# Synthesis and Properties of Novel Perfluorocyclohexylated Compounds with Bis(perfluorocyclohexane carbonyl) Peroxide

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**ABSTRACT:** Bis(perfluorocyclohexane carbonyl) peroxide was prepared by the reaction of the corresponding acyl fluoride and hydrogen peroxide. This peroxide was applied to the preparation of perfluorocyclohexylated end-capped oligomers via a radical process under very mild conditions. In cyclic perfluorocyclohexylated end-capped oligomers containing hydroxy segments, these oligomers could cause a gelation in water and in polar organic solvents such as MeOH, EtOH, dimethylformamide (DMF), and dimethylsulfoxide (DMSO), and the gelling ability of these oligomers was superior to that of the corresponding linear perfluorooxaalkylated oligomers. Furthermore, perfluroocyclohexylation of polystyrene or benzene was proceeded via a single electron transfer reaction by using this peroxide. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1101–1108, 1999

**Key words:** perfluorocyclohexyl group; oligomer; gelation; surface tension; peroxide

## INTRODUCTION

Recently, the increasing importance of fluorinated polymers in applications for new functional materials led to considerable interest in the development of partially fluoroalkylated polymers.[1] From such point of views, we have been actively studying the synthesis and application of perfluoroalkylated and perfluorooxaalkylated end-capped oligomers by using fluoroalkanoyl peroxides as key intermediates, and these partially fluorinated polymers were found to exhibit various unique properties such as a high solubility in various solvents and biological properties that set them apart from perfluorinated polymers and the corresponding nonfluorinated polymers.[2] Very recently, synthesis of perfluoroalkyl-terminated polymers were reported, and their interesting properties were also demonstrated.[3] Therefore, it is interesting to synthesize numerous novel partially fluoroalkylated macromolecules and to apply these fluorinated compounds to various fields.

**Scheme 1**



a) The yield is based on the starting material (ACA) and the decarboxylated peroxide unit ($R_F$-$R_F$).

**Scheme 2**

However, no direct introduction of hindered cyclic fluoroalkyl segments such as the perfluorocyclo-hexyl group into organic molecules was hitherto reported, but it is very interesting to explore such hindered cyclic fluoroalkylated compounds from the viewpoint of the development of new organofluorine chemistry. Furthermore, such novel hindered cyclic fluoroalkylated compounds are strongly expected to have greater application in a variety of fields. In a preliminary account, we reported the synthesis of a new bis(perfluorocy-clohexane carbonyl) peroxide (FCHPO), and this peroxide was shown to be useful for the direct introduction of perfluorocyclohexyl units into ACA oligomers and polystyrene or benzene.[4] In this article, we describe the synthesis and prop-erties of perfluorocylohexylated oligomers and perfluorocyclohexylated aromatic compounds with the use of FCHPO, with particular emphasis on the gelling ability of perfluorocyclohexylated oligomers.

## RESULTS AND DISCUSSION

FCHPO was prepared by the reaction of the cor-responding acylfluoride (FCHCF) and hydrogen peroxide under alkaline conditions as shown in Scheme 1.

FCHPO could not be isolated because of its thermal instability, but we succeeded in monitor-ing the thermal decomposition of FCHPO in $CF_2ClCFCl_2$ by iodometry at various tempera-tures ranging from 35.0 to 45.0°C. The rate of decomposition of FCHPO was found to conform well to a first-order equation; the results obtained are shown in Table I.

As shown in Table I, the values of the activation enthalpy and entropy for the thermal decomposi-tion of FCHPO were 105.4 kJ mol$^{-1}$ and 0 J K$^{-1}$ mol$^{-1}$, respectively. These values are similar to those of $(C_3F_7COO)_2$ and $[C_3F_7OCF(CF_3)COO]_2$, which are well known to decompose to afford the corresponding fluoroalkyl radicals with three-bond homolytic fissions as shown in Table I.[5] The result for this decomposition behavior suggests that a more stable perfluorocyclohexyl radical is likely to form by the concerted three-bond radical fission of FCHPO to afford the perfluorocyclohexylated oli-gomers with carbon–carbon bond formation via a radical process.

