SYNTHESIS OF BICYCLO [2.2.1] HEPT-2-ENES WITH MONO AND
DISUBSTITUTED LONG PERFLUORINATED CHAINS C_nF_{2n+1} (n = 4,6,8,10)

INVESTIGATION OF ASSOCIATION IN SOLUTION BY ^{19}F NMR
STUDY OF POLYMERIZATION VIA A METATHETIC REACTION

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SUMMARY

A method for the synthesis of mixed fluorinated and
hydrogenated derivatives: the bicyclo [2.2.1] hept-2-enes with
long chains C_nF_{2n+1} (n = 4,6,8 and 10) is described. Association
of these bicyclic derivatives in solution was demonstrated by
^{19}F NMR spectroscopy. In addition, these compounds were found to
polymerize readily by a metathetic reaction producing a new type
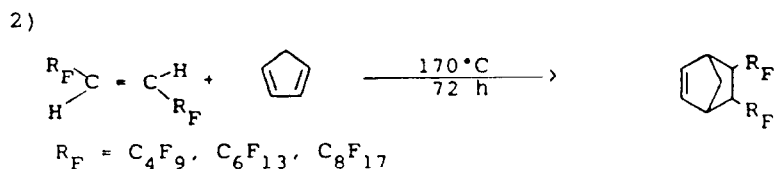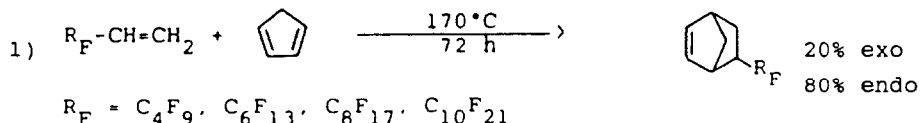of fluorinated polymer.

INTRODUCTION

One of the objectives of this laboratory has been the
development of novel mixed fluorinated and hydrogenated
molecules [1,2]. In order to investigate segregation and
microemulsion formation [3] we attempted the synthesis of
bicyclo [2.2.1] hept-2-enes, mono and disubstituted with long
chain perfluorinated groups. Blackmore and Feast [4] have recently
reported the polymerization of endo- and exo-5-trifluoromethyl

bicyclo [2·2·1] hept-2-ene. These authors have also mentioned

the preparation of similar products with long chains [5]

although no details were given of such compounds.

RESULTS AND DISCUSSION

Synthesis of bicyclo [2·2·1] hept-2-enes, mono and
disubstituted with long perfluorinated chains

These derivatives were synthesized by a Diels-Alder

reaction [6,5] between cyclopentadiene and olefins with

perfluorinated chains, R_F-CH=CH$_2$ and R_F-CH=CH-R$_F$

1) R_F-CH=CH$_2$ + ⬠ $\xrightarrow[\text{72 h}]{170°C}$ → ⬡R_F 20% exo
                 80% endo

    R_F = C_4F_9, C_6F_{13}, C_8F_{17}, $C_{10}F_{21}$

2)

  R_F\C = C/H + ⬠ $\xrightarrow[\text{72 h}]{170°C}$ → ⬡R_F R_F
  H/ \R_F

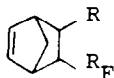 R_F = C_4F_9, C_6F_{13}, C_8F_{17}

For the monosubstituted bicyclic derivatives, we found 20% of

the exo isomer and 80% of the endo form for all lengths of chain

R_F.

The proportions of the two isomers were determined by ^{19}F, [13]C

and ^{1}H NMR [7] (cf. Experimental).

The yields obtained are shown in Table I.

TABLE I

Yields of derivatives

R_F	R	Compound	Yield (%)
C_4F_9	H	1	75
C_6F_{13}	H	2	65
C_8F_{17}	H	3	70
$C_{10}F_{21}$	H	4	55
C_4F_9	C_4F_9	5	60
C_6F_{13}	C_6F_{13}	6	55
C_8F_{17}	C_8F_{17}	7	40

^{19}F NMR analysis of the monosubstituted bicyclic derivatives

The ^{19}F NMR spectra of these derivatives carried out at the probe temperature (23°C) differed considerably for different chain lengths R_F, particularly in the CF_2 next to the CF_3 group at the end of the chain Figs. 1 and 2 [8]. For the long chain derivatives (R_F = C_8F_{17}, $C_{10}F_{21}$), this CF_2 forms a simple system: the two fluorine atoms appear as a singlet and can be considered to be magnetically equivalent.

For the shorter chains (R_F = C_4F_9, C_6F_{13}), the CF_2 at the end of the chain appears as a complex set of peaks with the exo isomer producing a split triplet in the center of an AB system corresponding to the endo isomer.

