Gelation of Fluoroalkylated End-Capped Oligomers Containing Triol Segments under Non-Crosslinked Conditions, and Binding or Releasing of Metal Ions by These Oligomers

Hideo Sawada,*,† Yutaka Nakamura, Shinsuke Katayama,† and Tokuzo Kawase††

Department of Chemistry, Nara National College of Technology, Yamatokoriyama, Nara 639-11

†Department of Chemistry, Faculty of Advanced Engineering, Nara National College of Technology, Yamatokoriyama, Nara 639-11

††Faculty of Human Life Science, Osaka City University, Sumiyoshi, Osaka 558

(Received May 23, 1997)

New fluoroalkylated end-capped oligomers containing triol segments were prepared by the reactions of *N*-tris(hydroxymethyl)methylacrylamide and fluoroalkanoyl peroxides. Under the non-crosslinked conditions, these fluoroalkylated oligomers were found to cause a gelation, where the aggregations of fluoroalkyl segments and the hydrogen-bonding interaction are involved in establishing a physical gel network not only in water, but also in organic solvents. Therefore, it was demonstrated that the aggregation of the end-capped fluoroalkyl segments in water and/or in organic media become a new driving factor for gelation as well as such well-known interactions as the hydrogen bond and ionic interaction. These thus-obtained fluorinated oligomer hydrogels had a high Cr^{3+} or Co^{2+} binding power, and the metal ions were easily released from the metal ions-bound oligomers into water.

Polyacrylamide gels, such as poly[*N*-tris(hydroxymethyl)methylacrylamide] gels crosslinked by *N*,*N*′-methylenebisacrylamide, have been widely used as anticonvective media for the electrophoretic separation of biomolecules,[1] and their derivatives have also been applied to a drug-delivery system.[2] Hitherto, there has been attractive interest in organofluorine compounds owing to possessing various unique properties which cannot be achieved by the corresponding non-fluorinated compounds.[3] Therefore, it is of particular interest to explore fluorinated polyacrylamide gels; however, although the preparation and application of these compounds have been limited, these compounds have been the subject of considerable research of both fundamental and applied nature. We have very recently discovered that fluoroalkylated end-capped betaine oligomers, $\{R_F\text{–}[CH_2\text{–}CH(=O)N^+H_2CMe_2CH_2SO_3^-]_n\text{–}R_F\}$, can cause a gelation derived from the synergistical interaction of the aggregations of fluoroalkyl segments and the ionic interactions of the betaine segments in water or organic media.[4] Therefore, the hydrogen-bonding interaction can be strongly expected to participate in the gelator which is constructed by the fluoroalkyl units.

From such points of view, we were interested in preparing new fluoroalkylated end-capped acrylamide oligomers which can cause physical gelation, the driving factors of which are intermolecular hydrogen bonding and the aggregations of fluoroalkyl segments. In this paper we report on the synthesis and properties of fluoroalkylated end-capped *N*-tris(hydroxymethyl)methylacrylamide oligomers by the reactions of fluoroalkanoyl peroxides with the corresponding monomers.

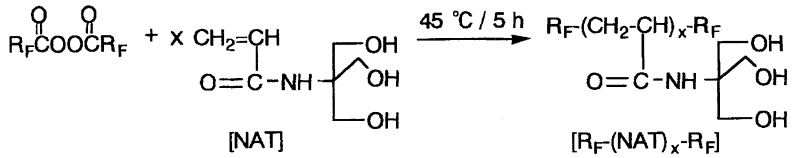
Results and Discussion

The reactions of fluoroalkanoyl peroxides with *N*-tris(hydroxymethyl)methylacrylamide [NAT] 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 were carried out at 45 °C for 5 h under nitrogen. The process is outlined in Scheme 1. NAT was found to react smoothly with the peroxides under mild conditions to give fluoroalkylated end-capped oligomers containing triol segments $[R_F\text{–}(NAT)_n\text{–}R_F]$.

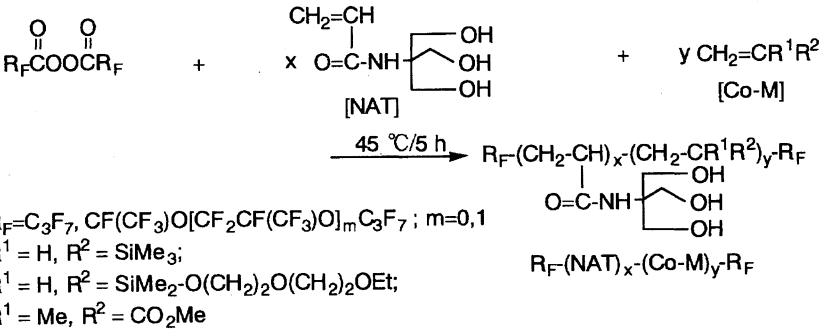
Similarly, co-oligomerization with co-monomers such as trimethylvinysilane, dimethyl-1,4,7-trioxanonylvinylsilane, and methyl methacrylate was found to proceed under mild conditions to afford the corresponding fluoroalkylated end-capped co-oligomers, as shown in the following Scheme 2.

The results for these reactions are summarized in Table 1.

