# Addition of difluorocarbene to poly(1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene). Thermal stability and characterization of microstructures by $^1$H, $^{13}$C, $^{19}$F and $^{29}$Si n.m.r. spectroscopy

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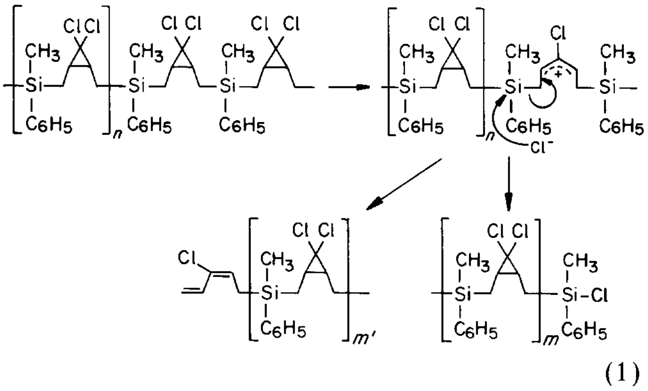
Excess difluorocarbene, generated by the sodium iodide catalysed decomposition of (trifluoromethyl)phenylmercury, adds in a stereospecific *cis* manner to the carbon–carbon double bonds of poly(1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene) (I) to yield poly(3,4-difluoromethylene-1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene) ($F_2C$-I). Similarly, a series of random copolymers has been prepared in which only some of the carbon–carbon double bonds of I have reacted with difluorocarbene. The microstructures of these difluorocyclopropanated polymers have been determined by $^1$H, $^{13}$C, $^{19}$F and $^{29}$Si n.m.r. spectroscopy. The glass transition temperatures of these copolymers are found to depend on the extent of difluorocyclopropanation. The thermal stability of $F_2C$-I has been determined by thermogravimetric analysis. The thermal stability of I, $F_2C$-I, poly(3,4-dichloromethylene-1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene) ($Cl_2C$-I) and (1-methyl-3,4-methylene-1-phenyl-1-sila-*cis*-pent-3-ene) ($H_2C$-I) are compared.

**(Keywords: difluorocarbene; copolymers; microstructure)**

## INTRODUCTION

There is considerable interest in the chemical modification of polymers[1–4]. Such reactions permit the preparation of polymers which cannot be prepared by monomer polymerization. In addition, partial chemical modification permits the synthesis of novel copolymers. Carbene addition to unsaturated polymers is one method for facile derivatization. For example, dichloro- and difluorocarbene add stereospecifically to the carbon–carbon double bonds of *cis*- and *trans*-1,4-polybutadiene[5–9].

We have previously added dichlorocarbene to the carbon–carbon double bonds of I and found the polymer $Cl_2C$-I to undergo facile chain scission at low temperature (95°C)[10]. This degradation process probably occurs by a two-step mechanism. The first involves ionization of one of the carbon–chlorine bonds with concerted disrotatory opening of the cyclopropane ring to yield an allylic cation. This symmetry-allowed process is accelerated due to stabilization of the allylic cation by the two adjacent methylphenylsilyl groups. It is well known that silicon has a profound stabilizing effect on $\beta$-carbocation centres[11]. Subsequent nucleophilic attack by the chloride anion on an adjacent methylphenylsilyl centre results in scission of the polymer chain (equation (1)). $F_2C$-I is expected to be more stable than $Cl_2C$-I if the first step in this process is rate determining since ionization of a carbon–fluorine bond will occur less readily than that of a carbon–chlorine bond[12]. On the other hand, if nucleophilic attack on one of the methylphenylsilyl centres that is $\beta$ to the allylic carbocation is rate limiting, then we might anticipate that the difluorocarbene adduct polymer would decompose *more* rapidly since a silicon–fluorine bond is much stronger than a silicon–chlorine bond[13].



(1)

A series of copolymers composed of 1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene(II) and 3,4-difluoromethylene-1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene(III) units has been prepared by controlling the extent of the difluorocyclopropanation of the carbon–carbon double bonds of I, in the hope that these will have predictable physical properties between those of I and $F_2C$-I.

