



# Synthesis of self-assembled fluoroalkyl end-capped oligomeric aggregates—Applications of these aggregates to fluorinated oligomeric nanocomposites

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## Abstract

Fluoroalkanoyl peroxide is a useful tool for the preparation of ABA triblock-type fluoroalkylated oligomers  $[R_F-(M)_n-R_F]$  by the reaction of the peroxide with a wide variety of radical polymerizable monomers under very mild conditions. Fluoroalkanoyl peroxide is also applied to the preparation of new dendritic fluoroalkyl end-capped polymers. Usually, it is well known that longer fluoroalkylated compounds exhibit a strong repellent property against water or hydrocarbons owing to the strong electronegativity of fluorine; however, end-capped fluoroalkyl groups in these fluorinated oligomers could aggregate easily each other rather than have repellent interactions in aqueous or organic media to afford nanometer size-controlled self-assembled molecular aggregates in these media. Interestingly, these fluorinated molecular aggregates could interact with a variety of guest molecules such as organic dyes, low-molecular biocides, metal nanoparticles, calcium carbonates, fullerenes, single-walled carbon nanotubes, nanodiamond and magnetites to afford stable fluorinated molecular aggregates-guest molecules nanocomposites. More interestingly, these fluorinated nanocomposites were applied to the surface modification of traditional organic polymers such as poly(methyl methacrylate) (PMMA) to exhibit not only a good surface active property imparted by fluorine but also a unique characteristic related to the guest molecules on their surface. Additionally, fluoroalkyl end-capped oligomers were applied to the preparation of fluoroalkyl end-capped oligomers-silica nanoparticles by the reactions of the corresponding oligomers with tetraethoxysilane and silica nanoparticles under alkaline conditions.

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**Keywords:** Fluorinated oligomer; End-capped fluoroalkyl group; ABA triblock; Molecular aggregates; Nanocomposites; Fluorinated dendritic polymer

**Abbreviations:** AK-225, 1:1 mixed solvents of 1,1-dichloro-2,2,3,3-pentafluoropropane and 1,3-dichloro-1,2,2,3,3-pentafluoropropane; DOBAA, *N*-(1, 1-dimethyl-3-oxobutyl)acrylamide; Pst, polystyrene; PMMA, poly(methyl methacrylate); CNT, carbon Nanotube; SW-CNT, single-walled carbon nanotube; ACMO, acryloylmorpholine; DMAA, *N, N*-dimethylacrylamide

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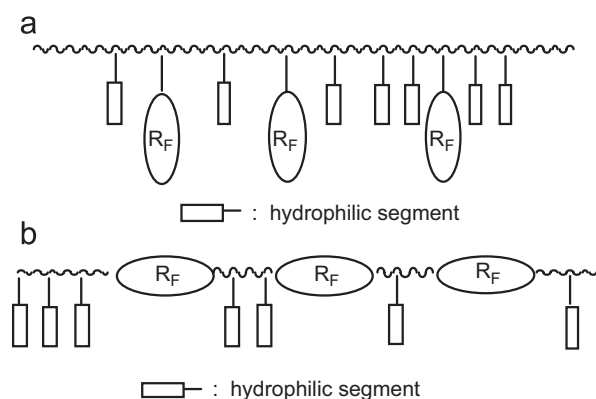
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## 1. Introduction

In general, fluorinated polysoaps can be classified into two types: randomly fluoroalkylated polysoaps, and AB block-type fluoroalkylated polysoaps (see Scheme 1). In these fluorinated polysoaps, there have hitherto been numerous reports on the synthesis and applications of randomly fluoroalkylated polysoaps [1–4]. For example, Lachewsky et al. reported on the synthesis of fluorinated cationic polysoaps in which fluoroalkyl groups were randomly introduced into polymeric molecules [5] (Scheme 2).

However, in these randomly fluoroalkylated polysoaps, these fluoroalkyl segments are introduced into polymeric molecules through the ester groups. Thus, these fluoroalkyl segments are likely to suffer the hydrolysis owing to the strong electron negativity of fluorine. In addition, these fluorinated



Scheme 1.

polysoaps in general (Scheme 3) possess a low solubility in various solvents and are not effective for reducing the surface tension of water.

Similarly, synthesis and applications of a wide variety of fluorinated AB block-type polysoaps, in which fluoroalkyl groups were introduced through the ester groups, have been hitherto reported [6–10]. For example, fluoroalkylated AB block-type polysoaps were prepared by using polymeric acyl peroxides (see Scheme 4) [11].

Hitherto, there have been some reports on the synthesis of fluoroalkyl end-capped polymers as follows:

- [I] Living radical polymerizations
  - I-a From nitroxide-mediated polymerization [12–14] (Scheme 5).
  - II-a From reversible addition-fragmentation chain transfer (RAFT) [15–17] (Scheme 6).
  - III-a From atom transfer radical polymerization (ATRP) [18–21] (Schemes 7 and 8).
- [II] Olefin metathesis [22] (Scheme 9).
- [III] Esterification with perfluoroacyl chloride [23,24] (Scheme 10).
- [IV] Reaction of isocyanates with fluoroalcohols [25,26] (Scheme 11).
- [V] Telomerizations with fluorinated mercaptan and fluorinated alky iodides [27,28] (Scheme 12).
- [VI] Iodine transfer polymerization [29] (Scheme 13).

In these fluoroalkyl end-capped polymers, fluoroalkyl groups are in general introduced into polymeric molecules through the ester, amide, and urethane bondings except for the ATRP technique

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