As shown in Table 1, not only perfluoropropylated, but also perfluoro-oxaalkylated NAT homo- and co-oligomers, were obtained under mild conditions, and the co-oligomerization ratios of these oligomers were determined by ^{1}H NMR analyses. We had a different reactivity in the co-oligomerization ratios of the obtained co-oligomers. This finding would depend upon that our present homo- and co-oligomerizations of NAT with fluoroalkanoyl peroxides are heterogeneous systems including water. In these fluoroalkylated NAT homo- and co-oligomers (Table 1) we could not measure each molecular weight of the oligomers by GPC (gel permeation



Scheme 1.



Scheme 2.

Table 1. Synthesis of Fluoroalkylated NAT Homo- and Co-oligomers at 45 °C for 5 h

No.	R_F in Peroxide	NAT	$CH_2=CR^1R^2$	Product	
	mmol	mmol	mmol	Yield (%)[a]	[x : y][b]
	C_3F_7			R_F–(NAT)$_n$–R_F	
1	5	21	—	55	
2	4	9	—	45	
	$CF(CF_3)OC_3F_7$				
3	4	20	—	43	
4	5	5	—	29	
	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$				
5	3	13	—	42	
6	3	5	—	48	
	C_3F_7		$CH_2=CHSiMe_3$	R_F–(NAT)$_x$–(CH_2–CR^1R^2)$_y$–R_F	
7	4	21	21	55	[83 : 17]
	$CF(CF_3)OC_3F_7$				
8	5	21	21	53	[67 : 33]
	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$				
9	3	13	15	50	[96 : 4]
	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$		$CH_2=CHSiMe_2$–O(CH_2)$_2$O(CH_2)$_2$OEt		
10	3	13	14	25	[95 : 5]
	$CF(CF_3)OC_3F_7$		$CH_2=CMeCO_2Me$		
11	4	21	22	52	[88 : 12]
	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$				
12	3	13	13	54	[90 : 10]

a) The yields are based on the starting materials [NAT, Co-monomers and the decarboxylated peroxide unit (R_F–R_F)].
b) Co-oligomerization ratio was determined by ^{1}H NMR.

chromatography) analyses under various conditions owing to the highly viscoelastic fluids or gel formation. In contrast, we have already reported that fluoroalkylated end-capped acrylic acid oligomers [R_F–(CH_2CHCO_2H)$_n$–R_F] can be prepared by the reactions of fluoroalkanoyl peroxides with acrylic acid under similar conditions, and that their molecular weights ($\overline{M}_n$: 5000—13000) are easily measured by GPC analyses.[5] To clarify this unique gelling behavior, we measured the viscosity of aqueous solutions of these fluoroalkylated end-capped oligomers at 30 °C. The results are shown in Fig. 1.

A shown in Fig. 1, the viscosities of non-fluorinated NAT oligomer [–(NAT)$_n$–] did not increase remarkably with increasing its concentration. On the other hand, fluoroalkylated NAT oligomer increased extremely with increasing the

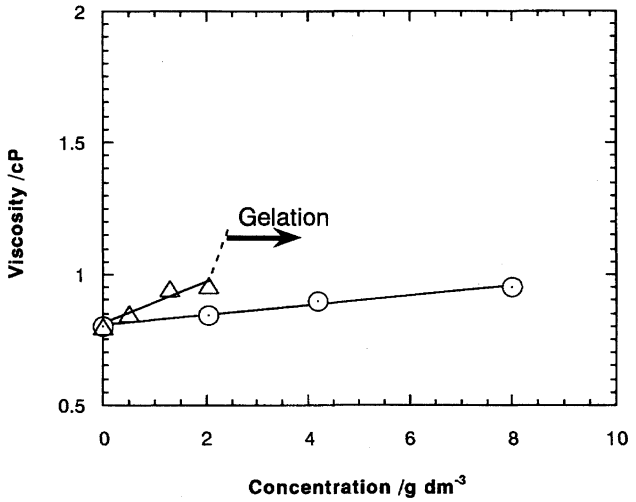


Fig. 1. Effect of concentration on viscosity of R_F–(NAT)$_n$–R_F and –(NAT)$_n$– at 30 °C. △ : R_F–(NAT)$_n$–R_F; $R_F = C_3F_7$ (No. 1 in Table 1), ○ : –(NAT)$_n$–.

concentration, and it became impossible to measure its viscosity owing to causing a gelation at concentrations above 2 g dm^{-3}.

Similarly, other fluoroalkylated end-capped oligomers were found to increase extremely with increasing the concentration to cause gelation in water. The striking characteristics of our fluoroalkylated NAT oligomers as gelling agents are to harden organic solvents, such as dimethyl sulfoxide (DMSO) and *N*,*N*-dimethylformamide (DMF). In contrast, non-fluorinated NAT oligomer was completely soluble not only in water, but also in organic solvents, such as DMSO and DMF.