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## EXPERIMENTAL

### *Characterization*

$^1$H, $^{13}$C and $^{19}$F n.m.r. spectra were obtained on a Bruker AM-360 spectrometer, while $^{29}$Si n.m.r. spectra were run on an IBM Bruker WP-270-SY spectrometer. Five per cent (w/v) solutions of polymer in chloroform-*d* were utilized for $^1$H, $^{13}$C and $^{19}$F n.m.r. spectra, while 20% (w/v) solutions were used to obtain $^{29}$Si n.m.r. spectra. $^{13}$C n.m.r. spectra were run with broad-band proton decoupling. Chloroform was used as an internal standard for $^1$H and $^{13}$C n.m.r. spectra. A DEPT[14] pulse sequence or a NONOE[15] with a pulse delay of 20 s was used to obtain $^{29}$Si n.m.r. spectra. These were externally referenced to TMS. $^{19}$F n.m.r. spectra were run with broad-band proton decoupling to eliminate $^1$H–$^{19}$F scalar coupling. $CCl_3F$ was used as an external standard for $^{19}$F n.m.r. spectra. *FT*i.r. spectra were obtained on an IBM FT IR/30S, DTGS/CSI spectrometer. These were taken of neat films on NaCl plates.

Gel permeation chromatographic (g.p.c.) analysis of the molecular weight distribution of the polymers was performed on a Waters system comprising a U6K injector, a 510 h.p.l.c. solvent delivery system, a R401 differential refractive index detector and a model 820 Maxima Control system. A Waters 7.8 mm × 30 cm, 10 $\mu$m particle size, mixed pore size, crosslinked polystyrene gel column was used for the separation. The elution solvent was h.p.l.c. grade THF at a flow rate of 0.6 ml min$^{-1}$. The retention times were calibrated against known monodisperse polystyrene standards: $M_p$ 212400; 110000; 20400; 4800 and 1350 whose $M_w/M_n$ were less than 1.09.

Thermogravimetric analysis (t.g.a.) of 97% substituted $F_2C$-I was carried out on a Perkin-Elmer TGS-2 instrument at a nitrogen flow rate of 40 cm$^3$ min$^{-1}$. The temperature programme for the analysis was 50°C for 10 min followed by an increase of 4°C min$^{-1}$ to 750°C. The glass transition temperatures of the polymers were measured on a Perkin-Elmer DSC-7 differential scanning calorimeter (d.s.c.). The melting points of samples of indium (156°C) and spectro grade n-hexane (−95°C) were used to calibrate the d.s.c. Temperature scans were begun at −100°C. Twenty min at −100°C was allowed for temperature equilibration. The temperature was then increased at a heating rate of 20°C min$^{-1}$ to 100°C.

### *Materials*

Tetrahydrofuran (THF) and hexane were distilled from sodium benzophenone ketyl immediately prior to use. All reactions were conducted under an atmosphere of purified nitrogen or argon.

(Trifluoromethyl)mercuric trifluoroacetate was prepared by pyrolysis of mercuric *bis*(trifluoroacetate), which was in turn obtained by the reaction of trifluoroacetic acid with mercury oxide[16,17].

(Trifluoromethyl)phenylmercury (IV) was prepared by an exchange reaction between diphenylmercury and (trifluoromethyl)mercuric trifluoroacetate. The crude product was recrystallized from hexane, m.p. 141–143°C (ref. 17).

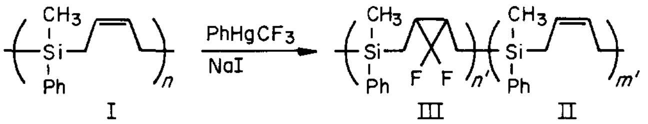
1-Methyl-1-phenyl-1-silacyclopent-3-ene was prepared by the reaction of methylphenyldichlorosilane, 1,3-butadiene and magnesium in THF. It had properties in complete agreement with literature values[18,19].