This AB system is further complicated by the various interactions of A and B with the two neighbouring fluorine atoms. This complexity underlines a strong magnetic inequality between the two fluorine atoms in the CF_2 group of the endo form.
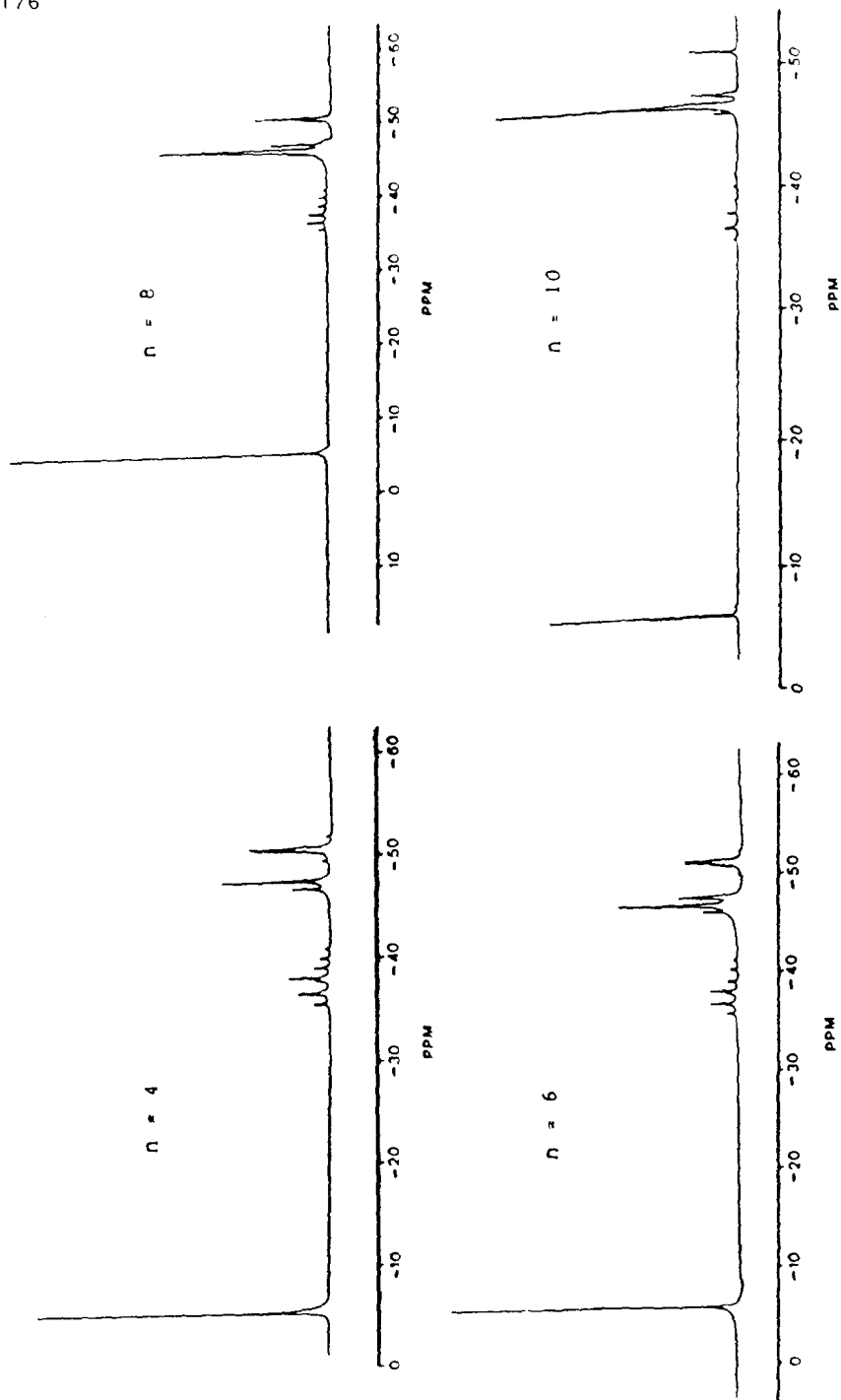
Fig. 1 . ^{19}F N.M.R. spectra of mixture of endo and exo isomers of C_nF_{2n+1} .
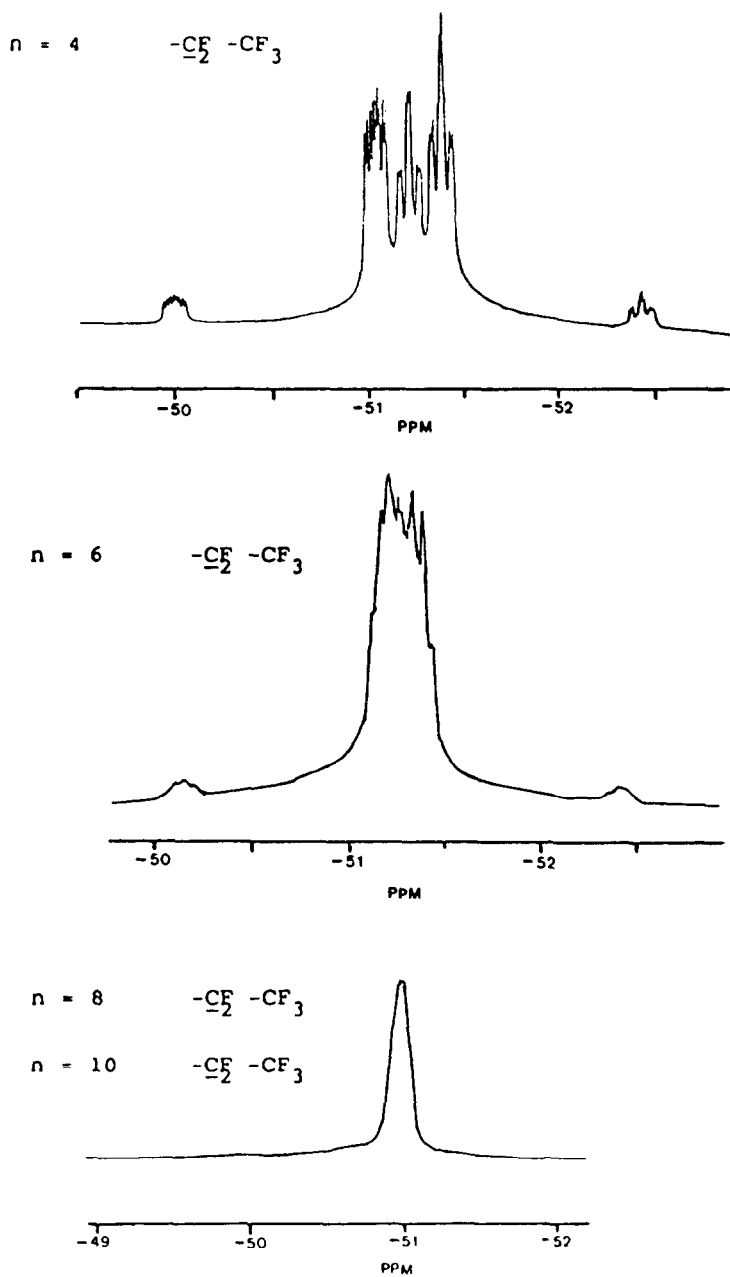
Fig. 2. High resolution ^{19}F N.M.R. spectra of $\underline{CF}_2$-CF_3 peaks for endo and exo forms of [bicyclic structure]$-C_nF_{2n+1}$.

