentafluoropropane), dimethylformamide, and acetone; although the parent  $\text{C}_{60}$  is in general insoluble in these solvents. Highly hydrophobic  $\text{C}_{60}$  is known to be moderately

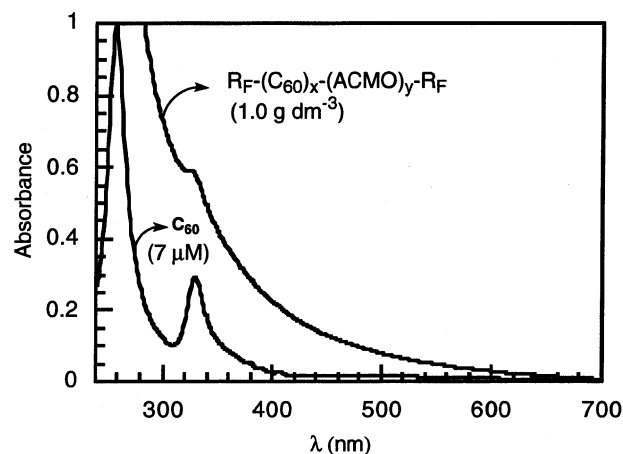


Fig. 1. UV-visible spectra of chloroform solutions of  $\text{R}_F-(\text{C}_{60})_x-(\text{ACMO})_y-\text{R}_F$  and  $\text{C}_{60}$ ;  $\text{R}_F = \text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$ .

soluble in nonpolar aprotic solvents, and insoluble in water [22–25]. Water solubilization of  $\text{C}_{60}$  becomes important, in view of the potential ability of the fullerene [22–25]. From such a point of view, our present water-soluble fluorinated  $\text{C}_{60}$  cooligomers are in particular interest. Therefore, our fluorinated  $\text{C}_{60}$  cooligomers are applicable to new fluorinated polymeric surfactants. In fact, these cooligomers were able to reduce the surface tensions of both water and benzene quite effectively from 72 to around 20 mN/m levels and from 29 to around 20 mN/m levels, respectively, with a clear break point resembling a CMC at 30°C. Therefore, not only fluoroalkyl units but also  $\text{C}_{60}$  segments in these fluorinated cooligomers should be arranged regularly above the water or organic surface. In order to clarify the surface property of these new fluorinated  $\text{C}_{60}$  cooligomers, we were interested in the formation of stable monolayers of these cooligomers at the air/water interface by the Langmuir–Blodgett method. A chloroform solution of  $\text{R}_F-(\text{C}_{60})_x-(\text{ACMO})_y-\text{R}_F$  [ $\text{R}_F = \text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$ ] was spread on the water surface, and the surface pressure–surface area ( $\pi$ -A) isotherm was measured. The  $\pi$ -A isotherm on pure water is shown in Fig. 2.

As shown in Fig. 2, this fluorinated  $\text{C}_{60}$  cooligomer was

Table 1  
Reactions of fluoroalkanoyl peroxide with  $\text{C}_{60}$  and comonomers

$\text{R}_F$ in $(\text{R}_F\text{CO}_2)_2$ (mmol)	$\text{C}_{60}$ (mmol)	Comonomer (mmol)	Product	
			Yield (%) <sup>a</sup>	$M_n(M_w/M_n)$
$\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$	0.21	ACMO	$\text{R}_F-(\text{C}_{60})_x-(\text{ACMO})_y-\text{R}_F$	
3.3		12	62	6520(1.34)
$\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$	0.21	12	55	3760(1.68)
3.3				
$\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$	0.21	DMAA	$\text{R}_F-(\text{C}_{60})_x-(\text{DMAA})_y-\text{R}_F$	
3.3		15	34	7390(1.11)
$\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$	0.21	ACA	$\text{R}_F-(\text{C}_{60})_x-(\text{ACA})_y-\text{R}_F$	
3.3		15	61	5080(1.85)

<sup>a</sup> The yields are based on the starting material [ $\text{C}_{60}$ , comonomer and the decarboxylated peroxide unit ( $\text{R}_F-\text{R}_F$ )].

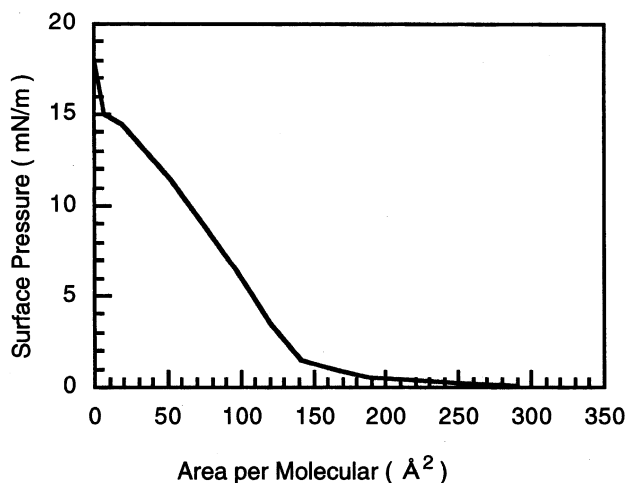


Fig. 2.  $\pi$ -A isotherm of  $R_F-(C_{60})_x-(ACMO)_y-R_F$ ;  $R_F = CF(CF_3)OCF_2CF(CF_3)OC_3F_7$  ( $M_n = 6520$ ).

