Stereoregular fluoropolymers: 2. The ring opening polymerization of some polyfluoroaryl polycyclic alkenes*

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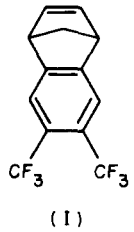
Three fluorinated derivatives of benzonorbornadiene have been shown to undergo ring opening polymerization at the unsubstituted double bond in the presence of $WCl_6/(CH_3)_4Sn$ and $MoCl_5/(CH_3)_4Sn$ in chlorobenzene solution at room temperature. The proportion of *cis*-vinylene units (σ_c) in the resultant polymers is a function of monomer structure and catalyst, and in one case σ_c approached zero; however, the distribution of meso- and racemic dyads in these polymers could not be determined with presently available techniques.

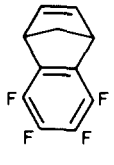
(Keywords: fluoropolymers; ring opening; polymerization; polyfluoroaryl poly cyclic alkenes)

INTRODUCTION

The background and context of this work was outlined in the introduction to the preceding paper[1]. During the last few years we have examined several kinds of fluorinated polycyclic alkenes as potential monomers for the preparation of stereoregular fluoropolymers via metathesis ring opening[2]. Our test of suitability was, in the first instance, that the polymers should be soluble and consequently amenable to conventional methods of characterization. In the event most of the systems examined gave products which were either insoluble in common solvents or gave spectroscopic data which were insufficiently well resolved and/or too complex for unambiguous interpretation. In this paper we report the polymerization of three polyfluoroaryl polycyclic alkenes (**I**, **II** and **III**) which proved reasonably amenable to investigation.



(I)



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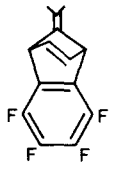
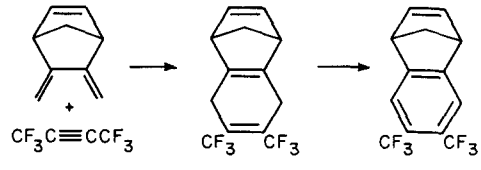


(III)

EXPERIMENTAL

Monomers

4,5-Bis(trifluoromethyl)tricyclo[6.2.1.$0^{2,7}$]undeca-2,4,6,9-tetraene (**I**) has not been previously reported. It was prepared by the sequence shown below:



(IV) (V) (I)

The triene (**IV**) has been prepared by two routes[3,4]. Both syntheses are satisfactory; however we found that of Bow and coworkers[4] more convenient and easier to scale up.

Hexafluorobut-2-yne (6.6 g, 40.8 mmoles), 5,6-dimethylenebicyclo[2.2.1]hept-2-ene (**IV**) (4.7 g, 4.4 cm^3, 39.83 mmoles) and hydroquinone (0.03 g) were sealed under vacuum in a Pyrex ampoule; after 17 h at room temperature the vessels was opened to give, white crystals from pentane, 4,5-bis(trifluoromethyl)tricyclo-[6.2.1.$0^{2,7}$]undeca-2(7),4,9-triene (**V**) (5.7 g, 20.4 mmoles, 51%; m.p. 44°C; found: C, 55.54; H, 3.31; F, 40.11%, $C_{13}H_{10}F_6$ requires C, 55.74; H, 3.57; F, 40.67%). The infra-red spectrum showed the expected vinylic (3050 cm^{-1}) and aliphatic (2800–2950 cm^{-1}) C–H stretching vibrations and the strong absorptions characteristic of C–F bonds in the 1400–1100 cm^{-1} region. The mass spectrum showed a parent ion at m/e 280 which was also the base peak, with major fragment ions at m/e 211 (80%, $P-CF_3$), 191, 185 and 142.