Similar findings were observed with the disubstituted derivatives, although the inequality of the two fluorine atoms was less pronounced. Such an inequality can be explained by preferred conformations at room temperature of the perfluorinated chain for the endo isomer with $R_F = C_4F_9$ or C_6F_{13}. This may be due to inter- or intra-molecular associations.

Intermolecular association

Intermolecular association is probably limited to segregation processes between the fluorinated and hydrogenated groups. This is a well known phenomenon in mixtures of perfluorinated and perhydrogenated compounds [5]. We also recently demonstrated this for aromatic amphiphiles with an ammonium polar head substituted with fluorinated and hydrogenated groups [10].

This process leads to the association of the bicyclic derivatives which behave as amphiphilic molecules with a large hydrogenated head (bicyclo moiety) and a long perfluorinated tail. Associations of this type can lead to the formation of micelles (Fig. 3).
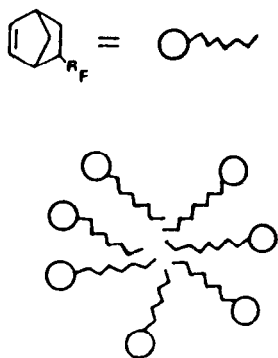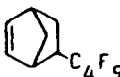

Fig. 3. Typical micelle structure.

It can also lead to blockade of the terminal region of the perfluorinated chain for molecules with short chains. For classical amphiphiles with polar heads and hydrocarbon chains, the terminal end of the chain is only genuinely flexible if the chain is long [7].

Effect of temperature

Since the micellar structures were sensitive to temperature, we carried out an investigation of the ^{19}F NMR spectrum of at different temperatures (Figs. 4 and 5).