found to form monomolecular film at the air/water interface, and the limiting area of this cooligomer at zero pressure ( $\pi_0$ ) was around  $150 \text{ \AA}^2$ . This finding suggests that the fluoroalkyl segments in cooligomers are perpendicular to the water surface and closely packed. Thus,  $C_{60}$  segments in this cooligomer should be arranged regularly above the surface. In general, the monolayers of water-soluble amphiphilic compounds are suggested to be very unstable. However, the monolayer of our present amphiphilic fluoroalkyl end-capped fullerene cooligomer was relatively stable because our present fluorinated cooligomer possesses strong hydrophobic fluoroalkyl and fullerene units.

Additionally, some fluorinated  $C_{60}$  cooligomers were tested for polystyrene (Pst) surface activity as a new type of  $C_{60}$ -containing fluorinated surface-active substances, and the results were listed in Table 2.

As shown in Table 2, contact angles for dodecane on the Pst surface treated with fluorinated  $C_{60}$  cooligomers [1% ( $m/m$ )] showed a significantly large value ( $41$ – $51^\circ$ ) compared with that ( $0^\circ$ ) of the nontreated Pst film, indicating that the

fluorinated  $C_{60}$ -cooligomers possess a higher oil-repellent property. On the other hand, the contact angles of water showed a considerably small value ( $10$ – $23^\circ$ ) and decreased dramatically to  $0$ – $13^\circ$  over 25 or 30 min with each fluorinated  $C_{60}$  cooligomer, although a constant value ( $86^\circ$ ) was obtained over 30 min in the nontreated Pst film. In contrast, contact angle measurements of dodecane and water on the Pst surfaces treated with fluoroalkyl end-capped  $N,N$ -dimethylacrylamide homo-oligomer [ $R_F-(DMAA)_n-R_F$ ] showed that fluorinated  $C_{60}$ -DMAA cooligomer possess slightly lower oleophobicity and hydrophilicity compared to  $R_F-(DMAA)_n-R_F$ . This finding would result from the presence of  $C_{60}$  segments on the Pst surface.

In this way, fluoroalkyl end-capped  $C_{60}$  cooligomers exhibit a markedly strong hydrophilicity above their surface, though these materials have highly hydrophobic fluoroalkyl and  $C_{60}$  segments. This finding suggests that at the interface with water, hydrophobic fluoroalkyl segments are replaced by the strongly hydrophilic morpholino or carboxdimethylamide [ $-C(=O)NMe_2$ ] segments. Such hydrophilic segments in fluorinated cooligomers are likely to be arranged more regularly at the air/Pst interface due to the bulkiness of  $C_{60}$  segments in cooligomers.

In particular interest, the above-mentioned results suggest strongly that  $C_{60}$  segments in fluorinated cooligomers should be arranged regularly above the Pst surface. Thus, it is very interesting to test the Pst surface treated with these fluorinated  $C_{60}$  cooligomers as a new type fluorinated-conducting polymer, because  $C_{60}$  segments are suggested to form well-ordered structures. The electrical conductivity in the plane of the Pst film treated with  $R_F-(C_{60})_x-(ACMO)_y-R_F$  ( $R_F = CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ ) listed in Table 2 was measured by a d.c. two-probe method. However, this Pst film and this Pst film doped with  $I_2$  or TCNQ (7,7,8,8-tetracyanoquinodimethane), which is a well-known electron-acceptor, had no conductivity. On the other hand, it was verified that this Pst film doped with 3,3',5,5'-tetramethylbenzidine, which is one of the most popular electron-donor substrate, has a conductivity of  $1.01 \times 10^{-10} \text{ S/cm}$  at room temperature. This finding

Table 2

Contact angles of dodecane and water on polystyrene films treated with fluoroalkyl end-capped fullerene cooligomers. (Concentration of oligomer based on polystyrene is 1% ( $m/m$ ))

$R_F$ in oligomer	Contact angle (degree)							
	Dodecane	Water 0 min	5 min	10 min	15 min	20 min	25 min	30 min
$R_F-(C_{60})_x-(ACMO)_y-R_F$								
$CF(CF_3)OC_3F_7$	41	10	9	9	9	5	3	2
$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	50	20	13	9	5	3	0	0
$R_F-(C_{60})_x-(DMAA)_y-R_F$								
$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	51	23	23	20	17	15	15	13
$R_F-(DMAA)_n-R_F$ ( $M_n = 2060$ )								
$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	57	10	7	3	0	0	0	0

suggests that C<sub>60</sub> segments should interact strongly with electron-donating substrates such as 3,3',5,5'-tetramethylbenzidine above the Pst surface to form the charge transfer complex between C<sub>60</sub> segments in the cooligomer and 3,3',5,5'-tetramethylbenzidine, since C<sub>60</sub> is known to possess a considerably low LUMO energy [26].

Our present amphiphilic fluoroalkyl end-capped C<sub>60</sub> cooligomers were demonstrated to have high potential for new fluorinated functional material through their unique surface and electrical properties. Further studies are actively in progress.

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