Triene (**V**) (8.27 g, 29.5 mmoles), chloranil (10.7 g, 43.1 mmoles) and xylene (400 ml) were refluxed together for 24 h. After removal of the solvent under reduced pressure the product was recovered by column chromatography (Kieselgel 60/cyclohexane), recrystallized from acetone, and dried under vacuum to give 4,5-bis(trifluoromethyl)tricyclo[6.2.1.$0^{2,7}$]undeca-2,4,6,9-tetraene (**I**) (6.1 g, 22.0 mmoles, 74%; m.p. 53°C; found: C, 56.28; H, 3.08; F, 41.20%; $C_{13}H_8F_6$ requires C, 56.13;

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Table 1 Polymerizations[a] of monomers **I**, **II** and **III**

Experiment number	Monomer (mmol)	$WCl_6(MoCl_5)$ (mmol)	Chlorobenzene (ml)	Reaction time (min)	Yield (%)
1	**I** (2.8)	0.014	8	20	64
2	**I** (2.6)	(0.013)	5	10	85
3	**II** (1.4)	0.0075	1.5	3	57
4	**II** (2.1)	(0.011)	3	4	61
5	**III** (5.6)	0.029	2	3	91
6	**III** (4.0)	(0.098)	3	5	84

[a] $(CH_3)_4Sn$ was added to the catalyst solution so as to make a 1:2, catalyst:$(CH_3)_4Sn$ molar ratio, prior to addition of monomer

H, 2.88; F, 40.99%). The infra-red spectrum showed the expected range of C–H and C–F stretching vibrations. The mass spectrum showed a parent ion at m/e 278 with major fragment ions at m/e 259 (P−F), 209 (100%, $P-CF_3$) and 183.

3,4,5,6-Tetrafluoro[6.2.1.$0^{2,7}$]undeca-2,4,6,9,-tetraene (**II**) and 3,4,5,6-tetrafluoro-11-isopropylidene-[6.2.1.$0^{2,7}$]undeca-2,4,6,9-tetraene (**III**) were both gifts from Dr G. M. Brooke (this Department); their preparation and characterization have been described elsewhere[5,6].

Polymerizations

Techniques, solvents and reagents were as previously described[1]. Monomers **I**, **II** and **III** were polymerized as solutions in chlorobenzene; two catalyst systems were used, $WCl_6/(CH_3)_4Sn$ and $MoCl_5/(CH_3)_4Sn$ with catalyst to activator ratios of 1:2 in both cases. The results are summarized in *Table 1*; yields are of polymers purified by successive reprecipitation and drying under vacuum. The products were characterized by elemental analysis (*Table 2*), gel permeation chromatography (*Table 3*), and spectroscopy (see later).

Table 2 Elemental analyses

Experiment number (Table 1)	Found			Calculated		
	C%	H%	F%	C%	H%	F%
1	56.0	3.2	40.5	56.1	2.9	41.0
4	62.5	2.7	30.4	61.7	2.8	35.5
5	67.2	3.8	28.1	66.2	3.9	29.9
6	67.1	3.5	29.4	—	—	—

Table 3 G.p.c. analyses[a]

Experiment number (*Table 1*)	$\bar{M}_n$[b] $\times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$
1	95	260	2.7
2	74	220	3.0
4	300	1700	5.6
5	42	100	2.4

[a] Perkin–Elmer 601 Syringe Pump Liquid Chromatography Apparatus, 3 PL Gel columns (10^5, 10^3 and 500Å) from Polymer Laboratories Ltd., THF stabilized with 2,6-di-tert-butylphenol as eluent, and a Knauer Differential Refractomer as detector

[b] 'Polystyrene equivalent values', see text for comment

RESULTS AND DISCUSSION

As would be expected from our earlier results on the polymerization of benzonorbornadiene and related hydrocarbon arylpolycyclic olefins[7] and the established polymerizability of fluorinated monomers[8], the polymerization of monomers **I**, **II** and **III** proceeded readily and in good yield. The results of elemental analyses (*Table 2*) and g.p.c. (*Table 3*) confirm that the products listed in *Table 1* are addition polymers of the monomers **I**, **II** and **III**. The analytical results, although in some instances far from perfect, are generally within the experimental error limits of the techniques used; the larger deviations between found and calculated values can probably be attributed to partial oxidation and/or to solvent contaminants, since all these polymers are susceptible to oxidation and have a tenacious hold on solvent even when stored for several days on a continuously pumped vacuum line.