The reactions of FCHPO with ACA were car-ried out for 10 h at 45°C. The results are shown in Scheme 2. The reactions of FCHPO with ACA proceeded smoothly to afford perfluorocyclohexy-lated ACA oligomers excellent to moderate iso-lated yields. It is suggested that mainly oligomers with two perfluorocyclohexylated end groups would be obtained via primary radical termina-tion or radical chain transfer to the peroxide un-der our oligomeric conditions, in which the con-centration of the peroxide was almost the same as

**Table I   Rate Constants and Activation Parameters for the Thermal Decomposition of 0.05 mol/dm$^3$ FCHPO in CF$_2$ClCFCl$_2$**

| Temp. (°C) | $k_d$ (s$^{-1}$) $\times 10^5$ | $\Delta H^{\neq}$ (kJ mol$^{-1}$) | $\Delta S^{\neq}$ (J K$^{-1}$ mol$^{-1}$) |
|---|---|---|---|
| 35.0 | 0.81 ± 0.01 | | |
| 40.0 | 1.67 ± 0.09 | 105.4 | 0 |
| 42.5 | 2.21 ± 0.16 | | |
| 45.0 | 3.09 ± 0.16 | | |
| $(C_3F_7COO)_2$[a] | | 101.7 | 16.3 |
| $[C_3F_7OCF(CF_3)COO]_2$[a] | | 100.0 | 12.6 |

[a] See Sawada.[5]

**Figure 1** Surface tension of aqueous solutions of fluorinated acrylic acid oligomers at 30°C.

$$R_F\text{-}(CH_2\text{---}CH)_n\text{---}R_F$$
$$|$$
$$CO_2H$$

●: $R_{F^-}$ = $\langle F \rangle$— ($\overline{M}_n$ = 1440); ■: $R_F$ = $C_3F_7OCF(CF_3)$—
($\overline{M}_n$ = 12000); △: —$(CH_2$—$CH)_n$— ($\overline{M}_n$ = 2000)
$$|$$
$$CO_2H$$

that of ACA. In fact, we previously reported that a series of ACA oligomers containing two perfluoroalkylated or perfluorooxaalkylated end groups are prepared by using the corresponding fluoroalkanoyl peroxides under similar conditions.[6]

Perfluorocyclohexylated end-capped ACA oligomer thus obtained was easily soluble in water and polar organic solvents such as MeOH, EtOH, THF, acetone, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). Thus, this oligomer can act as a new fluorinated oligosurfactant. The surface property of this oligomer was evaluated by measuring the reduction of the surface tension of aqueous solutions by the Wilhelmy plate method at 30°C; this result was shown in Figure 1. The surface tension of aqueous solutions of perfluoro-1-methyl-2-oxapentylated ACA oligomer and nonfluorinated ACA oligomer were also shown in Figure 1 for comparison.

As shown in Figure 1, a significant decrease in the surface tension of water, to $\sim 20$ mN m$^{-1}$, was observed for perfluorocyclohexylated ACA oligomer in contrast to the corresponding nonfluorinated oligomer. In particular, this oligomer exhib-

ited a clear break point resembling a critical micelle concentration (CMC). On the other hand, noncyclic fluoroalkylated (perfluoro-1-methyl-2-oxapentylated) ACA oligomer was able to reduce the surface tension of water more effectively. This finding suggests that perfluorocyclohexyl segments in this oligomer are not likely to be arranged regularly above the water surface owing to the steric hindrance compared to the perfluorooxaalkylated oligomer. Furthermore, we tried to prepare some perfluorocyclohexylated endcapped oligomers containing hydroxy segments.

As shown in Scheme 3, FCHPO reacted smoothly with 3-methacryloxy-2-hydroxypropyl trimethylammonium chloride (MHPTA) or 2-hydroxy-2-[(1-oxoprop-2-enyl)amino]acetic acid (HOPPA) to afford the corresponding perfluorocyclohexylated endcapped oligomers, respectively.

Interestingly, these perfluorocyclohexylated oligomers containing hydroxy segments were found to cause gelation not only in water but also in polar organic solvents such as DMSO, DMF, MeOH, and EtOH. We could not measure the molecular weights of these obtained oligomers by GPC analyses under various conditions owing to the highly viscoelastic fluids. We have already demonstrated that linear fluoroalkylated endcapped oligomers containing hydroxy segments can cause gelation where the aggregations of fluoroalkyl segments and the hydrogen-bonding interactions are involved in establishing the physical gel network.[7] Therefore, it is suggested that our present perfluorocylohexylated oligomer gel is also built up through the synergistic interactions of both the aggregations of perfluorocyclohexyl segments and the intermolecular hydrogen bondings between hydroxy segments.

