

# Synthesis and Gelation of Fluoroalkyl End-Capped Copolymers Containing Glucosyl Segments: Application to New Fluorinated Conductive Polymer Electrolytes

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Received 14 June 2001; accepted 30 November 2001

**ABSTRACT:** Fluoroalkyl end-capped copolymers containing glucosyl segments were prepared by the copolymerizations of fluoroalkanoyl peroxides with 2-glucosyoxethyl methacrylate (GEMA) and comonomers such as acrylic acid (ACA) and methacrylate monomer-containing poly(oxyethylene) units (PME). Under the non-cross-linked conditions, fluoroalkyl end-capped GEMA-ACA and GEMA-PME copolymers were found to cause a gelation in dimethyl sulfoxide (DMSO), where the aggregations of end-capped fluoroalkyl segments and the hydrogen-bonding interaction between hydroxyl segments are involved in establishing a physical gel network, although the corresponding non-fluorinated GEMA copolymers could cause no gelation in DMSO. More interestingly, it was demonstrated that these fluorinated polymeric gelling electrolytes containing lithium salts exhibit a considerably high ionic conductivity of  $10^{-3}$  S/cm level at room temperature. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2833–2838, 2002

**Key words:** fluorinated polymer; gelation; ionic conductivity; aggregation of fluorine; lithium ion

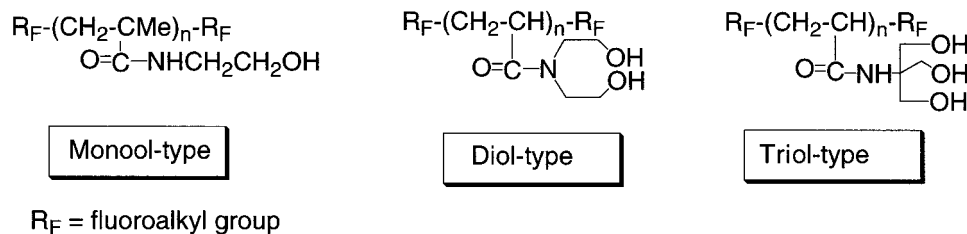
## INTRODUCTION

We have demonstrated recently that fluoroalkyl end-capped polymers can exhibit a variety of unique properties such as a high solubility, biological activities, and the formation of self-assembled molecular aggregates with the aggregations

of the terminally fluoroalkylated segments, which cannot be achieved by the corresponding randomly fluoroalkylated polymers and fluoroalkylated block polymers.<sup>1</sup> In these fluoroalkyl end-capped polymers, it was demonstrated that those containing monool, diol, and triol segments (shown in Scheme 1) can cause gelation under non-cross-linked conditions and that the strong aggregation of the end-capped fluoroalkyl segments in water and organic media becomes a new driving factor for gelation in addition to the hydrogen bonding interaction of the hydroxyl seg-

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*Journal of Applied Polymer Science*, Vol. 85, 2833–2838 (2002)  
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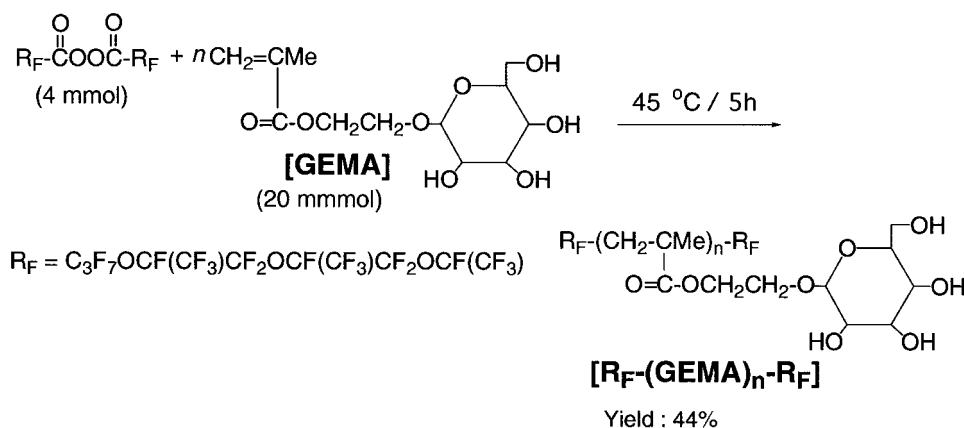
Scheme 1