We also tried to measure the temperature where the gel melts; however, the gel melted neither in water nor in DMSO, even when the gel was heated from 30 °C to around 95 °C. This suggests that the fluoroalkyl segments are strongly connected with the establishment of a gel network. For a similar gel formation of fluorinated compounds, Tweig et al reported that semifluorinated alkanes, such as $F(CF_2)_{10}(CH_2)_{12}H$, exhibit gel-like characteristics in hydrocarbon solvents, [H-$(CH_2)_p$H; $p = 8$, 10, 12, 14].[6] To study this gel-formation ability, we measured the minimum concentrations of fluoroalkylated NAT oligomers necessary for gelation according to a method reported by Hanabusa et al.[7] The results on the minimum concentrations for gelation (C_{min}) in water and in DMSO at 30 °C are given in Table 2.

There was no gel-formation ability for a non-fluorinated NAT oligomer owing to its good solubility. However, surprisingly, each fluoroalkylated oligomer in Table 1 can form a physical gel and harden not only water, but also organic polar solvents, such as DMSO at low concentrations, as shown in Table 2. In general, the gelling ability of fluoroalkylated homo-oligomers is superior to that of the co-oligomers, except for perfluoropropylated ones (Table 2), taking into account that C_{min}s are 18—47 g dm^{-3} for homo-oligomers and 34—82 g dm^{-3} for co-oligomers at 30 °C. This finding suggests that the fluoroalkylated homo-oligomers are likely to have stronger association through intermolecular hydrogen bondings between triol segments to cause physical gelation compared to those of the co-oligomers.

The non-fluorinated NAT oligomer could not cause gelation. Therefore, the physical gelling behavior for our fluorinated NAT oligomers is not governed by only the intermolec-

Table 2. Minimum Gel Concentration C_{min} of Fluoroalkylated NAT Homo- and Co-oligomers (in g per dm^{-3} Solvent) Necessary for Gelation at 30 °C

No.[a]	Oligomer	C_{min}	
		H_2O	DMSO
	R_F–(NAT)$_n$–R_F		
1	R_F=C_3F_7	72	72
2	=C_3F_7	38	73
3	R_F=$CF(CF_3)OC_3F_7$	18	24
4	=$CF(CF_3)OC_3F_7$	39	37
5	R_F=$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	42	47
6	=$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	31	19
	R_F–(NAT)$_x$–(CH_2–$CHSiMe_3$)$_y$–R_F		
7	R_F=C_3F_7	15	47
8	R_F=$CF(CF_3)OC_3F_7$	64	66
9	R_F=$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	57	63
	R_F–(NAT)$_x$–[CH_2–$CHSiMe_2$–$O(CH_2)_2O(CH_2)_2OEt$]$_y$–R_F		
10	R_F=$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	50	34
	R_F–(NAT)$_x$–(CH_2–$CMeCO_2Me$)$_y$–R_F		
11	R_F=$CF(CF_3)OC_3F_7$	82	63
12	R_F=$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	54	54

a) Each different from those of Table 1.

ular hydrogen bonding between triol segments, but the strong aggregations between end-capped fluoroalkyl segments in oligomers are essential for causing the gelation. Throughout these results, it is reasonable to assume that our present fluoroalkylated NAT oligomer gel is built up through the synergistical interactions of both the aggregations of fluoroalkyl segments and the intermolecular hydrogen bondings between triol segments. This feature is attributable to the fact that fluoroalkyl segments are solvophobic in aqueous and organic media, and enhance the aggregation due to the strong interaction between fluoroalkyl segments.

Much attention has been paid to the effect of metal ions or surfactants on the swelling equilibrium of polymer gels from both fundamental and technological standpoints.[8] For example, Osada et al. reported that poly(2-acryloylamino-2-methyl-1-propanesulfonic acid) gels crosslinked by *N*,*N*′-methylenebisacrylamide have high adsorptive properties against metal ions, such as Cr^{3+} and Co^{2+}.[9] Thus, it is very interesting to study the adsorptive properties against metal ions on the swelling equilibrium of our new fluoroalkylated NAT oligomer hydrogels. In fact, we have attempted to perform quantitative measurements of the uptake of Cr^{3+} by fluoroalkylated NAT oligomers. The metal-ion concentration of supernatant liquid after incubation (at 25 °C for 24 h) was spectrophotometrically determined from a calibration curve showing the relationship between the metal-ion concentration and absorbance at 580 nm (Cr^{3+}). These results are shown in Fig. 2.

As shown in Fig. 2, there was a decrease (a–b) in the absorbance of Cr^{3+} at 580 nm after the addition of the fluorinated hydrogel. This indicates that the Cr^{3+} ion strongly binds to R_F–$(NAT)_x$–$(CH_2CHSiMe_3)_y$–R_F hydrogel. A similar Cr^{3+} or Co^{2+} binding tendency was observed in poly(2-acryloylamino-2-methyl-1-propanesulfonic acid) gels crosslinked by *N*,*N*′-methylenebisacrylamide.[9]

More interestingly, as shown in Fig. 2, the results on the absorbance of Cr^{3+} released into water (c) and the absorbance of Cr^{3+} binding to gel (a–b) show that Cr^{3+} can be easily released from Cr^{3+}-bound R_F–$(NAT)_x$–$(CH_2CHSiMe_3)_y$–R_F hydrogel into water after incubation at 25 °C for 24 h.

Furthermore, the uptake and release of Cr^{3+} by various fluoroalkylated NAT oligomer hydrogels were studied for a wide range of metal-ion concentrations; these results are demonstrated in Figs. 3 and 4, respectively.

