Aggregation of fluoroalkyl units: synthesis of gelling fluoroalkylated end-capped oligomers containing hydroxy segments possessing metal ion binding and releasing abilities

Hideo Sawada,*[a,b] Toshihiro Tanimura,[a] Shinsuke Katayama[b] and Tokuzo Kawase[c]

[a] Department of Chemistry, Nara National College of Technology, Yamatokoriyama, Nara 639-11, Japan
[b] Department of Chemistry, Faculty of Advanced Engineering, Nara National College of Technology, Yamatokoriyama, Nara 639-11, Japan
[c] Faculty of Human Life Science, Osaka City University, Sumiyoshi, Osaka 558, Japan

New fluoroalkylated end-capped oligomers containing 2-hydroxypropyltrimethylammonium or carboxy(hydroxy)-methylamido segments, which are prepared from the reaction of fluoroalkanoyl peroxides with the corresponding monomers, can cause gelation where strong aggregation of the fluoroalkyl segments is involved in establishing the physical gel network, not only in water but also in organic media under the non-crosslinked conditions, and had a high metal ion binding and releasing power.

Recently there has been increased interest in organofluorinated polymeric materials, especially partially fluoroalkylated macromolecules, because of their unique properties such as high solubility, surface activity and biological activity, which cannot be achieved using the corresponding non-fluorinated macromolecules or perfluorinated polymers.[1] From such a viewpoint, we have been studying the synthesis of fluoroalkylated end-capped oligomers using fluoroalkanoyl peroxides as key intermediates,[2] and these partially fluoroalkylated compounds have been demonstrated to be able to reduce the surface tension of water,[3] and to be potent and selective inhibitors of HIV type-1 *in vitro*.[4] Therefore, it is of interest to develop such compounds. In the course of our studies for the synthesis and applications of fluoroalkylated end-capped oligomers, we have found that fluoroalkylated oligomers containing not only trimethylammonium and hydroxy segments but also hydroxy and carboxy segments can cause gelation in aqueous and organic media under non-crosslinked conditions. More interestingly, these fluoroalkylated oligomers were also found to have high metal ion binding and releasing power. The results are described herein.

A series of fluoroalkylated oligomers containing trimethylammonium and hydroxy segments [R_F–(MHPTA)$_n$–R_F] were prepared *via* the reactions of fluoroalkanoyl peroxides with 3-methacryloxy-2-hydroxypropyltrimethylammonium chloride (MHPTA).† Similarly, we succeeded in preparing a series of fluoroalkylated oligomers containing hydroxy and carboxy segments *via* the reaction of fluoroalkanoyl peroxides with 2-hydroxy-2-[(1-oxoprop-2-enyl)amino]acetic acid (HOPPA), as shown in Scheme 1.‡

The results for the reaction of fluoroalkanoyl peroxides with MHPTA and HOPPA are shown in Table 1. As shown, perfluoropropylated and perfluorooxaalkylated MHPTA or HOPPA oligomers were obtained in moderate to excellent yields under very mild conditions. The perfluoropropylated and perfluoro-1-methyl-2-oxapentylated MHPTA oligomers (entries 1–3, Table 1) were soluble in water, and we were able to measure their molecular weights by GPC analyses [$\bar{M}_n$ ($\bar{M}_w$/$\bar{M}_n$) = 2630 (3.02) (entry 1); 2060 (3.86) (entry 2); 6760 (11.0) (entry 3)]. However, in perfluoro-1-methyl-2-oxapentylated MHPTA oligomers, the oligomers with larger molar ratios of MHPTA to peroxide (entries 4–9) formed gels or became 'gel-like' with not only water but also MeOH, EtOH, DMF and

DMSO, and we were unable to measure their molecular weights owing to the high viscoelasticity of the fluids or the gel formation. A corresponding non-fluorinated MHPTA oligomer [–(MHPTA)$_n$–] was completely soluble in these solvents.

In fluoroalkylated HOPPA oligomers, not only perfluoropropylated but also perfluorooxaalkylated HOPPA oligomers were found to cause gelation with water, DMF and DMSO under non-crosslinked conditions. It is important to note that the corresponding non-fluorinated HOPPA oligomers [–(HOPPA)$_n$–] forms no gels with these solvents.