The $\bar{M}_n$ and $\bar{M}_w$ values quoted in *Table 3* were obtained from the raw data by drawing a baseline to the curve, tabulating peak height vs. elution volume, using a calibration curve derived from polystyrene standards run in the same solvent on the same column set, and computing the results in the standard way[9]. We were a little dubious about the objectivity of this procedure and so several different people conducted independent analyses of the raw data. There was very good agreement between the $\bar{M}_n$ values obtained but $\bar{M}_w$ values (and consequently also polydispersity values) were in considerably less good agreement. It seems that this is a consequence of the relatively large effect of the 'wing components' of the g.p.c. curve and the element of subjectivity in the analysis arises from the definition of where the baseline is drawn, small variations having a marked effect on the weighting attached to the 'wings' of the peak. Despite these reservations, the g.p.c. results provide unequivocal evidence for the formation of high polymers. The g.p.c. results reported in *Table 3* were obtained within a few days of the synthesis of the sample. Successive g.p.c. traces recorded for a particular polymer solution within a few hours were completely reproducible, but when solutions were stored for a few weeks the traces showed a gradual shift to larger retention volume and increasing peak width, consistent with a slow fragmentation of the polymers under these conditions.

The structural characterization of the polymers produced was heavily dependent on high resolution solution phase ^{13}C n.m.r. spectroscopy (see later) and some of the materials produced showed rather limited solubility which might have been a consequence of the high molecular weight or stereoregularity of the sample. We were therefore interested in the possibility of controlling molecular weight by including a chain transfer reagent during polymer synthesis. To investigate the effectiveness of *trans*-4-octene as a chain transfer agent in this type of system we examined the polymerization of **III**

with $WCl_6/(CH_3)_4Sn$; this reaction gave a soluble product in virtually 100% yield. The results are summarized in *Table 4*. As can be seen, the inclusion of *trans*-4-octene had the expected effect in that the molecular weight was progressively reduced as the proportion of octene was increased. It also appeared that the polydispersity increased with decreasing molecular weight but, in view of the reservations expressed above, this trend has to be regarded with some caution. In principle, it is possible to obtain the chain transfer constant (i.e. the ratio of the transfer rate constant to the propagation rate constant) as the slope of the plot of reciprocal number average degree of polymerization vs. the ratio of the concentrations of the transfer agent and monomer[10]. The limited data in *Table 4* give a fairly good straight line (intercept −0.0004, slope 1.4, correlation coefficient 0.99) indicating that the conventional chain transfer process was occurring, but the value of the chain transfer constant (1.4) is uncorrected ($\bar{M}_n$ values are polystyrene equivalent values) and no allowance has been made for competing reactions such as cyclization and polymer chain degradation via cross metathesis[11].

The first step in establishing the structure of these polymers is to demonstrate that the unsaturation of the monomers is retained in the polymers, as is required for metathesis ring opening, rather than lost, as would be required for vinyl polymerization. All the polymers could be cast as films from solution and were therefore readily obtained in a form suitable for infra-red spectroscopic investigation. Infra-red spectroscopy has been extensively used for the investigation of metathesis polymers; in particular the out-of-plane C–H vibrations of *cis* (730 cm^{-1}) and *trans* (970 cm^{-1}) vinylenes have proved very useful in assigning structures; unfortunately with these rather complex polymers there were several overlapping bands in this region of the spectrum and consequently, while the observed spectra were consistent with the structures assigned by other techniques, little unambiguous and useful structural information could be deduced from the infra-red spectra.

The ^1H n.m.r. spectra of several of the polymers were recorded; they were not well resolved and the data recorded in *Table 5* refer only to integrated intensities and the chemical shifts at the centres of broad unresolved bands. The data are, nevertheless, consistent only with the assumption that the products are formed by ring opening, and exclude the possibility of vinyl polymerization (see *Figure 1*). Comparison of the spectra of samples 1 and 2 revealed that the product from molybdenum-catalysed polymerization of monomer **I** displayed only one band for each type of proton environment whereas the spectrum of sample (**I**, W) showed resolvable bands in the tertiary proton region, which is consistent with the tungsten based catalyst giving a more disordered polymer than the molybdenum based system. Similarly, sample 5 (**III**, W) showed clearly resolved bands in the vinylic region whereas sample 6 (**III**, Mo) showed only one band, which is again consistent with the molybdenum based catalyst giving the more ordered polymer.