ments.<sup>2,3,4</sup> Therefore, it is expected that the synthesis of fluoroalkyl end-capped polymers containing tetraol segments could be derived into the development of fluorinated polymeric materials possessing a higher gelling ability. However, there has been a great interest in the development of the gelled polymer electrolyte-based rechargeable lithium battery, which can offer liquid-like values for the conductivity, and numerous studies on the gelling polymer electrolytes have been reported to date.<sup>5</sup> The development of fluorinated gelling polymer electrolytes has hitherto been very limited, but it is very important to explore novel fluoroalkylated gelling polymer electrolytes from the view points of the development of new fluorinated functional materials. Thus, it is deeply desirable to synthesize novel fluoroalkyl end-capped polymers containing tetraol segments. In this article, we report on the synthesis and gelation of novel fluoroalkyl end-capped copolymers containing glucosyl segments, using fluoroalkanoyl peroxide as a key intermediate, with particular emphasis on the application to new fluorinated gelling conductive polymer electrolytes.

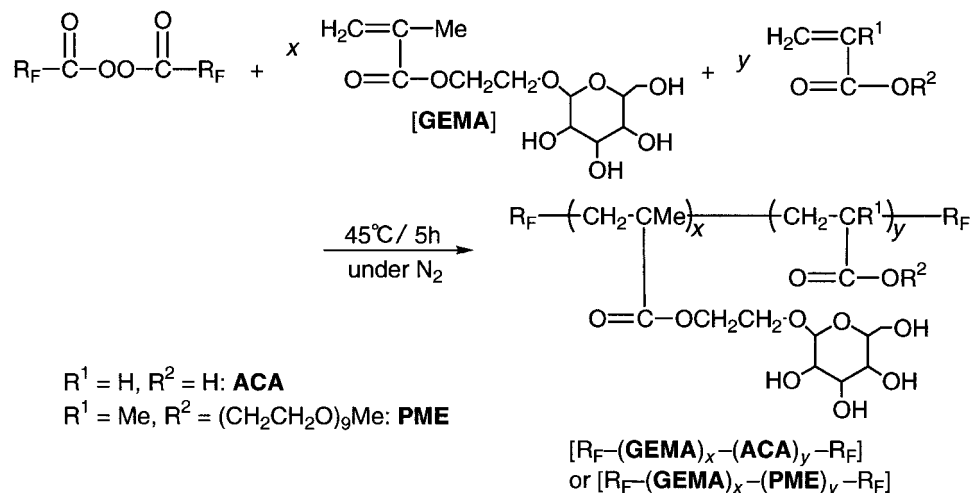
## RESULTS AND DISCUSSION

The reaction of fluoroalkanoyl peroxide with 2-glucosyloxyethyl methacrylate (GEMA) was carried out by heating the reaction mixtures at 45°C for 5 hours under nitrogen. The process is outlined in Scheme 2.

As shown in Scheme 2, GEMA was found to react smoothly with fluoroalkanoyl peroxide to give fluoroalkyl end-capped GEMA homo-polymer in a 44% yield. However, this fluorinated homo-polymer was not soluble in water or common organic solvents at all. This finding suggests that the aggregations between end-capped fluoroalkyl segments in polymer and the intermolecular hydrogen bonding between hydroxyl segments in GEMA are strongly governed in water and organic solvents. Therefore, the introduction of comonomer units into fluoroalkyl end-capped GEMA polymers could weaken the hydrogen bonding interactions to cause a gelation in these solvents. Then we tried to use acrylic acid (ACA) and methacrylate monomer-containing poly(oxyethylene) units (PME) as comonomers in the above reaction system; the results on the reactions of fluoroalkanoyl peroxides



Scheme 2



Scheme 3

with GEMA and ACA (or PME) are shown in Scheme 3 and Table I.