We have measured the minimum concentration ($C_{min}$) of these perfluorocyclohexylated oligomers necessary for gelation in water at 30°C according to the method reported by Hanabusa et al.[8] to clarify this gel formation; the results are



| FCH-PO (mmol) | R$^1$ | R$^2$(mmol) | Product (Yield, %)$^{a)}$ |
|---|---|---|---|
| 4 | Me | OCH$_2$CH(OH)CH$_2$N$^+$Me$_3$ Cl$^-$ 60 | 47 |
| 4 | H | NHCH(OH)CO$_2$H 40 | 48 |

a) The yield is based on the starting material and the decarboxylated peroxide unit (R$_F$-R$_F$).

**Scheme 3**

**Table II  Minimum Gel Concentration $C_{min}$ of Perfluorocyclohexylated and Perfluoro-1-methyl-2-oxapentylated Oligomers Containing Hydroxy Segments (in g/dm$^{-3}$ solvent) Necessary for Gelation at 30°C**

| Oligomer | $C_{min}$ |
|---|---|
| $c$-$C_6F_{11}$–(MHPTA)$_n$–$C_6F_{11}$–$c$[a] | 17 |
| $c$-$C_6F_{11}$–(HOPPA)$_n$—$C_6F_{11}$–$c$ | 44 |
| $C_3F_7OCF(CF_3)$–(MHPTA)$_n$—$CF(CF_3)OC_3F_7$ | 107 |
| $C_3F_7OCF(CF_3)$–(HOPPA)$_n$—$CF(CF_3)OC_3F_7$ | 517 |

[a] $c$–$C_6F_{11}$ indicates perfluorocyclohexyl group.

shown in Table II. Additionally, the values for $C_{min}$ of the corresponding perfluoro-1-methyl-2-oxapentylated oligomers,[7] which were prepared by the same reaction conditions in Scheme 3, were shown in Table II for comparison.

Of particular interest, as shown in Table II, the gelling ability of perfluorocyclohexylated oligomers is fairly superior to that of perfluoro-1-methyl-2-oxapentylated oligomers, taking into account that the minimum gel concentrations are $\sim$ 17–44 g dm$^{-3}$ for perfluorocyclohexylated oligomers and $\sim$ 107–517 g dm$^{-3}$ for perfluoro-1-methyl-2-oxapentylated oligomers. This strong gelling ability would depend on the fact that a hydrogen-bonding interaction between perfluorocyclohexyl segments and hydroxy segments in oligomers is essential for causing the gelation in addition to the synergistic interactions of both the



a) Calculated from styrene monomer units.
b) $R_F$–ratio was determined by $^{19}F$ NMR in comparison with the peak area of the perfluorocyclohexyl groups of polymer with that of PhCF$_3$ as the internal standard.

**Scheme 4**

aggregations of perfluorocyclohexyl segments and the intermolecular hydrogen bonding of hydroxy segments as in Figure 2.

FCHPO was calculated by using the MNDO-PM3 semiempirical molecular orbital (MO) method, the semiempirical calculations of which were carried out by using the CaChe MOPAC, to have a similar lowest unoccupied MO (LUMO) energy level ($-2.613$ eV) as that of $(C_3F_7COO)_2$ ($-2.513$ eV). Therefore, it is suggested that FCHPO becomes a useful electron acceptor even from well-known poor electron-donor aromatic compounds such as benzene. In fact, we already succeeded in preparing a series of perfluoroalkyl-



**Figure 2**  Schematic illustration for gelation of perfluorocyclohexylated oligomers containing hydroxy segments.

[phenyl equatorial]                    [phenyl axial]

**Scheme 5**

ated and perfluorooxaalkylated aromatic compounds by the use of the corresponding fluoroalkanoyl peroxides.[9] Thus, we tried to react FCHPO with aromatic compounds such as benzene and polystyrene. These results were shown in Schemes 4 and 5.