We have measured the minimum concentrations (C_{min}) of these oligomers necessary for gelation in water at 30 °C according to the method reported by Hanabusa *et al.*,[5] and the results are shown in Table 1.

As shown, the amount (C_{min}) of a fluoroalkylated oligomer necessary to gel 1 l of water was 7–330 g, and the oligomers with greater molar ratios of MHPTA (or HOPPA) to peroxide or longer perfluorooxaalkylated oligomers were found to exhibit higher gelling ability. These results strongly suggest that the main driving forces for gelation are the synergistic interactions between aggregations of fluoroalkyl units in oligomers and the intermolecular hydrogen bonding between hydroxy or carboxy segments, including the interactions of OH and N$^+$ groups. On the other hand, the corresponding non-fluorinated oligomers could not form a physical gel network in these media owing to the absence of the aggregation of fluoroalkyl units. Hitherto, it was known that some macromolecules cause chemical and physical gelation in aqueous solutions, but the application of these compounds to organogels has been limited. The striking characteristic of our present oligomers as gelling agents is the
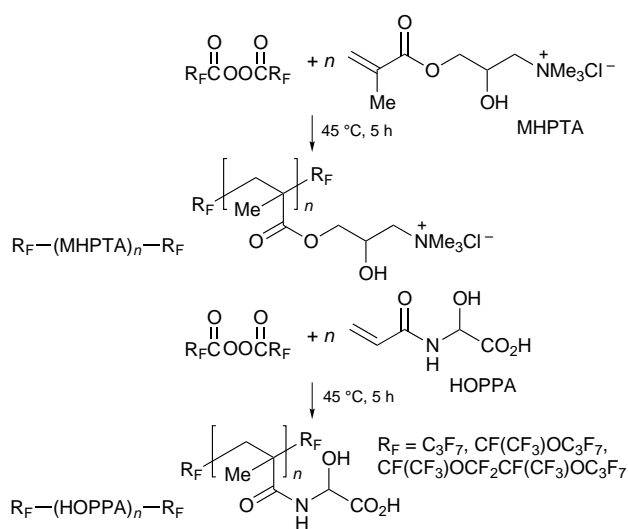
Scheme 1

Table 1 Reactions of fluoroalkanoyl peroxides $R_FC(O)OOC(O)R_F$ with MHPTA or HOPPA and minimum gel concentration of fluoroalkylated MHPTA or HOPPA oligomers for gelation at 30 °C

Entry	Peroxide R_F	Central segment	Ratio peroxide : central segment	Yield (%)[a]	C_{min}/g dm^{-3} [b]
1	C_3F_7	MHPTA	4 : 21	21	soluble
2	C_3F_7	MHPTA	4 : 42	30	soluble
3	$CF(CF_3)OC_3F_7$	MHPTA	4 : 11	17	soluble
4	$CF(CF_3)OC_3F_7$	MHPTA	5 : 25	36	gel-like
5	$CF(CF_3)OC_3F_7$	MHPTA	4 : 42	12	gel-like
6	$CF(CF_3)OC_3F_7$	MHPTA	4 : 65	39	102
7	$CF(CF_3)OC_3F_7$	MHPTA	4 : 85	25	7
8	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	MHPTA	4 : 22	32	330
9	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	MHPTA	4 : 43	88	51
10	C_3F_7	HOPPA	4 : 41	83	88
11	$CF(CF_3)OC_3F_7$	HOPPA	4 : 8	8	100
12	$CF(CF_3)OC_3F_7$	HOPPA	4 : 20	20	93
13	$CF(CF_3)OC_3F_7$	HOPPA	5 : 50	71	91
14	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	HOPPA	3 : 5	15	94
15	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	HOPPA	3 : 13	50	87
16	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	HOPPA	3 : 26	85	53