As shown in Fig. 3, the uptake of Cr^{3+} increased linearly with an increase in the initial concentration of Cr^{3+}, and fluorinated hydrogels possessing lower C_{min} values (i.e., No. 7: $C_{min} = 15\ g\,dm^{-3}$) were found to have a stronger Cr^{3+} binding power with ca. 40% binding ratio (the ratio based on the relative amount of Cr^{3+} binding to gel and relative amount of initial Cr^{3+}).

On the other hand, as shown in Fig. 4, the release of

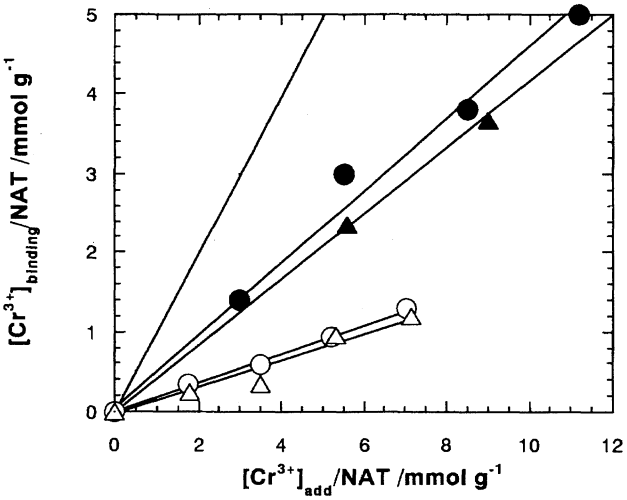


Fig. 3. Relationship between relative amount of Cr^{3+} binding to fluoroalkylated NAT oligomer hydrogels and relative amount of initial Cr^{3+} •: No. 7 in Table 1. ▲: No. 3 in Table 1. ○: No. 13 in Table 1. △: No. 11 in Table 1. —: Theoretical line (corresponds to a 100% binding ratio).

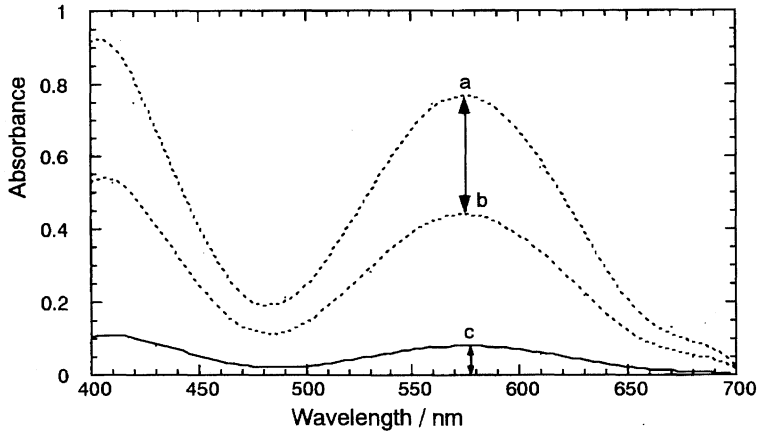


Fig. 2. The UV-visible spectra of aqueous solutions of $Cr(NO_3)_3$ in the presence (b) and absence (a) of R_F–$(NAT)_x$–$(CH_2CHSiMe_3)_y$–R_F gel, and the UV-visible spectra of aqueous solution in the presence of Cr^{3+} binding to R_F–$(NAT)_x$–$(CH_2CHSiMe_3)_y$–R_F gel (c) after the incubation at 25 °C for 24 h. (a) $Cr(NO_3)_3$: 60 mmol dm^{-3}. (b) Cr^{3+} binding to R_F–$(NAT)_x$–$(CH_2CHSiMe_3)_y$–R_F gel, ($R_F = C_3F_7$; No. 7 in Table 1; 6.57 g dm^{-3}). (c) Cr^{3+} released in water from Cr^{3+} binding to R_F–$(NAT)_x$–$(CH_2CHSiMe_3)_y$–R_F gel.

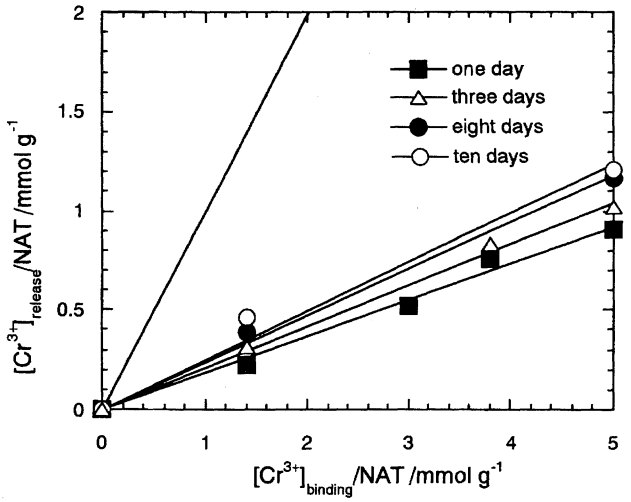


Fig. 4. Relationship between relative amount of released Cr^{3+} in water and relative amount of Cr^{3+} binding to No. 7 hydrogel under various incubation conditions.