As shown, the copolymerizations of fluoroalkyl peroxides with GEMA and ACA (or PME) proceeded under very mild conditions to afford fluoroalkyl end-capped GEMA copolymers in 32%~88% isolated yields. A series of fluoroalkyl end-capped GEMA-ACA and GEMA-PME copolymers thus obtained were not soluble in water or common organic solvents such as methanol, ethanol, dimethylformamide, chloroform, ethyl acetate, benzene, toluene, acetone, and hexane. However, these fluorinated GEMA copolymers were found to cause a gelation in dimethyl sulfoxide (DMSO), although the corresponding nonfluorinated GEMA copolymers could not cause a gelation in DMSO. In these fluoroalkylated GEMA copolymers, we could not measure each copolymerization ratio or the molecular weight of the

copolymer by NMR (nuclear magnetic resonance) and GPC (gel permeation chromatography), respectively, under various conditions, owing to the gel formation. The result for their solubilities that is, the hydrophobicity of our present fluoroalkyl end-capped GEMA copolymers, is suitable to provide the new fluorinated gelling polymeric electrolytes with a good stability. In contrast, our previously reported fluoroalkyl end-capped polymers containing monool, diol, and triol segments, as in Scheme 1, have been shown to cause a gelation in water.<sup>2-4</sup>

To study this gel-formation ability, we have measured the minimum concentrations of the fluoroalkyl end-capped GEMA copolymers necessary for gelation according to a method reported by Hanabusa et al.<sup>6</sup> The results on the minimum concentration for gelation ( $C_{\min}$ ) in DMSO at 30°C are as follows:

**Table I** Reactions of Fluoroalkanoyl Peroxides with 2-Glucosyloxyethyl methacrylate (GEMA) and Acrylic Acid (ACA) (or PME) at 45°C for 5 Hours

$R_F$ in Peroxide	$R_F$ in Peroxide (mmol)	GEMA (mmol)	Comonomer (mmol)	Product Yield (%) <sup>a</sup>
$C_3F_7OCF(CF_3)$	5	25	ACA	$R_F-(GEMA)_x-(ACA)_y-R_F$ 55
$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$	4	20	ACA	88
$C_3F_7OCF(CF_3)$	5	24	PME	$R_F-(GEMA)_x-(PME)_y-R_F$ 54
$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$	2	12	PME	32

<sup>a</sup> The yield is based on the starting materials (GEMA, PME, and the decarboxylated peroxide unit [ $R_F-R_F$ ]).

**Table II** Ionic Conductivities ( $\sigma$ [S/cm]) of  $R_F-(GEMA)_x-(ACA)_y-R_F$  and  $R_F-(GEMA)_x-(PME)_y-R_F$  at Room Temperature

Co-oligomer	Li Salt (2.7 mmol/g [co-oligomer])		
	$(CF_3SO_2)_2NLi$	$CF_3SO_3Li$	$PF_6Li$
$R_F-(GEMA)_x-(ACA)_y-R_F$			
$R_F = CF(CF_3)OC_3F_7$	$1.07 \times 10^{-3}$	$1.39 \times 10^{-3}$	$2.70 \times 10^{-3}$
$= CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	$2.12 \times 10^{-3}$	$2.56 \times 10^{-3}$	$8.60 \times 10^{-4}$
$R_F-(GEMA)_x-(PME)_y-R_F$			
$R_F = CF(CF_3)OC_3F_7$	$5.09 \times 10^{-4}$	$5.20 \times 10^{-4}$	$2.45 \times 10^{-3}$
$= CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	$1.49 \times 10^{-3}$	$2.33 \times 10^{-3}$	$7.15 \times 10^{-4}$

GEMA = 2-glucosyoxoethyl methacrylate; ACA = acrylic acid; PME = poly(oxyethylene).

Copolymer	$C_{min}$ [g/dm <sup>3</sup> ]
$R_F-(GEMA)_x-(ACA)_y-R_F$	
$R_F = CF(CF_3)OC_3F_7$	177
$= CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	173
$R_F-(GEMA)_x-(PME)_y-R_F$	
$R_F = CF(CF_3)OC_3F_7$	156
$= CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	177

$C_{min}$ s of a series of fluoroalkyl end-capped GEMA copolymers necessary to gel 1 L of DMSO were 156–177 g dm<sup>-3</sup>, and the  $C_{min}$ s of  $R_F-(GEMA)_x-(ACA)_y-R_F$  were similar to those of  $R_F-(GEMA)_x-(PME)_y-R_F$ . This result indicates that the main driving force for gelation is the synergistical interactions with the aggregation of end-capped fluoroalkyl units in copolymers and the intermolecular hydrogen bonding between tetraol segments in GEMA. However, it is suggested that the intermolecular hydrogen bonding between carboxyl segments cannot participate strongly in the gelator, which is constructed by the aggregations of the fluoroalkyl units, since the carboxyl segments in  $R_F-(GEMA)_x-(ACA)_y-R_F$  were directly introduced into the main polymer chains.