As shown in Scheme 4, perfluorocyclohexylated benzene was obtained in 56% isolated yield by the reaction of benzene and FCHPO under very mild conditions. Furthermore, direct aromatic perfluorocyclohexylation of polystyrene with FCHPO was found to proceed smoothly under mild conditions, even though this reaction was carried out in a heterogeneous system. The molecular weight of perfluorocyclohexylated polystyrene was increased by perfluorocyclohexylation, and the $\bar{M}_w/\bar{M}_n$ of perfluorocyclohexylated polystyrene did not change to that of the parent polystyrene. This finding indicates that the degradation of the polymer chain did not occur under this reaction condition. From these results, the perfluorocyclohexylation of benzene and polystyrene with FCHPO would be accounted for by a single electron transfer reaction from the substrates to the antibonding $(2p\sigma^*)$ O—O bond of the peroxide, as was proposed in perfluoroalkylations or perfluorooxaalkylations with corresponding fluorinated alkanoyl peroxides.[9]

We have measured the contact angles for water and dodecane on glass treated with the perfluorocyclohexylated polystyrenes. The contact angles for water (102°) and dodecane (34°) on the glass were found to increase significantly compared with that of parent polystyrene [water (90°) or dodecane (0°)], indicating that this polymer possesses good water- and oil-repellent properties imparted by fluorine, although perfluorocyclohexyl segments are partially introduced into aromatic nuclei of polystyrene.

Usually, it is not possible to separate conformers from one another above room temperatures, and hindered cyclohexanes such as $t$-butylcyclo-

hexane exist in a single conformation with the $t$-butyl group equatorial. In fact, in the conformational isomers of phenylcyclohexane, only isomers with phenyl group equatorial should be isolated. However, GC analyses from 30 to 150°C of phenylperfluorocyclohexane in Scheme 4 showed the presence of two conformational isomers (equatorial : axial = 53 : 47). From the results of GC mass spectrometry (MS) (exact MS), GC–FTIR, and $^{19}$F-NMR analyses, two isomers of phenylperfluorocyclohexane (PhC$_6$F$_{11}$) were suggested to correspond to cyclohexanes with the perfluorocyclohexyl group equatorial and axial, respectively, as in Scheme 5. In contrast, $^{19}$F-NMR analyses of perfluorocyclohexylmethyl ether) showed that the bulky perfluoromethoxy substituent of the favored conformer is in the equatorial position, and there is an additional signal that could be assigned to the minor conformer (axial position) in the low-temperature region ($\sim$ 217 K).[10]

As shown in Scheme 5, the presence of the axial isomer may be ascribed to the hydrogen bond formation between the hydrogen atoms in the phenyl group and the fluorine atoms, which stablizes the axial isomer. The similar hydrogen bond formation between the hydrogen atom and fluorine atom was observed in the fluorinated compounds such as fluorinated $\beta$-keto-$\gamma$-butyrolactones.[11] We also proposed the similar hydrogen bond formation between perfluorocyclohexyl segments and hydroxy segments in perfluorocyclohexylated oligomers containing hydroxy groups as illustrated in Figure 2. Additionally, the $p$–$p$ orbital overlap in the $p$ electrons of fluorines with the $p$ system of the benzene ring, including the contributing resonance form describing a 1,6-interaction



should stabilize the axial isomer. Fluorine $p$ orbitals in benzotrifluoride and pentafluoroethylbenzene give optimum overlap with carbon $p$ orbitals at the benzene ring because fluorine $p$ or-

bitals are of comparable size and compactness with large atoms such as bromine.[12]

Furthermore, it was shown that there are two conformational isomers in perfluorocyclohexylated polystyrene (equatorial : axial by ^{19}F-NMR is 56 : 44) by ^{19}F-NMR analyses.

In this way, it was verified that FCHPO is a convenient tool for the introduction of perfluorocyclohexyl segments into not only aromatic compounds such as polystyrene and benzene, but also various oligomers such as ACA, MHPTA, and HOPPA oligomers. More interestingly, perfluorocyclohexylated compounds were found to exhibit unique behaviors (high gelling ability and conformational isomers) that set them apart from linear perfluoroalkylated and perfluorooxaalkylated compounds. Therefore, from the viewpoints of the development of new organofluorine chemistry, our present perfluorocyclohexylated compounds are expected to be widely applicable in various fields as new attractive fluorinated materials.

## EXPERIMENTAL

NMR spectra were measured using a Varian Unity-Plus 500 (500 MHz) spectrometer, whereas IR spectra were recorded on a Horiba FT-300 FTIR spectrophotometer. Molecular weights were calculated by using a Shodex DS-4–Shodex-RI-71 gel permeation chromatography calibrated with standard polystyrene by using THF as the eluent. GC analyses were performed on a Shimadzu GC-8A gas chromatograph, and GC–FTIR spectra were measured with a Jeol JIR-7000. GC–MS spectra were measured with a Jeol HP6890(GC)–Automass 15(MS) spectrometer and a Hitachi M-2000 spectrometer.