[a] Yields are based on the starting materials (MHPTA or HOPPA) and the decarboxylated peroxide unit (R_F–R_F). [b] gel-like = highly vicoelastic fluid.
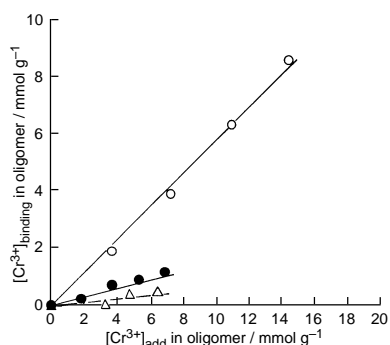

Fig. 1 Relationship between relative amounts of Cr^{3+} binding to fluoroalkylated oligomers and initial Cr^{3+}: (○) R_F–(MHPTA)$_n$–R_F [R_F = $CF(CF_3)OC_3F_7$ (entry 7)], (●) R_F–(HOPPA)$_n$–R_F [R_F = $CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (entry 16) and (△) R_F–(MHPTA)$_n$–R_F [R_F = $CF(CF_3)OC_3F_7$ (entry 6)]

ability to harden not only water but also organic polar solvents. This feature is attributable to the fact that fluoroalkyl segments are solvophobic in aqueous and organic media, and enhance aggregation due to strong interaction between the fluoroalkyl segments.

From both fundamental and technological standpoints, it is interesting to study the adsorptive properties against metal ions of our new fluoroalkylated oligomer gels. Thus, we performed quantitative measurements of the uptake of Cr^{3+} (15–60 mmol dm^{-3}) by the R_F–(MHPTA)$_n$–R_F (entry 7, Table 1) hydrogel. The metal ion concentration of the supernatant liquid after the incubation (at 25 °C for 24 h) was determined spectrophotometrically using a calibration curve, and the results are shown in Fig. 1.

As shown, Cr^{3+} was found to bind strongly to the fluoroalkylated oligomer hydrogel with *ca.* 60% binding ratio [based on the relative amount of Cr^{3+} binding to gel ([Cr^{3+}]$_{binding}$/oligomer) and relative amount of initial Cr^{3+}([Cr^{3+}]$_{add}$/oligomer)]. The R_F–(MHPTA)$_n$–R_F (entry 6, Table 1) hydrogel possessing a higher C_{min} value than entry 7 had a weaker Cr^{3+} binding power (*ca.* 10% binding ratio) under similar conditions. The R_F–(HOPPA)$_n$–R_F (entry 16, Table 1) hydrogel was also shown to have a Cr^{3+} binding power (*ca.* 17% binding ratio) as shown in Fig. 1. However, fluoroalkylated oligomers (entries 8 and 11) possessing higher C_{min} values than entries 6, 7 or 16 were found to have poor Cr^{3+} binding power. From these results, it can be said that the fluoroalkylated oligomer networks in the hydrogels possessing lower C_{min} values are likely to bind strongly to the metal ion, since stronger aggregation of the fluoroalkyl

segments is necessary for the establishment of the physical gel network to exhibit lower C_{min} value.

More interestingly, it was found that Cr^{3+} can be easily released from the Cr^{3+}-bound R_F–(MHPTA)$_n$–R_F (entry 7, Table 1) hydrogel into water with *ca.* 60% releasing ratio (the ratio based on the relative amount of Cr^{3+} released into water and relative amount of Cr^{3+} binding to gel) after the incubation at 25 °C for 24 h. On the other hand, Cr^{3+} was not released from the Cr^{3+}-bound R_F–(HOPPA)$_n$–R_F hydrogels under similar conditions. This is because the interaction of Cr^{3+} and R_F–(HOPPA)$_n$–R_F hydrogels is ionic, whereas the main driving force for Cr^{3+} binding to R_F–(MHPTA)$_n$–R_F is coordination between Cr^{3+} and OH segments.

Thus it has been demonstrated that our new fluoroalkylated oligomers containing hydroxy segments can cause gelation under non-crosslinked conditions, and that the aggregation of fluoroalkyl units in water and/or organic media becomes a new driving factor for gelation in addition to well-known interactions such as hydrogen bond and ionic interactions. In addition, it has been shown that these new fluoroalkylated oligomer hydrogels have high metal-binding or releasing power. Thus, these fluorinated oligomer gels are expected to prove useful in various fields as novel fluorinated functional materials.

Footnotes

References

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