Cr^{3+} increased linearly along with an increase in the initial concentration of Cr^{3+} binding to the fluoroalkylated hydrogels; it was clarified that Cr^{3+} can be released from Cr^{3+}-bound fluoroalkylated NAT oligomer hydrogels into water with ca. 18% (No. 7) or 25% (No. 3:C_{min} = 18 g dm^{-3} ; data not shown) releasing ratio after the incubation at 25 °C for 1 d. This releasing ratio is based on the relative amount of Cr^{3+} released into water and the relative amount of Cr^{3+} binding to gel. Thus, a oligomer hydrogel possessing a lower C_{min} value (No. 7) was clarified to have a lower metal-ion releasing power.

Furthermore, the release of Cr^{3+} from Cr^{3+}-bound fluoroalkylated NAT oligomer hydrogel (No. 7) possessing the lowest C_{min} was studied at 25 °C under various incubation conditions. The results are shown in Fig. 4.

As shown in Fig. 4, the releasing ratios were found to increase along with an increase in the incubation times from 18% (1 d) to 24% (10 d).

Similar results for the uptake and release of Co^{2+} ($CoCl_2$) by fluoroalkylated NAT oligomer hydrogels were obtained under the same spectrometrical conditions at 510 nm, and the uptake and release of Co^{2+} increased linearly with an increase in the initial concentration of Co^{2+} (data not shown), and an increase in the initial concentration of Co^{2+} binding to the hydrogels (data not shown) to afford ca. 50% (No. 7) and ca. 40% (No. 3) binding ratios, and ca. 18% (No. 7) and ca. 23% (No. 3) releasing ratios, respectively.

From these results, it can be said that the fluoroalkylated NAT oligomer hydrogels possessing lower C_{min} values enable the metal ions to bind more strongly to the triol segments in the oligomer networks via the coordinate interaction, since the stronger aggregation of fluoroalkyl segments and the intermolecular hydrogen bondings are necessary for the establishment of the physical gel network to exhibit lower C_{min} values. In contrast, the metal ions are likely to release easily from metal ions-bound fluorinated hydrogels possessing higher C_{min} values into water. This finding would depend on that the binding of metal ions to oligomer hydrogels is via the coordinate interaction, and the oligomer gels possessing higher C_{min} values have a weaker interaction among the oligomer networks in the gel.

The uptake of Cr^{3+} by fluoroalkylated NAT hydrogel (No. 7) was studied at 25 °C for a wider range (ca. 44 mmol g^{-1}) of Cr^{3+} concentrations than that of Fig. 3 in order to determine the binding number of Cr^{3+} to the hydrogel by applying the Langmuir isotherm. The results are shown in Fig. 5.

However, as shown in Fig. 5, the uptake of Cr^{3+} increased linearly with an increase in the initial concentration of Cr^{3+}. Thus, we can prefer to apply the following equilibrium reaction rather than Langmuir isotherm:

$$m\mathrm{M}^{n+} + \mathrm{R_F\text{–}Gel} \underset{K_2}{\overset{K_1}{\rightleftarrows}} \mathrm{R_F\text{–}Gel\ (M^{n+})}_m, \quad (1)$$

where R_F–Gel, M^{n+}, and R_F–Gel $(M^{n+})_m$ denote the fluoroalkylated NAT oligomer hydrogel, metal ion, and the fluoroalkylated NAT oligomer hydrogel with metal ions, respectively.

The equilibrium constant (K) can be then defined as

$$K = \frac{[\mathrm{R_F\text{–}Gel\ (M^{n+})}_m]}{[\mathrm{M}^{n+}]^m[\mathrm{R_F\text{–}Gel}]}, \quad (2)$$

where the brackets signify the equilibrium concentration of the species. Taking into account the fact that the degree of saturation (Y) of metal ion binding is given by

$$Y = \frac{[\mathrm{R_F\text{–}Gel\ (M^{n+})}_m]}{[\mathrm{R_F\text{–}Gel\ (M^{n+})}_m] + [\mathrm{R_F\text{–}Gel}]} \quad (3)$$

and also that $[M^{n+}]=C$, we obtain the following relation which is useful in determining the m and K values:

$$\log\left(\frac{Y}{1-Y}\right) = m\log C + \log K. \quad (4)$$

We can determine the m and K values in the Cr^{3+} uptake or release of No. 7 hydrogel from plots of $\log[Y/(1-Y)]$

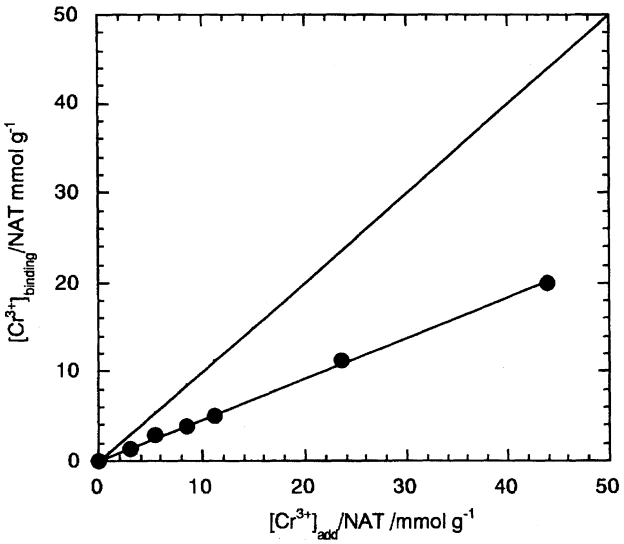


Fig. 5. Relationship between relative amount of Cr^{3+} binding to No. 7 hydrogel and relative amount of initial Cr^{3+}.

vs. log C using both Eq. 4 and the results shown in the data for No. 7 hydrogel in Fig. 4 (Cr^{3+} release) and Fig. 5 (Cr^{3+} uptake).