### Materials

FCHPO was prepared as follows. To a solution of potassium carbonate (3.3 g) in 17.7 g of water, 30% hydrogen peroxide (24 mmol) and then $CF_2ClCFCl_2$ (130 g) was added at 5°C. The two-phase solution was cooled to $-5$°C, stirred, and then the solution of FCHCF (11 mmol) in $CF_2ClCFCl_2$ (20 g) was added drop by drop. The reaction mixture was then kept at $-5$°C for 30 min. The $CF_2ClCFCl_2$ layer was separated and the concentration of the peroxide determined iodometrically (yield, 81%).

IR $\nu$ (cm$^{-1}$): 1865, 1830 (C=O)

Because of its instability, the solution of the peroxide in $CF_2ClCFCl_2$ thus obtained was used without further purification.

Perfluorocyclohexane carbonyl fluoride used in the synthesis was supplied by SynQuest Laboratories, Inc. (Alachua, FL). MHPTA was supplied by NOF Corp. (Tokyo, Japan). HOPPA was purchased from Acros Organics, Inc. (Geel, Belgium).

### General Procedure for the Synthesis of Perfluorocyclohexylated Oligomers

FCHPO (2.4 mmol) in $CF_2ClCFCl_2$ solution (60 g) was added to a mixture of ACA (11.0 mmol) and 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 (60 g). The solution was stirred at 45°C for 10 h under nitrogen. The white powder obtained was reprecipitated from methanol–ethyl acetate to give an $\alpha,\omega$-bis(perfluorocyclohexylated) ACA oligomer (0.90 g). This oligomer exhibited the following spectral characteristics.

IR (cm$^{-1}$): 3367 (OH), 1722 (C=O), 1238 (CF$_2$); ^{1}H-NMR: (D$_2$O) $\delta$ 1.30 $\sim$ 2.09 (CH$_2$), 2.12 $\sim$ 2.83 (CH); ^{19}F-NMR: (D$_2$O, ext. CF$_3$CO$_2$H) $\delta$ 5.72 $\sim$ $-7.98$ (2F, 1$a$), $-39.98 \sim -44.68$ (4F, 2,6$a$), $-45.98 \sim -51.08$ (6F, 3,5$a$, 4$a$), $-56.48 \sim -60.08$ (4F, 2,6$e$), $-61.98 \sim -71.68$ (6F, 3,5$e$, 4$e$), $-107.19 \sim -111.98$ (2F, 1$e$).

Similarly, perfluorocyclohexylated MHPTA and HOPPA oligomers were prepared by the oligomerizations with FCHPO. These exhibited the following IR spectral characteristics; however, their NMR spectra were not measured due to the gelling (highly viscoelastic) samples.

IR (cm$^{-1}$); $c$-C$_6$F$_{11}$–(MHPTA)$_n$–C$_6$F$_{11}$–$c$]: 3451 (OH), 1726 (C=O), 1269 (CF$_2$); IR [cm$^{-1}$; $c$-C$_6$F$_{11}$–(HOPPA)$_n$–C$_6$F$_{11}$–$c$]: 3435 (OH), 1747, 1670 (C=O), 1228 (CF$_2$).

### A Typical Procedure for Gelation Test

A procedure for studying the gel-formation ability was based on a method reported by Hanabusa et al.[8] Briefly, weighted perfluorocyclohexylated MHPTA oligomer was mixed with water 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.

## Surface Tension Measurements

The surface tensions of aqueous solutions of the fluorinated ACA oligomers were measured at 30°C using a Wilhelmy-type surface tensiometer (ST-1, Shimadzu Co.) with a glass plate.

## Contact Angle Measurements

The contact angles were measured with the use of the goniometer-type contact angle meter (Erma G-1-1000), according to our previously reported method.[13]

## Synthesis of Perfluorocyclohexylated Benzene

FCHPO (8 mmol) in $CF_2ClCFCl_2$ solution (200 g) was added to benzene (40 mmol) and the solution was stirred at 45°C for 10 h under nitrogen atmosphere. The reaction mixture was then washed with 5% sodium hydrogen carbonate and water. The separated organic layer was dried over anhydrous magnesium sulfate and the solvent was evaporated. $PhC_6F_{11}$ (1.58 g) was isolated by distillation [boiling point (bp): $\sim$ 41–43°C/3 mmHg] and identified by IR, GC–MS (exact MS); $^1H$-, $^{13}C$-, and $^{19}F$-NMR. GC (a 2-m column packed with 20% SE-30) analyses of the isolated products showed the presence of two conformational isomers (equatorial and axial); however, we could not isolate each product under various conditions.