Poly(1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene) (I) was obtained by the anionic ring opening polymerization of 1-methyl-1-phenyl-1-silacyclopent-3-ene. It had properties in agreement with literature values[20,21], and was stored at 0°C under argon.

**Table 1** Effect of molar ratio of $PhHgCF_3$ to I on percentage difluorocyclopropanation of I, $M_w/M_n$ of I and %$F_2C$-I, and glass transition temperature ($T_g$)

| Ratio $PhHgCF_3$ | Percentage composition[a] | $M_w/M_n \times 10^{-3}$ I | $M_w/M_n \times 10^{-3}$ %$F_2C$-I | $T_g$ (°C) |
|---|---|---|---|---|
| 0.0 | 0 | 249/93 | | −15.0 |
| 0.5 | 16 | 249/93 | 194/100 | −1.7 |
| 1.0 | 34 | 44/22 | 10/7 | 0.3 |
| 3.0 | 55 | 44/22 | 10/6 | 9.9 |
| 7.0 | 80 | 44/22 | 30/15 | 22.0 |
| 12.0 | 97 | 44/22 | 11/7 | 24.9 |

[a] Percentage composition = $\frac{n'}{n' + m'}$



*Addition of difluorocarbene to I.* In a 50 ml round bottom flask equipped with a reflux condenser and a Teflon covered magnetic stirring bar was placed I (60 mg), IV (*Table 1*) and a three-fold molar excess of sodium iodide with respect to IV. To this mixture was added 15 ml benzene. The solution was degassed by bubbling a stream of argon through it to remove any dissolved oxygen, and heated at reflux with vigorous stirring for 40 h. The mixture was then cooled to room temperature and filtered. Benzene was removed by evaporation under reduced pressure. The polymer was dissolved in 3 ml THF. It was precipitated by addition of methanol to the THF solution. This procedure was repeated, and the polymer was then dried under vacuum for 24 h. Yields between 80 and 86% of copolymer were obtained. N.m.r. data are given below. I.r.$\nu$: 3071, 3050, 3011, 2961, 2929, 2892, 1461, 1428, 1411, 1297, 1259, 1113, 1084, 978, 849, 821, 734, 699 cm$^{-1}$.

## RESULTS AND DISCUSSION

While several difluorocarbene precursors are known, we have chosen to utilize the sodium iodide catalysed decomposition of (trifluoromethyl)phenylmercury developed by Seyferth[17,22], since this reagent functions at low temperature (80°C) under neutral conditions. These conditions were attractive since we have previously found[21] that poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) undergoes chain scission by hydroxide under phase transfer catalysis conditions utilized to generate dichlorocarbene. The reaction solutions were carefully degassed to eliminate the oxidation of iodide anion to iodine, since it is well known that monomeric allylic silanes undergo electrophilic scission of the allylic carbon–silicon bond on treatment with iodine[23]. Despite these precautions, polymer degradation was a problem (*Table 1*).

The stereospecific *cis*-addition of difluorocarbene to the carbon–carbon double bonds of I yields random copolymers comprised of II units and III units. $^{19}$F n.m.r.

provides conclusive evidence that the addition of difluorocarbene to the carbon–carbon double bonds of I proceeds in a stereospecific *cis* manner. Thus, the two fluorine atoms of the difluoromethylene units of $F_2C$-I are nonequivalent. Two doublets are observed in the $^{19}F$ n.m.r. at $-124.9$ and $-151.3$ ppm, $J_{FF} = 150$ Hz[24].

The percentage of III units in a particular copolymer will be expressed as %$F_2C$-I. This value can be easily determined by $^1H$ n.m.r. spectroscopy by comparison of the integral due to phenyl groups bonded to silicon at 7.46 (s, 2H) and 7.34 (s, 3H) ppm which are present in both II and III units compared to the integral of the resonance at 5.25 ppm due to the vinyl hydrogens of the II units. This can be confirmed by comparison of the integral of the signal at 1.64 ppm, which is assigned to the allylic hydrogens of II units, with the integral of the resonances at 7.46 and 7.34 ppm. As expected, the intensity of this signal at 1.64 ppm is consistently twice that of the signal at 5.25 ppm. The signal at 1.36 (br.s) ppm (assigned to the methine hydrogens of the difluorocyclopropane rings of III), and that at 0.74 ppm (which results from the methylene hydrogens adjacent to the difluorocyclopropane groups of III) are consistently found to be in a 1:2 intensity ratio. The percentage of difluorocyclopropane units in the polymer can also be confirmed by comparison of the intensities of the resonances at 1.36 and 0.74 ppm with those at 7.46 and 7.34 ppm (*Figure 1*).