The m and K values were estimated by means of the slope of each straight line. The m and K_1 values for binding (incubation time: 1 d) estimated by means of the slope of the straight line were 0.9 and 12.3 $dm^3\ g^{-1}$, respectively. In contrast, the m and K_2 values for release estimated by means of the slope of each straight line were as follows:

Incubation time/d	m	K_2/$dm^3\ g^{-1}$
1	1.1	9.2
3	0.9	4.5
8	0.8	4.4
10	1.1	3.0

From these results, we can say that one molecule of metal ion was bound to one binding site in the gel. Thus, this result suggests that the metal ions bind only to the oligomer networks lying near to the gel surface due to the presence of a strong hydrophobic fluoroalkyl segment in the oligomers. The equilibrium constants K_2 (9.2—3.0 $dm^3\ g^{-1}$) were smaller than K_1 value (12.3 $dm^3\ g^{-1}$). This finding corresponds well with the results for the binding and the release ratios of the No. 7 hydrogel in Figs. 4 and 5.

In this way, it was clarified that fluoroalkylated end-capped oligomers containing triol segments can be prepared under very mild conditions by using fluoroalkanoyl peroxides as the key intermediates. Very interestingly, these fluoroalkylated oligomers were demonstrated to cause a physical gelation not only in water, but also in organic solvents, whose behavior is governed by the synergistical interaction of strong aggregations of fluoroalkyl segments in oligomers and intermolecular hydrogen bonding between triol segments under non-crosslinked conditions. Thus, it was demonstrated that the aggregation of fluoroalkyl segments in polymeric compounds in water and/or in organic media become a new driving factor for gelation as well as the well-known interactions, such as hydrogen bond and ionic interaction. Hitherto, 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, since fluoroalkyl groups are introduced into only oligomer end-sites, these fluoroalkyl segments could aggregate easily each other rather than have repellent interactions in aqueous or organic media. In fact, Kunitake et al. reported that the fluorocarbon tails in the fluorinated amphiphiles should provide the solovophobic property to form stable bilayer membrances in water[10—12] and in organic solvents.[13,14] Thus, such unique aggregate in these media would be remarkably enhanced due to the stability by the self-organization of oligomers to cause gelation in these media. Additionally, these fluoroalkylated oligomer hydrogels were demonstrated to have not only a metal ion binding, but also a metal-ion releasing power. Especially, these oligomer hydrogels possessing lower C_{min} values had a higher metal binding power, whereas, the hydrogels possessing higher C_{min} values had a higher releasing power. Therefore, these fluoroalkylated oligomers would be applicable to various fields, such as water softening, scale removal, and metal cleaning.

Experimental

NMR spectra were measured using a Varian Unity-plus 500 (500 MHz) spectrometer, while IR spectra were recorded on a Horiba FT-300 FT-IR spectrophotometer. Absorption spectra were recorded on a Shimadzu UV-240 spectrophotometer. Solution viscosities were measured by using a falling-sphere Haake Viscometer D1-G.

Materials. A series of fluoroalkanoyl peroxides [$(R_FCOO)_2$] were prepared by the reactions of the corresponding acyl halides and hydrogen peroxide in the presence of aqueous sodium hydroxide according to our previously reported method.[15] *N*-Tris(hydroxymethyl)methylacrylamide was purchased from Acros Organics Inc.. Trimethylvinylsilane and dimethyl-1,4,7-trioxanonylvinylsilane were purchased from Shin-Etsu Co., Ltd. Chromium(III) nitrate and cobalt(II) chloride were purchased from Wako Chemicals.

General Procedure for The Synthesis of Fluoroalkylated NAT Oligomers. Perfluor-2-methyl-3-oxahexanoyl peroxide (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 (50 g) was added to an aqueous solution (50%, w/w) of NAT (20 mmol). The heterogeneous solution was stirred vigorously at 45 °C for 5 h under nitrogen. The crude product obtained was washed with methanol well to remove the unreacted NAT monomer, and dried over in vacuo to give a bis(perfluoro-1-methyl-2-oxapentylated) *N*-tris(hydroxymethyl)methylacrylamide (3.45 g). This oligomer exhibited the following spectra characteristics: IR 3355 (OH, NH), 1652 (C=O), 1394 (CF_3), 1270 cm^{-1} (CF_2); ^{1}H NMR (D_2O) δ = 1.02—2.22 (CH_2, CH), 3.28—4.19 (CH_2); ^{19}F NMR (D_2O, ext. CF_3CO_2H) δ = −5.82——10.82 (16F), −54.65 (6F).