At a concentration of 0.4 mole.l^{-1} in CDCl$_3$, the AB system of the CF$_2$ terminal was observed to shift towards that of an A$_2$ system. The two fluorine atoms became equivalent at a temperature of 91°C and above. This temperature (T) was obtained by extrapolation at $\Delta v = 0$ of the plot $\Delta v = f(T)$ (Figure 6). Δv is the value $vA - vB$ of the AB system of the CF$_2$terminal, and $\Delta v = 0$ corresponds to magnetic equivalence of the two fluorine atoms. Above 91°C, there is either total destruction of the aggregate with liberation of free molecules, or an alteration in the aggregate leading to a greater mobility of the CF$_2$ terminal. Effects of temperature were also studied for the derivatives with R$_F$ = C$_6$F$_{13}$, C$_8$F$_{17}$ and C$_{10}$F$_{21}$ (Fig. 6 and Table II).
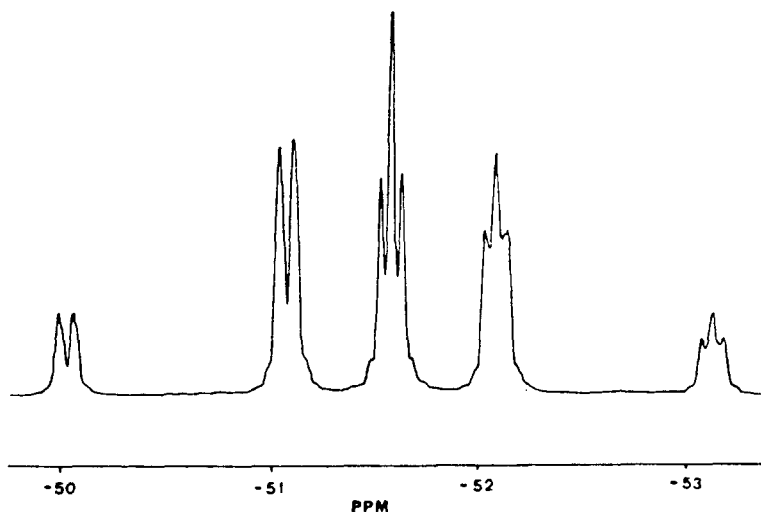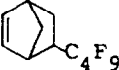
Fig. 4. ^{19}F NMR spectra of C$\underline{F}_2$-CF$_3$ in a mixture of endo and exo
isomers of [structure] 0.4 mole/liter in CDCl$_3$ at -60°C.
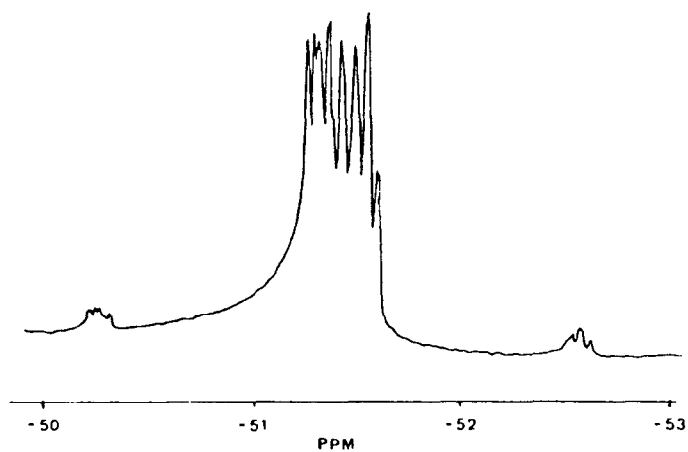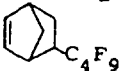
Fig. 5. ^{19}F NMR spectra of C$\underline{F}_2$-CF$_3$ in a mixture of endo and exo
isomers of [structure] 0.4 mole/liter in CDCl$_3$ at +50°C.
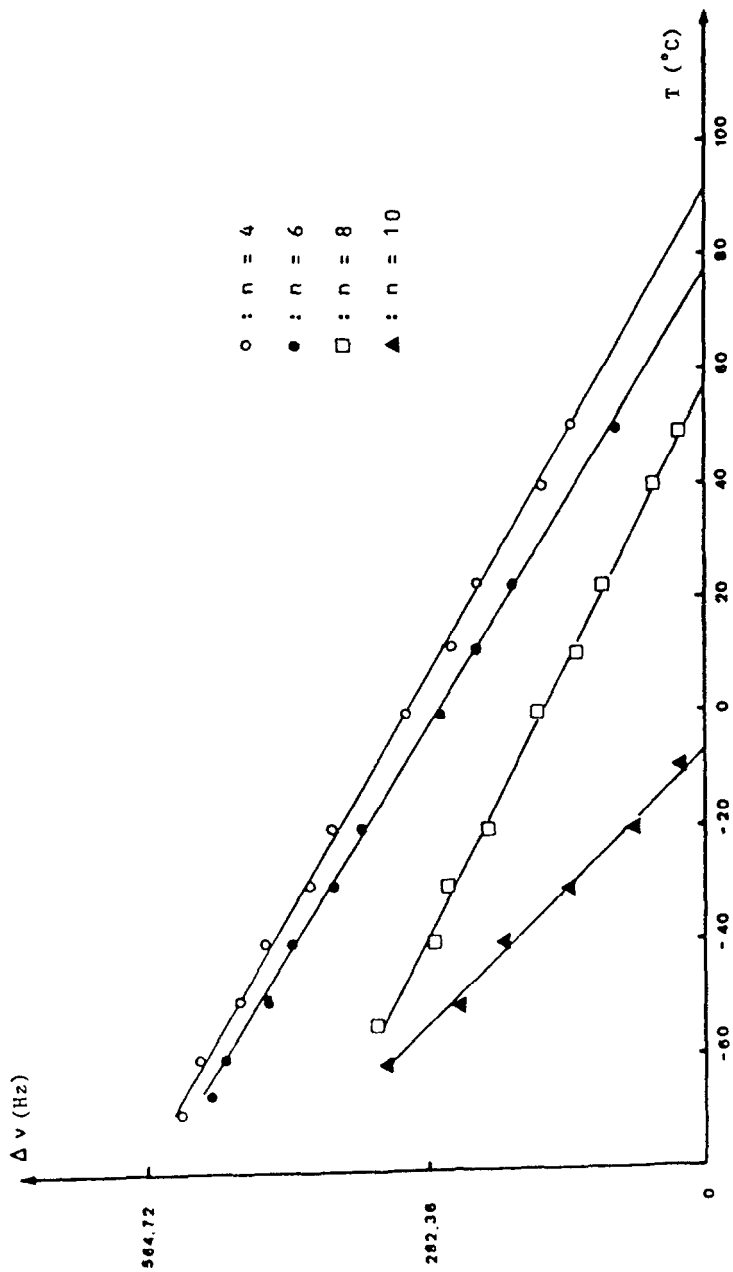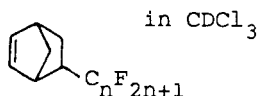
Fig. 6. Plot of Δv for the AB system of $C\underline{F}_2-CF_3$ in a mixture of endo and exo isomers of C_nF_{2n+1} as a function of temperature.