The most useful structural information was derived from high field ^{13}C n.m.r. spectroscopy. *Figure 2* shows the spectrum of the polymer produced from monomer **I** using $WCl_6/(CH_3)_4Sn$ (i.e. **I**, W) as an illustration of the quality of spectra obtained and also of the procedure for assigning the observed resonances. Thus, the relatively high intensity signals assigned to C-1, C-2, C-3 and C-5 arise from carbons bearing hydrogen and experience a large NOE, whereas the quaternary signals due to C-4, C-6 and C-7 are of low intensity; these assignments were confirmed by DEPT[12] spectra (not shown) where

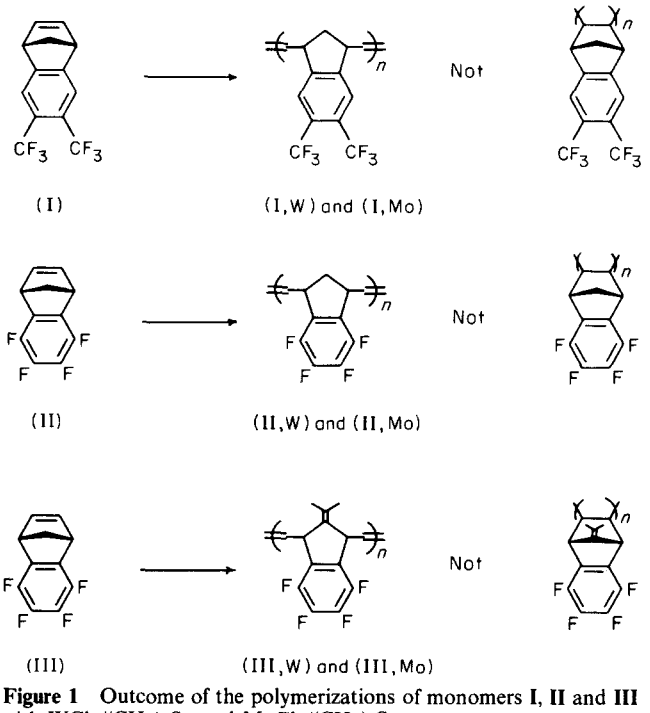


Figure 1 Outcome of the polymerizations of monomers **I**, **II** and **III** with $WCl_6/(CH_3)_4Sn$ and $MoCl_5/(CH_3)_4Sn$

Table 4 Polymerization of **III** in the presence of *trans*-4-octene

Expt. no.	WCl_6:$(CH_3)_4Sn$:III:octene[a] (molar ratio)	$\bar{M}_n^b \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$
1	1:2:200:0	340	560	1.6
2	1:2:200:2	17	61	3.6
3	1:2:200:5	8.8	36	4.1
4	1:2:200:10	3.6	21	5.8

[a] In chlorobenzene solution at *ca.* 0.6 M in **III**; reaction time 10 min, terminated by CH_3OH
[b] As for results reported in *Table 3*

Table 5 ^1H n.m.r. spectra data for ring opened polymers[a] of monomers **I**, **II** and **III** (chemical shifts)

Sample origin expt. number, (see *Table 1*)	Methyl	Methylene	Tertiary	Vinyl	Aryl
1 (**I**, W)	–	2.98 (2)	4, 4.5 (2)	5.86 (2)	7.65 (2)
2 (**I**, Mo)	–	2.99 (2)	4 (2)	6 (2)	7.8 (2)
4 (**II**, Mo)	–	3.9 (2)	4.76 (2)	5.62 (2)	–
5 (**III**, W)	1.7 (6)	–	4.56 (2)	5.6, 5.14 (2)	–
6 (**III**, Mo)	1.7 (6)	–	4.4 (2)	5.6 (2)	–