The other products obtained exhibited the following spectral characteristics:

C_3F_7–(NAT)$_x$–C_3F_7 (No. 1 in Table 1): IR 3361 (OH, NH), 1648 (C=O), 1386 (CF_3), 1280 cm^{-1} (CF_2); ^{1}H NMR (D_2O) δ = 1.10—2.24 (CH_2, CH), 3.28—4.15 (CH_2); ^{19}F NMR (D_2O, ext. CF_3CO_2H) δ = −5.64 (6F), −43.18 (4F), −54.65 (4F).

C_3F_7–(NAT)$_x$–C_3F_7 (No. 2 in Table 1): IR 3424 (OH, NH), 1648 (C=O), 1388 (CF_3), 1261 cm^{-1} (CF_2); ^{1}H NMR (D_2O) δ = 1.04—2.48 (CH_2, CH), 3.33—3.98 (CH_2); ^{19}F NMR (D_2O, ext. CF_3CO_2H) δ = −5.77 (6F), −43.18 (4F), −54.52 (4F).

$C_3F_7OCF(CF_3)$–(NAT)$_x$–$CF(CF_3)OC_3F_7$ (No. 4 in Table 1): IR 3378 (OH, NH), 1650 (C=O), 1392 (CF_3), 1245 cm^{-1} (CF_2); ^{1}H NMR (D_2O) δ = 1.03—2.24 (CH_2, CH), 3.03—4.28 (CH_2); ^{19}F NMR (D_2O, ext. CF_3CO_2H) δ = −6.93——7.74 (16F), −54.05 (6F).

$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$–(NAT)$_x$–$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (No. 5 in Table 1): IR 3386 (OH, NH), 1650 (C=O), 1390 (CF_3), 1245 cm^{-1} (CF_2); ^{1}H NMR (D_2O) δ = 1.01—2.21 (CH_2, CH), 2.78—4.18 (CH_2); ^{19}F NMR (D_2O, ext. CF_3CO_2H) δ = −3.99——7.74 (26F), −54.36 (6F), −72.28 (2F).

$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$–(NAT)$_x$–$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (No. 6 in Table 1): IR 3390 (OH, NH), 1648 (C=O), 1392 (CF_3), 1267 cm^{-1} (CF_2); ^{1}H NMR (D_2O) δ = 1.04—2.54 (CH_2, CH), 3.40—4.12 (CH_2); ^{19}F NMR (D_2O, ext. CF_3CO_2H) δ = −3.99——6.93 (26F), −54.60 (6F), −71.21 (2F).

Similarly, a series of fluoroalkylated NAT co-oligomers were prepared by co-oligomerizations with fluoroalkanoyl peroxides. These exhibited the following spectral characteristics:

C_3F_7–(NAT)$_x$–($CH_2CHSiMe_3$)$_y$–C_3F_7 (No. 7 in Table 1): IR 3337 (OH, NH), 1648 (C=O), 1390 (CF_3), 1268 cm^{-1} (CF_2); ^{1}H NMR (D_2O) δ = −0.22——0.01 (CH_3), 0.98—2.47 (CH_2, CH),

3.34—4.36 (CH_2); ^{19}F NMR (D_2O, ext. CF_3CO_2H) δ = −5.71 (6F), −43.25 (4F), −52.24 (4F).

$C_3F_7OCF(CF_3)$–(NAT)$_x$–($CH_2CHSiMe_3$)$_y$–$CF(CF_3)OC_3F_7$ (No. 8 in Table 1): IR 3411 (OH, NH), 1648 (C=O), 1392 (CF_3), 1245 cm^{-1} (CF_2); ^{1}H NMR (D_2O) δ = −0.13—0.11 (CH_3), 0.74—2.65 (CH_2, CH), 3.28—4.22 (CH_2); ^{19}F NMR (D_2O, ext. CF_3CO_2H) δ = −3.97——7.74 (16F), −54.68 (6F).

$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$–(NAT)$_x$–($CH_2CHSiMe_3$)$_y$–$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (No. 9 in Table 1): IR 3415 (OH, NH), 1649 (C=O), 1392 (CF_3), 1245 cm^{-1} (CF_2); ^{1}H NMR (D_2O) δ = −0.24——0.08 (CH_3), 0.82—2.22 (CH_2, CH), 2.90—4.21 (CH_2); ^{19}F NMR (D_2O, ext. CF_3CO_2H) δ = −3.99——7.50 (26F), −54.70 (6F), −62.75 (2F).

$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$–(NAT)$_x$–[$CH_2CHSiMe_2$–$O(CH_2)_2O(CH_2)_2OCH_2CH_3$]$_y$–$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (No. 10 in Table 1): IR 3405 (OH, NH),1650 (C=O), 1386 (CF_3), 1247 (CF_2); ^{1}H NMR (D_2O) δ = −0.29—0.11 (CH_3), 0.52—2.44 (CH_2, CH), 3.27—4.18 (CH_2); ^{19}F NMR (D_2O, ext. CF_3CO_2H) δ = −3.78——10.78 (26F), −55.82 (6F), −70.98 (2F).