TABLE II

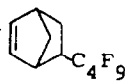Temperatures at $\Delta v = 0$ for endo and exo mixtures of

in $CDCl_3$

C_nF_{2n+1}

n	T °C	Concentration * mole/liter
4	91	0.4
6	77	0.3
8	57	0.2
10	- 8	0.07

* These concentrations were chosen on solubility criteria

Effect of concentration

The structure of the micelles was also sensitive to
concentration. The ^{19}F NMR spectrum of C_4F_9 was recorded at
different concentrations. At 23°C and in the concen-
tration range studied (0.4 to 2.10^{-7} mole.l^{-1} in $CDCl_3$), the
spectrum remained the same. The association process appeared to
persist (Figs. 7 and 8). This result along with those obtained
at different temperatures indicate that the aggregates, once
formed, are stable. They thus have a low critical micellar
concentration (CMC). The CMC is defined as the concentration
above which micellization is observed. However, at a given
temperature, the association falls with increasing length of the
perfluorinated chain. This is contrary to classical micelliza-
tion since in general, micelles increase in stability with
increasing length of hydrophobic chain. Moreover, intermolecular
association does not readily account for the fact that this
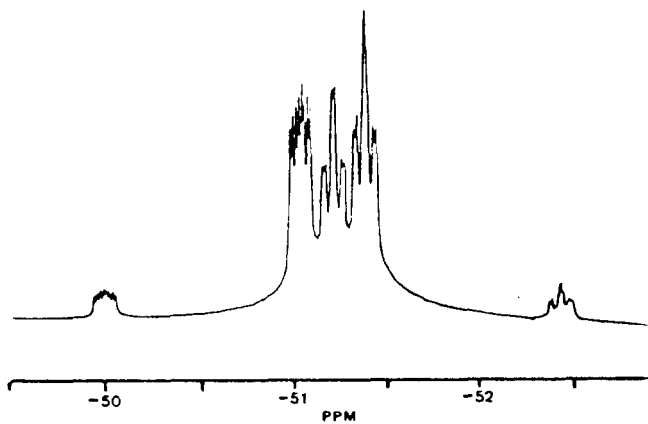
Fig. 8. ^{19}F NMR spectra of $C\underline{F}_2-CF_3$ in a mixture of endo and exo isomers of [structure] C_4F_9 0.4 mole/liter in $CDCl_3$ at 23°C.
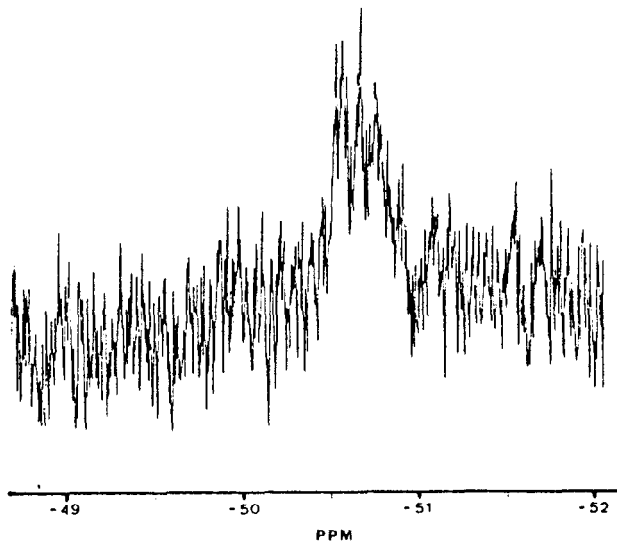
Fig. 7 ^{19}F NMR spectra of $C\underline{F}_2-CF_3$ in a mixture of endo and exo isomers of [structure] C_4F_9 2×10^{-7} mole/liter in $CDCl_3$ at 23°C.

phenomenon was only observed for the endo isomer. However, the perfluorinated chain is sufficiently long (even where $R_F = C_4F_9$) and distant from the ring for there to be, at least in theory, exo-exo and endo-exo interactions.

Intramolecular associations

In this case, the perfluorinated chain is bent towards the ring. The end CF_2 group could thus interact with the protons in the ring. F..H bonds could thus hold the perfluorinated chain in a new conformation (Fig.9).
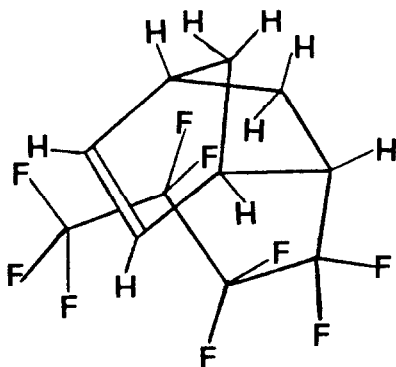
Fig. 9. Intramolecular association.

This conformation could account for the fact that the phenomenon is only observed for the endo isomer where there is no steric hindrance. It is also supported by the fact that the process is not affected by dilution. Steric factors can also explain why the phenomenon disappears with increasing chain length, since perfluorinated chains are known to be rather inflexible.

This explanation does not rule out intermolecular association which may take place albeit to a lesser extent. The

perfluorinated chains are thus enclosed by the hydrogenated rings, and micellization is due to a kind of inter-intramolecular association.

Polymerization of the mono and disubstituted bicyclic derivatives

Most of the fluorinated polymers are characterized by exceptional chemical inertness; the presence of fluorine makes them refractory, non-toxic and non-biodegradable. These properties along with a strong water repellant nature make these polymers particularly useful as protective films for various materials [11].

We were interested to examine the polymerization by a metathetic reaction involving a ring opening of the partially fluorinated bicyclo [2.2.1] hept-2-enes described above.

1)   n

$R_F = C_4F_9$, C_6F_{13}, C_8F_{17}, $C_{10}F_{21}$

2)   n

$R_F = C_4F_9$, C_6F_{13}, C_8F_{17}
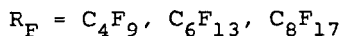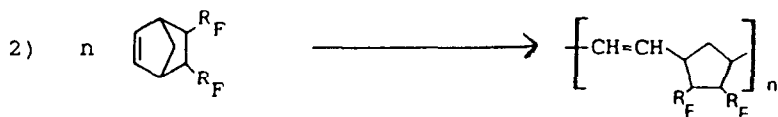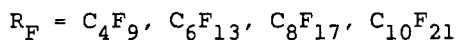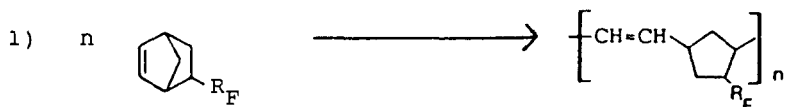
By altering the fluorinated part, we hoped to relate the characteristics of these polymers to the length of the perfluorinated chain.