The microstructure of the partially difluorocyclopropanated copolymers can be analysed by $^1H$, $^{13}C$, $^{19}F$ and $^{29}Si$ n.m.r. spectroscopy. For example, the methyl groups bonded to silicon give rise to three resonances at 0.22, 0.29 and 0.36 ppm. These can be assigned on the basis of a dyad analysis based on the observed changes in their intensities with the extent of difluorocyclopropanation. The signal at 0.22 ppm is due to methylphenylsilylene groups whose nearest neighbours are *cis*-1,4-but-2-ene (V) groups. The signal at 0.29 ppm is due to methylphenylsilylene units which have V on one side and a *cis*-2,3-difluoromethylene-1,4-but-2-ene (VI) unit on the other. Finally the resonance at 0.36 ppm is due to methylphenylsilylene units which have VI group on both sides. Apparently, $^1H$ n.m.r. is neither sensitive to whether the difluorocyclopropanes of adjacent VI units are on the same or opposite sides of the polymer chain, nor to the stereochemistry at the chiral silyl centre.

Three groups of resonances are likewise observed in the $^{29}Si$ n.m.r.. Their intensities vary with the extent of difluorocyclopropanation and can be analysed by application of a similar dyad analysis (*Figure 2*). The signal at $-4.31$ ppm is due to methylphenylsilylene units which are bonded to V groups on both sides. Two signals of equal intensity at $-2.71$ and $-2.93$ ppm are assigned to methylphenylsilylene units which have a V group on one side and a VI group on the other. Finally two signals in a 1:3 intensity ratio at $-0.94$ and $-1.18$ ppm result from methylphenylsilylene units which have VI groups on either side. Dyad analysis predicts four microenvironments (*Figure 3*). Apparently, three of these signals fortuitously overlap.