$C_3F_7OCF(CF_3)$–(NAT)$_x$–(CH_2CMeCO_2Me)$_y$–$CF(CF_3)OC_3F_7$ (No. 11 in Table 1): IR 3397 (OH, NH), 1650 (C=O), 1322 (CF_3), 1241 cm^{-1} (CF_2); ^{1}H NMR (D_2O) δ = 0.62—2.52 (CH_3, CH_2, CH), 3.28—4.22 (CH_3, CH_2); ^{19}F NMR (D_2O, ext. CF_3CO_2H) δ = −5.64——10.13 (16F), −54.36 (6F).

$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$–(NAT)$_x$–[$CH_2CMeCO_2CH_3$]$_y$–$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (No. 12 in Table 1): IR 3423 (OH, NH), 1646 (C=O), 1394 (CF_3), 1243 cm^{-1} (CF_2); ^{1}H NMR (D_2O) δ = 0.84—2.39 (CH_3, CH_2, CH), 3.31—4.18 (CH_3, CH_2); ^{19}F NMR (D_2O, ext. CF_3CO_2H) δ = −3.99——9.18 (26F), −54.57 (6F), −70.64 (2F).

Viscosity Measurements. The viscosities of aqueous solutions of fluoroalkylated NAT homo- and co-oligomers were measured at 30 °C using a falling-sphere viscometer (Haake Viscometer D1-G).

A Typical Procedure for Gelation Test. A procedure for studying the gel-formation ability was based on a method reported by Hanabusa et al.[7] Briefly, weighted fluoroalkylated NAT oligomer was mixed with water or organic fluid 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 h, and then the gelation was checked out visually. When it was formed, the gel was stable and the tube was able to be inverted without changing the shape of the gel.

Metal Ions Binding or Releasing by Fluoroalkylated NAT Oligomer Hydrogels. Fluoroalkylated NAT oligomer hydrogels were swelled with water in a measuring flask. After the addition of the required amount of aqueous metal ion solution into the flask, the flask was allowed to stand for 1 d at 25 °C. The metal-ion concentration of supernatant liquid after the incubation was spectrophotometrically determined.

The metal ion was released from the metal binding to the hydrogel into water for 1 d at 25 °C, and then the metal ion concentration of supernatant liquid was determined spectrophotometrically.

This work was partially supported by a Grant-in-Aid for Scientific Research No. 09650945 from the Ministry of Education, Science and Culture, for which the authors are grateful.

References

1) M. Kozulic, B. Kozulic, and K. Mosbach, *Anal. Biochem.*, **163**, 506 (1987).

2) a) S. Kitano, K. Kataoka, Y. Koyama, T. Okano, and Y. Sakurai, *Makromol. Chem., Rapid Commun.*, **12**, 227 (1991); b) S. Kitano, Y. Koyama, K. Kataoka, T. Okano, and Y. Sakurai, *J. Control Release*, **19**, 162 (1992).

3) H. Sawada, *Chem. Rev.*, **96**, 1779 (1996).

4) H. Sawada, S. Katayama, Y. Nakamura, T. Kawase, and Y. Hayakawa, *Polymer*, in press.

5) a) H. Sawada, Y.-F. Gong, Y. Minoshima, T. Matsumoto, M. Nakayama, M. Kosugi, and T. Migita, *J. Chem. Soc., Chem. Commun.*, **1992**, 537; b) H. Sawada, Y. Minoshima, and H. Nakajima, *J. Fluorine Chem.*, **65**, 169 (1993).

6) R. J. Twieg, T. P. Russell, R. Siemens, and J. F. Rabolt, *Macromolecules*, **18**, 1361 (1985).

7) K. Hanabusa, Y. Watanabe, M. Kimura, T. Koyama, and H. Shirai, *Sen'i Gakkaishi*, **52**, 129 (1996).

8) a) A. R. Khokhlov, E. Y. Kramarenko, E. E. Makhaeva, and S. G. Starodubtzev, *Macromolecules*, **25**, 4779 (1992); b) H. Inomata, S. Goto, K. Otake, and S. Saito, *Langmuir*, **8**, 1030 (1992).

9) Y. Osada and M. Takase, *Nippon Kagaku Kaishi*, **1983**, 439.

10) T. Kunitake, Y. Okahata, and S. Yasunami, *J. Am. Chem. Soc.*, **104**, 5547 (1987).

11) T. Kunitake and N. Higashi, *J. Am. Chem. Soc.*, **107**, 692 (1985).

12) T. Kunitake and N. Higashi, *Macromol. Chem. Phys. Suppl.*, No. 14, 81 (1985).

13) Y. Ishikawa, H. Kuwahara, and T. Kunitake, *Chem. Lett.*, **1989**, 1737.

14) Y. Ishikawa, H. Kuwahara, and T. Kunitake, *J. Am. Chem. Soc.*, **111**, 8530 (1989).

15) a) H. Sawada and M. Nakayama, *J. Fluorine Chem.*, **51**, 117 (1990); b) H. Sawada, M. Yoshida, H. Hagii, K. Aoshima, and M. Kobayashi, *Bull. Chem. Soc. Jpn.*, **59**, 215 (1986).