[a] Recorded at 60 MHz in $CDCl_3$ with internal TMS as reference; shifts in ppm with integrated intensities in parentheses

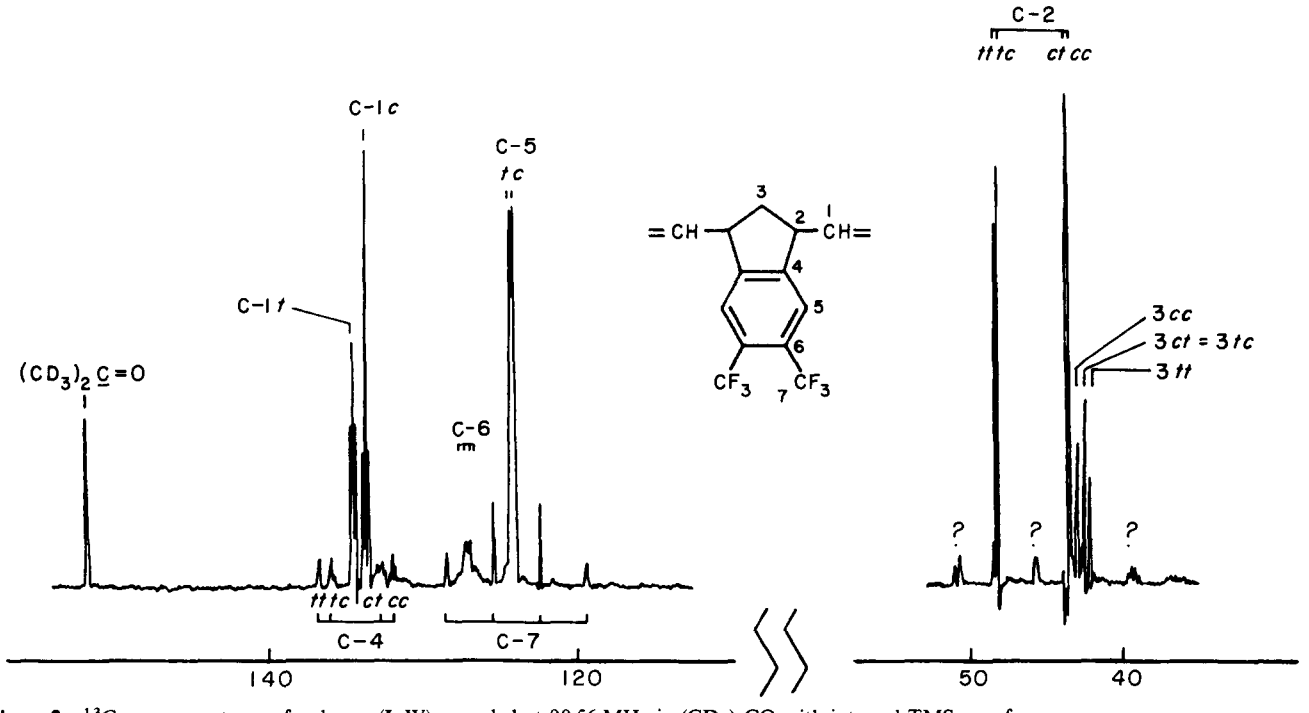
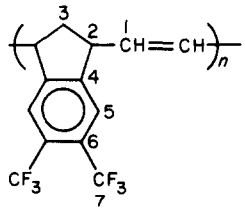