In the case of the substituted bicyclo [2·2·1] hept-2-enes where the ring is already strained, ring opening is highly favored. Under classical conditions of metathesis [12], we were therefore able to obtain the polymers corresponding to ring opening of all the monomers with long perfluorinated chains in good yield (Table III).

TABLE III

Yields for the polymerization reaction

$$n \quad \text{[structure]} \xrightarrow[25°C]{C_6H_5Cl} \text{[-CH=CH ... structure]}_n$$

$R = H;\ C_nF_{2n+1}\ (n = 4,6,8)$

$R_F = C_nF_{2n+1}\ (n = 4,6,8,10)$
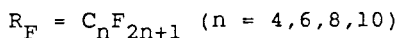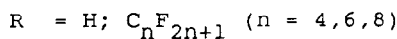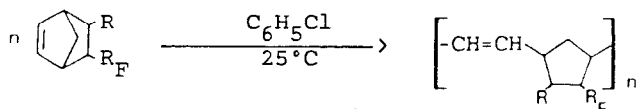
R_F	R	Compound	Yield (%)
C_4F_9	H	8	65
C_6F_{13}	H	9	75
C_8F_{17}	H	10	85
$C_{10}F_{21}$	H	11	80
C_4F_9	C_4F_9	12	45
C_6F_{13}	C_6F_{13}	13	60
C_8F_{17}	C_8F_{17}	14	40

The following catalytic conditions were employed:

Catalyst : $W(CO)_3$ (mesitylene)

$C_2H_5AlCl_2$

O_2
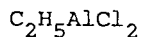
Molar ratios : catalyst/olefin/cocatalyst/O_2 (1/50/4/6)

There was a considerable difference in reactivity between the mono and disubstituted bicyclic monomers. Since the cata-

lytic attack is on the exo side [13], the lower reactivity of the disubstituted derivatives was probably due to greater steric hindrance from the chain in the exo position.

The polymers obtained were elastomers with a glass transition temperature ranging from -10°C to -20°C, and with a decomposition temperature of 300°C. Most of them were amorphous.

We also measured their intrinsic viscosity. The results are shown in Tables IX and X. They exhibited good water repellant properties on textile fibers [14]. A more detailed analysis of their physical properties is currently in progress.

CONCLUSION

In this report, we describe a general method for the synthesis of bicyclo [2.2.1] hept-2-enes, mono and disubstituted with long perfluorinated chains C_nF_{2n+1} (n = 4,6,8,10). Mechanisms of molecular association were investigated by ^{19}F NMR spectroscopy. The compounds were also found to polymerize readily by a metathetic reaction producing further examples of polymers with promising physical properties.

EXPERIMENTAL

The high resolution ^{19}F and ^{13}C NMR spectra were recorded on a Bruker AM 300WB (nominal frequency 282.38 MHz for ^{19}F and 75.47 MHz for ^{13}C). The ^{1}H spectra were recorded at 60 MHz on a Varian T60. The spectra and the microanalysis results (CNRS central facilities, Vernaison, France) were in good agreement with the proposed structures. Measurements of intrinsic viscosity were carried out using a capillary viscosimeter of the Ubbelohde type [15].
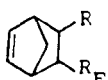
The bicyclo [2·2·1] hept-2-enes with long fluorinated chains were obtained by reacting freshly distilled cyclopentadiene (0.2 moles) with the corresponding freshly distilled olefins (0.2 moles). The reaction was carried out in the presence of hydroquinone (1.8 g) in an autoclave maintained at 170°C for 72 h. After filtration of the crude product, the compounds were purified by distillation under reduced pressure.

Polymerization of the bicyclic derivatives

The metathetic catalytic reaction was carried out under an atmosphere of argon using standard anaerobic conditions. All solvents and reagents after purification were dried, degassed and kept under argon. The complex $W(CO)_3$ (mesitylene) was supplied by Research Organic and Inorganic Chemical Corp. $C_2H_5AlCl_2$ was supplied by the Ethyl Corp. The mixed olefins with long perfluorinated chains were kindly provided by Atochem.

The typical reaction was carried out as follows: 0.01 moles of long chain perfluorinated bicyclo [2·2·1] hept-2-ene were added to 50 ml of chlorobenzene containing 2×10^{-4} moles of $W(CO)_3$ (mesitylene). Then 1.2×10^{-3} moles of oxygen were introduced into the reactor. The reaction was initiated at 25°C by the addition of 8×10^{-4} moles of $C_2H_5AlCl_2$. After a few minutes, the reaction was stopped by addition of 5 ml of methanol. The mass of polymer was collected and dissolved in a minimum quantity of Freon 113, and then released into methanol. The purified polymer was finally dried under vacuum at 50°C.