IR ($\nu$/cm$^{-1}$) axial $PhC_6F_{11}$: 3078, 1342, 1288, 1257, 1226, 1200, 1165, 1153, 1119, 1072, 1041, 984, 922, 837; equatorial $PhC_6F_{11}$: 3078, 1504, 1454, 1319, 1257, 1207, 1145, 1038, 1018, 972, 926, 852, 744. MS ($m/z$) axial $PhC_6F_{11}$: 358 (M$^+$), 339, 208, 189, 158, 127 (base), 69 (found: M$^+$, 358.0174). $C_{12}H_5F_{11}$: requires M, 358.0214; equatorial $PhC_6F_{11}$: 358 (M$^+$), 339, 250, 189, 158, 127 (base), 69 (found: M$^+$, 358.0200). $C_{12}H_5F_{11}$: requires M, 358.0214. $^1H$-NMR (CDCl$_3$) $\delta$ 7.51 (2$H$, $t$, $J$ = 8 Hz), 7.57 (1$H$, $tt$, $J$ = 8 Hz, 2 Hz), 7.65 (2$H$, $m$); $^{19}F$-NMR (CDCl$_3$, ext. CF$_3$CO$_2$H) $\delta$ 2.49 (1$F$, $d$, $J$ = 24 Hz, 1$a$), $-42.49$ (2$F$, $d$, $J$ = 291 Hz, 2,6$a$), $-46.29$ (2$F$, $d$, $J$ = 291 Hz, 3,5$a$), $-47.40$ (1$F$, $d$, $J$ = 277 Hz, 4$a$), $-57.29$ (2$F$, $d$, $J$ = 306 Hz, 2,6$e$), $-62.97$ (2$F$, $d$, $J$ = 282 Hz, 3,5$e$), $-66.09$ (1$F$, $d$, $J$ = 277 Hz, 4$e$), $-105.33$ (1$F$, $t$, $J$ = 37 Hz, 1$e$). $^{13}C$-NMR (CDCl$_3$) $\delta$ 124.41 [C$_1$(Ph $e$), $d$, $J$ = 20.6 Hz], 127.06 [C$_2$(Ph $e$), $d$, $J_{CCCF}$ = 11.9 Hz], 127.23 [C$_2$(Ph $a$), m], 128.93 [C$_3$ (Ph $e$), $d$, $J$ = 2.6 Hz], 129.03 [C$_3$(Ph $a$), $d$, $J$ = 2.1 Hz], 131.41 [C$_4$(Ph $e$)], 131.55 [C$_4$(Ph $a$)].

## Synthesis of Perfluorocyclohexylated Polystyrene

FCHPO (0.8 mmol) in $CF_2ClCFCl_2$ solution (22 g) was added to the mixture of polystyrene 0.83 g (8 mmol calculated from styrene monomer unit) and AK-225 (75 g). The heterogeneous solution was stirred vigorously at 45°C for 10 h under nitrogen. Dichloromethane (50 mL) was added to the reaction mixture and the solution was stirred for 5 min, then 5% of aqueous sodium hydrogen carbonate (100 mL) was added. The separated organic layer was washed with water (100 mL) and dried over anhydrous magnesium sulfate, and the removal of the solvent gave the crude product. This product was reprecipitated from chloroform–methanol to give perfluorocyclohexylated polystyrene (0.95 g). This polymer showed the following spectral data.

IR ($\nu$/cm$^{-1}$) 1278 (CF$_2$); $^{19}F$-NMR (CDCl$_3$, ext. CF$_3$CO$_2$H) $\delta$ 2.49 (1$F$, 1$a$), $-42.97$ (2$F$, $d$, $J$ = 293 Hz, 2,6$a$), $-46.29$ (2$F$, $d$, $J$ = 293 Hz, 3,5$a$), $-44.59$ (1$F$, $d$, $J$ = 281 Hz, 4$a$), $-57.39$ (2$F$, $d$, $J$ = 305 Hz, 2,6$e$), $-62.94$ (2$F$, $d$, $J$ = 281 Hz, 3,5$e$), $-66.05$ (1$F$, $d$, $J$ = 293 Hz, 4$e$), $-105.01$ (1$F$, 1$e$).

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