Figure 2 ^{13}C n.m.r. spectrum of polymer (I, W) recorded at 90.56 MHz in $(CD_3)_2CO$ with internal TMS as reference

quaternary signals vanish and methines and methylenes are readily distinguished. The carbon atom of the trifluoromethyl group, C-7, was assigned to the quartet centred at $\delta = 123.65$ ppm ($^1J_{CF} = 280$ Hz). The aromatic carbon C-6 couples to the fluorine atoms of the trifluoromethyl group and hence appears as a quartet at $\delta = 126.74$ ppm ($^2J_{CF} \simeq 33$ Hz). The other low intensity signals, recorded at 136.29, 135.56 and 131.67 ppm and visible but not recorded by the computer at *ca.* 131, were assigned to the aromatic quaternary carbon atom C-4, and correspond to *cc*, *ct*, *tt* and *tc* environments. The integration of these poorly resolved low intensity peaks was not sufficiently reliable to calculate a σ_c value but inspection indicates a roughly 50:50 *cis*:*trans* distribution. The olefinic resonance was split into two sets of overlapping resonances centred at 134.10 ppm (*trans*) and 133.4 ppm (*cis*), giving a σ_c value of 0.51. The fine structure of these two signals suggested that they were partially resolved into triplets, although the computer again did not recognize one of the peaks. This triplet splitting may arise from olefinic sequence and/or tacticity effects of the kind discussed previously[1]. A similar splitting patern for the vinylene carbons has been reported in the high resolution spectra of some polynorbornenes[13]. In those cases the multiplicity was unambiguously assigned to *cis*/*trans* vinylene sequence effects extending over three repeat units. The aromatic carbon at C-5 was split into two signals at 123.94 and 124.09 ppm, assigned as *cis* and *trans*, respectively; the *cis* content calculated from these absorptions was $\sigma_c = 0.47$. In the aliphatic region the signals at 43.02, 43.20, 47.60 and 47.76 ppm corresponding to the methine carbon were assigned as 2*cc*, 2*ct*, 2*tc* and 2*tt* respectively, the line order being in agreement with that observed in the spectra of polynorbornadiene reported by Ivin and co-workers[14]. This assignment is confirmed in the spectrum of the $MoCl_5$ derived 'high *trans*' polymer (see *Table 6*, below). The line order parallels that noted for poly(3,5-(1,2-bis(trifluoromethyl)cyclopentenylene)vinylene)s[1]. From the intensities of the C-2 absorptions the calculated *cis* content was $\sigma_c = 0.59$. The CH_2 carbon, C-3, appeared as a triplet, with resonances observed at 41.75, 42.06 and 42.54 ppm assigned to 3*tt*, 3*tc*/3*ct* and 3*cc* environments; the calculated *cis* content from these absorptions is 0.65. However, computation of σ_c from C-2 and C-3 must be regarded as somewhat suspect because the groups of resonances due to these two carbons overlap, making accurate integration difficult. Thus, for the WCl_6/Me_4Sn derived polymer, we are able to assign all the resonances observed in this high field and high resolution spectrum except those marked with a question mark in *Figure2*. There was invariably some delay between the synthesis (in Durham) and the ^{13}C n.m.r. examination (in Edinburgh) of these polymers and these minor unassigned peaks in the aliphatic region of the spectrum may have been due to a low level of oxidative degradation, or partial crosslinking. Thus, for polymer (I, W) there appears to be a roughly 50:50 distribution of *cis* and *trans* vinylenes and the multiplicity of observed lines is consistent only with an atactic polymer.

An analogous analytical procedure was applied to the spectra obtained for polymers (I, Mo), (II, W), (II, Mo), (III, W) and (III, Mo) and the spectral data are collected in *Tables 6*, *7* and *8* for comparison purposes. In all cases the polymers prepared using the $MoCl_5/(CH_3)_4Sn$ catalyst contained a higher proportion of *trans* vinylene units and also displayed simpler spectra consistent with a higher degree of order in these polymers as compared with those derived from the same monomers using $WCl_6/(CH_3)_4Sn$ as the initiator. The resolution and signal to noise ratio for these spectra was variable and integrated intensities have been quoted only when they could be confidently assigned. The outcome of these polymerizations with respect to vinylene stereochemistries is summarized in *Table 9*, from which it is clear that dependence of double bond geometry for the polymer on the monomer structure increases in the order **II** < **I** < **III** for both kinds of catalyst, and that the molybdenum based catalyst always gives the