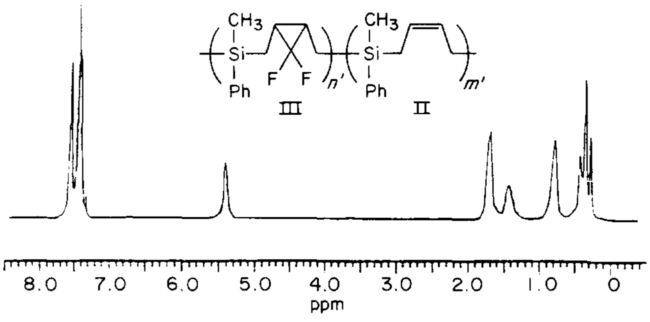


Figure 1 $^1H$ n.m.r. spectrum of 55% difluorocyclopropanated $F_2C$-I

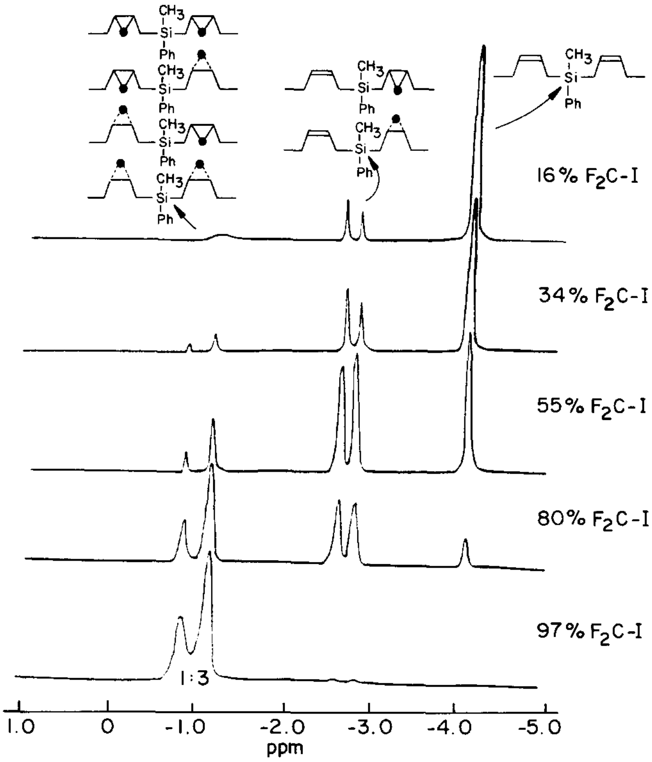
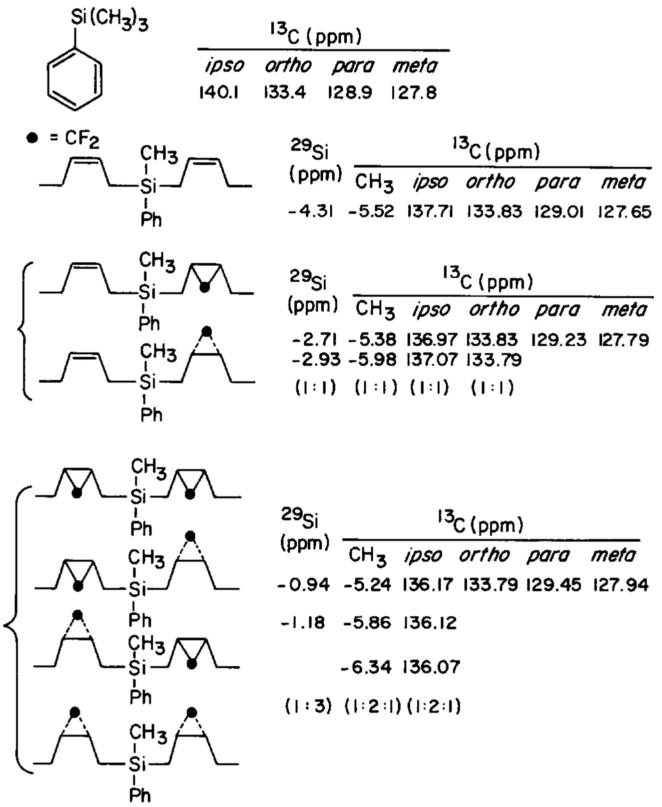


Figure 2 The intensities of $^{29}Si$ n.m.r. resonances vary with the extent of difluorocyclopropanation

The $^{13}C$ n.m.r. signals which result from the methyl carbons of methylphenylsilylene units vary in intensity with the extent of difluorocyclopropanation and can be assigned on the basis of a dyad analysis. The resonance at $-5.52$ ppm results from methylphenylsilylene units which have V groups on either side. Two signals of equal intensity at $-5.38$ and $-5.98$ ppm are assigned to methylphenylsilylene units which have a V unit on one side and a VI unit on the other. Finally three signals at $-5.24$, $-5.86$ and $-6.34$ ppm in a 1:2:1 intensity ratio result from methylphenylsilylene units which have VI units on either side. The dyad analysis predicts four signals in this situation. Apparently, two of the resonances are fortuitously coincident. The *ipso* carbons of phenyl groups bonded to silicon likewise give rise to six signals which vary in intensity with the extent of difluorocyclopropanation as described above (*Figure 3*). On the other hand, the *ortho*, *meta* and *para* carbons give rise to three sets of three resonances. These have been assigned on the basis of their variation with the extent of difluorocyclopropanation. Apparently, they are not sensitive to differences in microenvironments.