TABLE IV

Elemental analysis of compounds

R_F	R	Elemental analyses (% weight)			
			C	H	F
C_4F_9	H	C	42.30	2.88	54.82
		E	42.41	2.90	53.64
C_6F_{13}	H	C	37.86	2.18	59.96
		E	37.72	2.21	58.23
C_8F_{17}	H	C	33.15	1.76	63.09
		E	35	1.70	62.19
$C_{10}F_{21}$	H	C	33.33	1.47	65.20
		E	33.42	1.45	62.34
C_4F_9	C_4F_9	C	33.96	1.50	64.54
		E	34	1.47	61.36
C_6F_{13}	C_6F_{13}	C	31.23	1.09	67.68
		E	31.12	1.10	63.54
C_8F_{17}	C_8F_{17}	C	29.67	0.86	69.47
		E	30	0.94	64.53

C : Calculated
E : Experimental

TABLE V

^{1}H and ^{19}F NMR spectra of compounds

C$_n$F$_{2n+1}$ (n=4,6,8,10)

Compound	B.P. °C/mmHg	^{1}H NMR δ ppm [a]	^{19}F NMR δ ppm [b]
R$_F$ = C$_4$F$_9$ 1	34/0.01	m (4H)=1.4, m (4H)=1.8 m (1H)=2.9, m (2H)=3.2 m (4H)=6.1	sys. AB endo (2F), A=-38.9, B=-36.7, J$_{AB}$=280 Hz sys. AB exo (2F), A=-40.9, B=-37.9, J$_{AB}$=275 Hz s (2F) exo =-49.2, s (2F) =-48 m (4F)=-51.1, s (6F)=-6.3
R$_F$ = C$_6$F$_{13}$ 2 endo + exo	47/0.01	m (4H)=1.3, m (4H)=1.8 m (4H)=2.9, m (2H)=3.1 m (4H)=6	sys. AB endo (2F), A=-38.4, B=-36.6, J$_{AB}$=275 Hz sys. AB exo (2F), A=-40.8, B=-36.63, J$_{AB}$=275 Hz s (2F) exo =-46.2, s (2F) =-47, s (4F)=-47.8 m (4F)=-51.2, s (6F)=-6.1
R$_F$ = C$_8$F$_{17}$ 3 endo + exo	62/0.01	m (4H)=1.4, m (4H)=1.7 m (4H)=2.9, m (2H)=3.2 m (4H)=6.2	sys. AB endo (2F), A=-38.4, B=-36.4, J$_{AB}$=280 Hz sys. AB exo (2F), A=-40.5, B=-36.0, J$_{AB}$=280 Hz s (2F) exo =-46, s (14F) =-46.7, s (4F)=-47.5 s (4F)=-50.9, s (6F)=-5.7
R$_F$ = C$_{10}$F$_{21}$ 4 endo + exo	78/0.01	m (4H)=1.4, m (4H)=1.8 m (4H)=2.8, m (2H)=3 m (4H)=6.1	sys. AB endo (2F), A=-38.3, B=-36.4, J$_{AB}$=280 Hz sys. AB exo (2F), A=-40.5, B=-37.4, J$_{AB}$=280 Hz s (2F) exo =-46, s (22F) =-46.5, s (4F)=-47.5 s (4F)=-50.9, t (6F)=-5.7 J$_3$ F-F=10 Hz

a 60 MHz in CDCl$_3$, internal reference : TMS

b 282.386 MHz in CDCl$_3$, internal reference : CF$_3$COOH

TABLE VI

¹H and ¹⁹F NMR spectra of compounds

$$\text{[structure with } C_nF_{2n+1}, C_nF_{2n+1}]$$

(n=4,6,8,10)
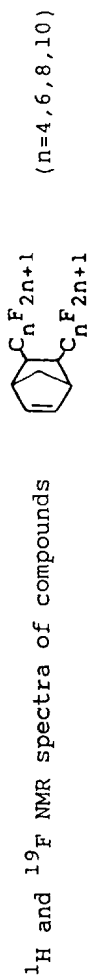
Compound R_F	B.P. °C/mmHg	^1H NMR δ ppm [a]	^{19}F NMR δ ppm [b]
$R_F = C_4F_9$ **5**	76/0.01	m (4H)=1.5, m (4H)=2.2 m (4H)=2.7, m (2H)=3.1 m (4H)=6.1	sys. AB ant. (2F), A=-28.9, B=-28.3, J_{AB}=191 Hz sys. AB sup.(2F), A=-43.8, B=-41.9, J_{AB}=288 Hz s (2F) sup.=-49.4, s (2F) ant. =-48.1, m (4F)=-51.2, s (6F)=-6.7
$R_F = C_6F_{13}$ **6**	98/0.01	m (4H)=1.6, m (1H)=2.2 m (4H)=2.6, m (2H)=3.1 m (4H)=6	sys. AB ant. (2F), A=-29.5, B=-28.3, J_{AB}=189 Hz sys. AB sup.(2F), A=-43.7, B=-42.3, J_{AB}=297 Hz s (2F) sup.=-46.4, s (6F)=-46.9 s (4F) =-48, m (4F)=-51.3, s (6F)=-6.5
$R_F = C_8F_{17}$ **7**	123/0.01	m (4H)=1.5, m (1H)=2.2 m (4H)=2.6, m (2H)=3.2 m (4H)=6.2	sys. AB ant. (2F), A=-30.2, B=-28.4, J_{AB}=225 Hz sys. AB sup. (2F), A=-43.5, B=-41.6, J_{AB}=285 Hz s (2F) sup.=-47.3, s (14F)=-48.5 s (4F)=-49.5, s (4F)=-53.1, s (6F)=-5.4

a 60 MHz in CDCl₃, internal reference : TMS
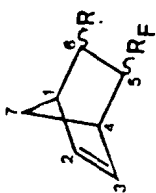
b 282.386 MHz in CDCl₃, internal reference : CF₃COOH