In this way, it was verified that our present fluoroalkyl end-capped GEMA copolymers possess gelling ability in DMSO. Especially, fluoroalkyl end-capped GEMA–PME copolymers possess not only the gelling ability but also poly(oxyethylene) units. Therefore, it is very interesting to apply these fluorinated polymers to new gelling fluorinated polymer electrolytes. We have tested these fluorinated GEMA copolymers for ionic conductivity. Gelling fluorinated GEMA copolymer electrolytes were formed by heating DMSO solutions of the copolymers and lithium salts at 30°C

under ultrasonic conditions. The ionic conductivities  $\sigma$  [(S/cm)] in fluoroalkylated GEMA copolymer gels in the presence of some lithium salts were measured by a AC impedance method at room temperature.

As shown in Table II,  $R_F-(GEMA)_x-(PME)_y-R_F$  gels in the presence of lithium ions (2.7 mmol/g [copolymer]) exhibited good ionic conductivities of  $10^{-4}$ – $10^{-3}$  levels. Three kinds of lithium ions, such as  $(CF_3SO_2)_2NLi$ ,  $CF_3SO_3Li$ , and  $PF_6Li$  were found to exhibit similar ionic conductivities in these fluorinated gels. This finding suggests that the interaction between poly(ethylene oxide) and lithium ions could lead to relatively high ionic conductivities. However,  $R_F-(GEMA)_x-(ACA)_y-R_F$  gels were found to exhibit considerable high-ionic conductivities of  $10^{-3}$  levels compared with those of  $R_F-(GEMA)_x-(PME)_y-R_F$ . This finding suggests that carboxyl segments in  $R_F-(GEMA)_x-(ACA)_y-R_F$  should interact with lithium ions as well as the poly(oxyethylene) units to give a higher ionic conductivity. In the absence of lithium ions, room temperature proton conductivity of  $1.42 \times 10^{-4}$  S/cm has been obtained in the case of  $R_F-(GEMA)_x-(ACA)_y-R_F$  ( $R_F = CF([CF_3]OC_3F_7)$  gel).

In summary, it was demonstrated that fluoroalkanoyl peroxide is a convenient tool for the synthesis of a variety of fluoroalkyl end-capped GEMA polymers. Fluoroalkyl end-capped GEMA homo-polymer was not soluble in water or various organic solvents at all; however, fluoroalkyl end-capped GEMA–ACA and GEMA–PME copolymers were found to cause gelation in DMSO. However, the corresponding nonfluorinated GEMA copolymers could cause no gelation in DMSO. This suggests that fluoroalkyl end-capped

GEMA copolymers can cause gelation derived from the synergistical interaction of the strong aggregations of the end-capped fluoroalkyl segments and the intermolecular hydrogen bonding interactions between tetraol segments in GEMA. In these fluoroalkyl end-capped GEMA copolymers,  $R_F-(GEMA)_x-(ACA)_y-R_F$  gels in lithium ions exhibited higher ionic conductivities at  $10^{-3}$  S/cm levels. In addition, this fluorinated GEMA-ACA copolymer gel exhibited a proton conductivity at a  $10^{-4}$  S/cm level. Therefore, our present fluoroalkyl end-capped GEMA-ACA copolymers are applicable to not only lithium ions but also proton conductive polymer electrolytes, especially new fluorinated ionic conductive materials.

## EXPERIMENTAL

### Measurements

Fourier-transform infrared (FTIR) spectra were measured using a Shimadzu FTIR-8400 spectrophotometer (Kyoto, Japan). We attempted to measure NMR spectra and molecular weights using a Varian Unity-plus 500 (500 MHz) spectrometer (Palo Alto, CA) and a Shodex DS-4 (pump) and Shodex RI-71 (Detector) gel permeation chromatographer (Tokyo, Japan), respectively. The ionic conductivities were determined by AC impedance measurement using a Hi Tester HIOKI-3520 (Nagano, Japan).