The $^{13}C$ n.m.r. signals due to the V units vary with the extent of difluorocyclopropanation and can be assigned on the basis of a triad analysis. Four signals due to vinyl carbons and four signals due to allylic carbons are observed. The resonances at 123.24 and 15.23 ppm arise from V units which have V units on



| $^{13}C$ (ppm) ipso | ortho | para | meta |
|---|---|---|---|
| 140.1 | 133.4 | 128.9 | 127.8 |

| $^{29}Si$ (ppm) | $^{13}C$ (ppm) $CH_3$ | ipso | ortho | para | meta |
|---|---|---|---|---|---|
| -4.31 | -5.52 | 137.71 | 133.83 | 129.01 | 127.65 |

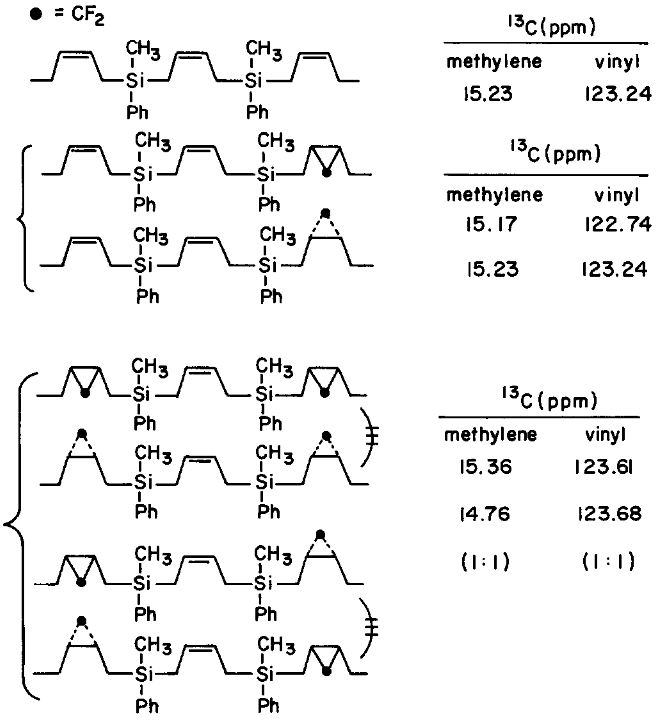
| $^{29}Si$ (ppm) | $^{13}C$ (ppm) $CH_3$ | ipso | ortho | para | meta |
|---|---|---|---|---|---|
| -2.71 | -5.38 | 136.97 | 133.83 | 129.23 | 127.79 |
| -2.93 | -5.98 | 137.07 | 133.79 | | |
| (1:1) | (1:1) | (1:1) | (1:1) | | |

| $^{29}Si$ (ppm) | $^{13}C$ (ppm) $CH_3$ | ipso | ortho | para | meta |
|---|---|---|---|---|---|
| -0.94 | -5.24 | 136.17 | 133.79 | 129.45 | 127.94 |
| -1.18 | -5.86 | 136.12 | | | |
| | -6.34 | 136.07 | | | |
| (1:3) | (1:2:1) | (1:2:1) | | | |

**Figure 3** Dyad microstructures of %$F_2$C-I and model compound, trimethylsilylbenzene

either side. Apparently, these carbon atoms are not sensitive to the stereochemical relationship (*meso* or *d, l*) of the two methylphenylsilylene units. The four resonances: 15.17, 15.23, 122.74 and 123.24 ppm can be assigned to the carbons of V which have a V unit on one side and a VI unit on the other. The signals at 15.23 and 123.24 ppm result from the allyl and vinyl carbons of V units which are adjacent to a V unit. On the other hand, the signals at 15.17 and 122.74 ppm result from the allyl and vinyl carbons of V units which are close to VI units. Finally, the four resonances at 15.36 and 14.76 ppm (1:1); and 123.61 and 123.68 ppm (1:1) result from V units which have VI units on either side (*Figure 4*).