TABLE VII

^{13}C NMR spectra of compounds

R_F	R		$\delta^{13}C$ / TMS (ppm)						
			C_1	C_2	C_3	C_4	C_5	C_6	C_7
C_4F_9	H	E	42.13	137.17	131.76	43.74	40.4	27.46	49.57
		X	41.36	138.23	136.30	42.53	41.14	26.72	46.29
C_6F_{13}	H	E	42.05	137.21	131.77	43.67	40.31	27.49	49.61
		X	41.28	138.24	136.33	42.43	41.05	26.73	46.32
C_8F_{17}	H	E	42.08	137.01	131.70	43.72	40.50	27.39	49.46
		X	41.32	138.12	136.25	42.49	41.25	26.64	46.18
$C_{10}F_{21}$	H	E	40.89	136.42	130.65	42.54	39.01	26.27	48.43
		X	40.12	137.33	135.30	41.27	39.76	25.51	45.07
C_4F_9	C_4F_9		43.10	135.95	135.60	43.72	42.92	42.43	47.58
C_6F_{13}	C_6F_{13}		42.96	136	135.66	43.64	43.14	42.45	47.62
C_8F_{17}	C_8F_{17}		42.95	136	135.64	43.66	43.18	42.44	47.53

Frequency 75.469 MHz

E : Endo isomer   X : Exo isomer

TABLE VIII

Elemental analysis of polymers $\left[CH=CH \underset{R \quad R_F}{\bigcirc} \right]_n$
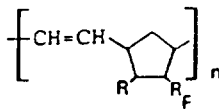
R_F	R	Elemental analyses (% weight)		
			C	H	F
C_4F_9	H	C	42.30	2.88	54.82
		E	42.38	2.85	51.18
C_6F_{13}	H	C	37.86	2.18	59.96
		E	37.92	2.16	55.80
C_8F_{17}	H	C	33.15	1.76	63.09
		E	32.80	1.75	61.67
$C_{10}F_{21}$	H	C	33.33	1.47	65.20
		E	33.27	1.51	60.92
C_4F_9	C_4F_9	C	33.96	1.50	64.54
		E	34.20	1.53	60.07
C_6F_{13}	C_6F_{13}	C	31.23	1.09	67.68
		E	31.30	1.07	62.15
C_8F_{17}	C_8F_{17}	C	29.67	0.86	69.47
		E	29.48	0.91	61.71

C : Calculated
E : Experimental

TABLE IX

^{1}H, ^{19}F NMR spectra and viscosity of polymers

C_nF_{2n+1} (n=4,6,8,10)
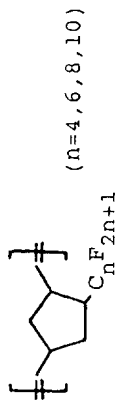
| Compound	$[\eta]$ ^{a} dl/g	^{1}H NMR ^{b} δ ppm	^{19}F NMR ^{c} δ ppm
$R_F = C_4F_9$ **8**	0.19	m (7H) = 1.3 - 3 m (2H) = 5.1	m (2F) = 35.1, s (2F) = 45.7 s (2F) = 50.2, s (3F) = 4.7
$R_F = C_6F_{13}$ **9**	0.35	m (7H) = 1.2 - 3 m (2H) = 5.2	m (2F) = 35.5, s (6F) = 45.3 s (2F) = 50.6, s (3F) = 5.3
$R_F = C_8F_{17}$ **10**	0.85	m (7H) = 1.2 - 3 m (2H) = 5.2	m (2F) = 35, s (10F) = 45.5 s (2F) = 50.6, s (3F) = 4.7
$R_F = C_{10}F_{21}$ **11**	0.14	m (7H) = 1.3 - 3.1 m (2H) = 5.2	m (2F) = 35.7, s (14F) = 45.7 s (2F) = 50.8, s (3F) = 5.1

a   intrinsic viscosity at 30°C in F113 ($CF_2Cl-CFCl_2$)
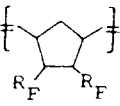
b   60 MHz in F113, internal reference : TMS

c   84.6 MHz in F113, internal reference : CF_3COOH

TABLE X

^{1}H NMR^a spectra and viscosity of polymers (n = 4,6,8)

$$\left[\text{...cyclopentane ring with } C_nF_{2n+1} \text{ and } C_nF_{2n+1} \right]$$
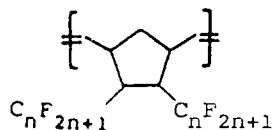
Compound $\left[\text{ring } R_F, R_F \right]$	$[n]^b$ dl/g	^{1}H NMR^c δ ppm
$R_F = C_4F_9$ <u>12</u>	0.03	m (6H) = 1.8 - 3.3 m (2H) = 5.2
$R_F = C_6F_{13}$ <u>13</u>	0.08	m (6H) = 1.6 - 3.1 m (2H) = 5.2
$R_F = C_8F_{17}$ <u>14</u>	0.13	m (6H) = 1.8 - 3.2 m (2H) = 5.1

a   The ^{19}F NMR spectra are not given due to their complexity, and difficulty of interpretation

b   intrinsic viscosity at 30°C in F113 ($CF_2Cl-CFCl_2$)

c   60 MHz in F113, internal reference : TMS

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