Table 6 Chemical shifts and integrated intensities in the ^{13}C n.m.r. spectra of poly(4,5-bis-trifluoromethyltricyclo[6.2.1.$0^{2,7}$]undeca-2,4,6,9-tetraene)s (I, W) and (I, Mo)



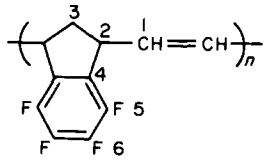
Chemical shift			Integral		σ_c	
I, W	I, Mo	Assignment	I, W	I, Mo	I, W	I, Mo
41.75	41.76	3*tt*	3.540	2.760		
42.06	42.06	3*tc* ≡ *ct*	9.113	2.405		
42.54	42.54	3*cc*	10.192	1.591	0.65	0.41
43.02	43.00	2*cc*	22.732	3.050		
43.20	not recorded	2*ct*	19.371	–		
47.60	47.59	2*tc*	13.038	5.155	0.59	0.26
47.76	47.74	2*tt*	16.061	3.606		
123.65 q J_{CF} = 280 Hz	123.66 q J_{CF} = 280 Hz	7				
123.94		5*c*	25.474			
124.09	124.10	5*t*	29.242		0.47	
126.74 $^2J_{CF}$ = 33 Hz	126.64 $^2J_{CF}$ = 33 Hz	6				
ca. 131		4*tc*				
131.67		4*tt*				
133.24 133.40 133.56	133.41	1*c*	6.069 14.651 7.978	2.346	0.51	0.25
134.03 134.20	134.19	1*t*	6.465 21.203	7.174		
135.56		4*ct*				
136.29	136.26	4*cc*				

lower σ_c. Thus, the most 'selective system' would appear to be the polymerization of monomer **III** with $MoCl_5/Me_4Sn$ and consequently, for the set examined in this study, we might expect polymer (**III**, Mo) to have the highest chance of proving stereoregular. This was fortunate since the detailed examination of polymers from monomers **I** and **II** was complicated by the fact that the resonances due to methylene and allylic carbons overlap and, even with the aid of DEPT, obtaining unambiguous assignments and integrations was difficult, whereas the methyl (C-1) and allylic (C-4) carbons in polymers of **III** show well resolved environmental shift effects and are well separated from other resonances. Thus, the data for (**III**, W) and (**III**, Mo), recorded in *Table* 8, indicate that four methyl signals (C-1) were detected for (**III**, W) whereas only one was detected for (**III**, Mo) although in the spectrum a very small C-1(*c*) could be distinguished from background noise; also the methine carbons (C-4) show a similar lack of multiplicity in (**III**, Mo) as compared to (**III**, W). Examination of the vinylene carbon (C-5) resonance of (**III**, Mo) under high resolution showed that in this high *trans* polymer ($\sigma_c \leqslant 0.05$) there appeared to be two predominant lines with some further fine structure. These signals must all have been due to *trans* vinylenes and the observed multiplicity is inconsistent with a totally stereoregular (i.e. all m or all r dyads) structure, unless the splitting is due to a remarkably large (~ 27 Hz) long range C–F coupling. Unfortunately the spectrum recorded for polymer (**III**, W) showed an unresolved broad band in the vinylene region and no useful comparisons could be made. The sample of polymer (**III**, Mo) used for obtaining ^{13}C n.m.r. spectroscopic data was produced in the presence of the chain transfer agent *trans*-oct-4-ene in order to increase its solubility and reduce its molecular weight and solution viscosity; however, the spectrum showed no evidence for butenyl chain ends so that this procedure seems unlikely to have had a significant effect on the polymer microstructure. We therefore conclude that polymer (**III**, Mo) is all-*trans* and atactic.

CONCLUSIONS

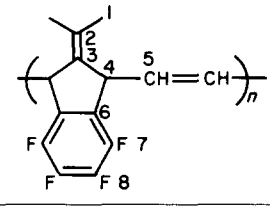
The first conclusion to be drawn is that all these monomers underwent ring opening polymerization. Gel permeation chromatography results demonstrated that the products are genuine high polymers and spectroscopic analysis, especially n.m.r. spectroscopy, established that the product polymers had the expected structures. It has also been demonstrated that for these polymerizations the molecular weight of the polymer can be regulated by carrying out the polymerization in the presence of oct-4-ene.