### Materials

GEMA and methacrylate monomer containing were used as received from Nippon Fine Chemical Co. Ltd. (Hyogo, Japan) and NOF corporation (Tokyo, Japan), respectively. Acrylic acid was purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan).  $(CF_3SO_2)_2NLi$ ,  $CF_3SO_3Li$ , and  $PF_6Li$  were purchased from Kishida Chemical Co., Ltd. (Osaka, Japan). A series of fluoroalkanoxy peroxides  $[(R_FCOO)_2]$  were prepared by the method described in the literature.<sup>7,8</sup>

### General Procedure for the Synthesis of Fluoroalkyl End-Capped GEMA Copolymers

Perfluoro-2-methyl-3-oxahexanoxy peroxide (5 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 (100 g), and acrylic acid (25 mmol) were added to an aqueous

solution (50%, w/w) of GEMA (25 mmol). The heterogeneous solution was stirred vigorously at 45°C for 5 hours under nitrogen. The crude product obtained was washed with methanol well to remove the unreacted GEMA monomer and acrylic acid and dried over *in vacuo* to give a bis(perfluoro-1-methyl-2-oxapentylated) GEMA-acrylic acid copolymer (6.58 g). This polymer exhibited the following spectra characteristics: IR ( $cm^{-1}$ ) 3420 (OH), 1717 (C=O), 1310 ( $CF_3$ ), 1250 ( $CF_2$ ).

Similarly, a series of fluoroalkyl end-capped GEMA homo- and copolymers were prepared by homo- and copolymerizations with fluoroalkanoxy peroxides. These exhibited the following spectral characteristics:

$C_3F_7OCF(CF_3)CF_2OCF(CF_3)-(GEMA)_n-CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ : IR ( $cm^{-1}$ ) 3346 (OH), 1715 (C=O), 1308 ( $CF_3$ ), 1251 ( $CF_2$ ).

$C_3F_7OCF(CF_3)CF_2OCF(CF_3)-(GEMA)_x-(ACA)_y-CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ : IR ( $cm^{-1}$ ) 3450 (OH), 1720, 1711 (C=O), 1310 ( $CF_3$ ), 1242 ( $CF_2$ ).

$C_3F_7OCF(CF_3)-(GEMA)_x-(PME)_y-CF(CF_3)OC_3F_7$ : IR ( $cm^{-1}$ ) 3400 (OH), 1717 (C=O), 1354 ( $CF_3$ ), 1252 ( $CF_2$ ).

$\sim C_3F_7OCF(CF_3)CF_2OCF(CF_3)-(GEMA)_x-(PME)_y-CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ : IR ( $cm^{-1}$ ) 3430 (OH), 1717 (C=O), 1352 ( $CF_3$ ), 1254 ( $CF_2$ ).

### Typical Procedure for Gelation Test

A procedure for studying gel-formation ability was based on a method reported by Hanabusa et al.<sup>6</sup> Briefly, weighted fluoroalkyl end-capped GEMA copolymer was mixed with DMSO in a tube. The mixture was treated under ultrasonic conditions until the solid was dissolved. The resulting solution was kept at 30°C for 1 hour, and gelation was checked visually. The gel was stable, and the tube could be inverted without changing the shape of the gel.

### Ionic Conductivity Measurements

The ionic conductivities of fluorinated gel electrolytes were determined by AC impedance measurement between 40 Hz and 100 kHz using a Hi Tester HIOKI-3520. Fluorinated gels (0.98 cm in diameter) were sandwiched between two copper electrodes in a sealed cell under a dry argon atmosphere. Measurements were carried out over room temperature. Bulk resistance was derived from the Cole-Cole plot of the complex impedance

data of the fluorinated gel, where the imaginary impedance is zero. Conductivity was calculated from the bulk resistance according to the following equation:

$$\sigma = D/A \times R_b,$$

where  $\sigma$  is conductivity,  $D$  is the thickness of the sample,  $A$  is the section area of the sample, and  $R_b$  is bulk resistance.

We thank Nippon Fine Chemical Co. Ltd. and NOF Corporation for supply of GEMA and PME, respectively.

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