Table 7 Chemical shifts and integrated intensities in the ^{13}C n.m.r. spectra of poly(3,4,5,6-tetrafluoro[6.2.1.$0^{2,7}$]undeca-2,4,6,9-tetraene)s (**II**, W) and (**II**, Mo)



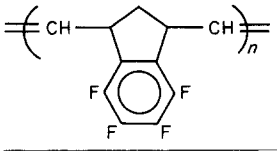
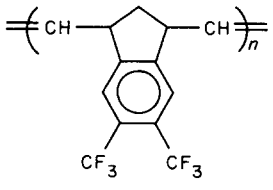
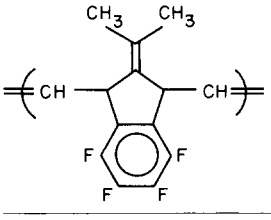
Chemical shifts			Integral		σ_c	
II, W	**II**, Mo	Assignment	**II**, W	**II**, Mo	**II**, W	**II**, Mo
40.04 40.18	40.21	3*tt*				
40.31	40.32	3*tc* ≡ 3*ct*				
41.72 41.83	41.14	3*cc*				
40.75	40.75	2*cc*	21.964	13.94		
40.99	41.02	2*ct*	52.105	13.937	0.60	0.25
45.39 45.57	45.40	2*tc* 2*tt*	28.994 21.401	81.468		
127.71 127.87	127.53 127.62	4				
130.61 130.96 131.18	130.62 130.84 130.98 131.21	1*c*	10.847 27.51 18.23	7.137 7.876 6.98 15.687	0.57	0.36
131.55 131.76	131.56 131.74	1*t*	22.34 20.998	42.014 25.696		
139.86d J_{CF} = 250 Hz	139.86d J_{CF} = 250 Hz	6				
143.83d J_{CF} = 250 Hz	143.83d J_{CF} = 250 Hz	5				

Table 8 Chemical shifts and integrated intensities in the ^{13}C n.m.r. spectra of poly(3,4,5,6-tetrafluoro-9-isopropylidene[6.2.1.$0^{2,7}$]undeca-2,4,6,9-tetraene)s, (**III**, W) and (**III**, Mo)



Chemical shifts			Integral		σ_c	
III, W	**III**, Mo	Assignment	**III**, W	**III**, Mo	**III**, W	**III**, Mo
19.63 19.83	19.71	1*t*	50.138 15.673	51.45	0.37	
20.04 20.85	not recorded by computer	1*c*	5.389 32.786	–		
43.63	43.58	4*c*	50.302	3.519		
47.99 48.08	48.12	4*t*	52.033 50.286	78.59	0.33	0.04
126.24 126.35	126.14 126.39	6				
129.44 centre of broad band	129.24 129.54	5				
133.0 133.75 136.0	133.08 133.71 133.95	2 and 3				
138.51d J_{CF} = 250 Hz	139.51d J_{CF} = 250 Hz	8				
143.16d J_{CF} = 250 Hz	143.16d J_{CF} = 250 Hz	7				

Table 9 Proportion of *cis* vinylene units (σ_c) in the polymers of **I**, **II** and **III**

Polymer repeat unit	Average σ_c values	
	WCl_6/Me_4Sn	$MoCl_5/Me_4Sn$
	0.6	0.3
	0.5	0.2
	0.3	≤0.05

Although this work has not resulted in the preparation of completely stereoregular polymers the detailed analysis of ^{13}C n.m.r. spectroscopic data for pairs of polymers derived from the same monomer using either tungsten or molybdenum based catalysts shows clear differences in microstructure with a tendency towards the formation of polymers having a high *trans* vinylene content with molybdenum based catalyst and much less ordered products with tungsten based catalyst.

We believe that the evidence presented in this paper indicates that further study of monomers of the type described has a high probability of leading to stereoregular fluoropolymers.

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