Likewise, most of the $^{13}C$ n.m.r. signals due to VI units vary with the extent of difluorocyclopropanation and can be assigned on the basis of a triad analysis. The difluoromethylene carbon is *not* sensitive to the extent of difluorocyclopropanation. A signal at 115.27 ppm is split to a triplet by the two geminal fluorine atoms which fortuitously have identical coupling constants at 288 Hz. Three signals are observed for the methine carbons: 21.34, 21.44 and 21.45 ppm. The signal at 21.44 ppm results from VI units which have V units on either side. It is split into a triplet with a coupling constant of 9.8 Hz by the two geminal fluorine atoms. The broad signal at 21.45 ppm is assigned to V units which have a V unit on one side and a VI unit on the other. Finally, the broad resonance at 21.34 ppm results from VI units which have VI units on either side. The methylene carbons of VI units are significantly more sensitive to differences in microenvironment. A total of eight distinct resonances are observed. Two signals of equal intensity at 5.56 and 5.41 ppm are assigned to methylene units of VI which have V units on either side. Apparently, the methylene groups are sensitive to the stereochemical relationship (*meso* or *d, l*) of the adjacent methylphenylsilylene units. Similarly, two equally intense resonances at 5.53 and 5.40 ppm are ascribed to the methylenes of VI units which have a V unit on one side and a VI unit on the other. Finally, four signals of equal intensity are observed at 5.78, 5.46, 5.08 and 4.96 ppm. These are attributed to methylenes of VI units which have VI units on either side. Apparently, the methylenes are sensitive not only to the stereochemical relationship (*meso* or *d, l*) of the adjacent methylphenylsilylene units but also to the

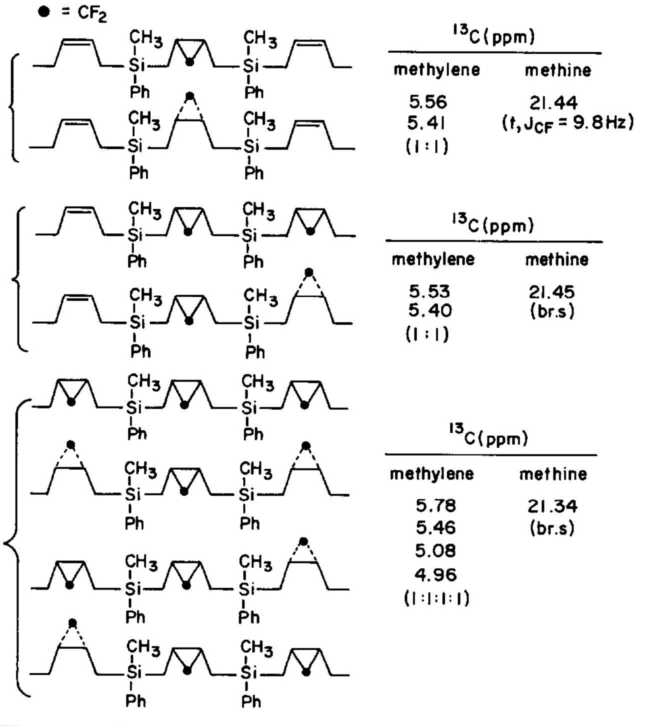


| $^{13}C$(ppm) methylene | vinyl |
|---|---|
| 15.23 | 123.24 |

| $^{13}C$(ppm) methylene | vinyl |
|---|---|
| 15.17 | 122.74 |
| 15.23 | 123.24 |

| $^{13}C$(ppm) methylene | vinyl |
|---|---|
| 15.36 | 123.61 |
| 14.76 | 123.68 |
| (1:1) | (1:1) |

**Figure 4** Triad microstructures of V units of %$F_2$C-I



| $^{13}C$(ppm) methylene | methine |
|---|---|
| 5.56 | 21.44 |
| 5.41 | (t, $J_{CF}$ = 9.8Hz) |
| (1:1) | |

| $^{13}C$(ppm) methylene | methine |
|---|---|
| 5.53 | 21.45 |
| 5.40 | (br.s) |
| (1:1) | |

| $^{13}C$(ppm) methylene | methine |
|---|---|
| 5.78 | 21.34 |
| 5.46 | (br.s) |
| 5.08 | |
| 4.96 | |
| (1:1:1:1) | |

**Figure 5** Triad microstructures of VI units of $F_2$C-I

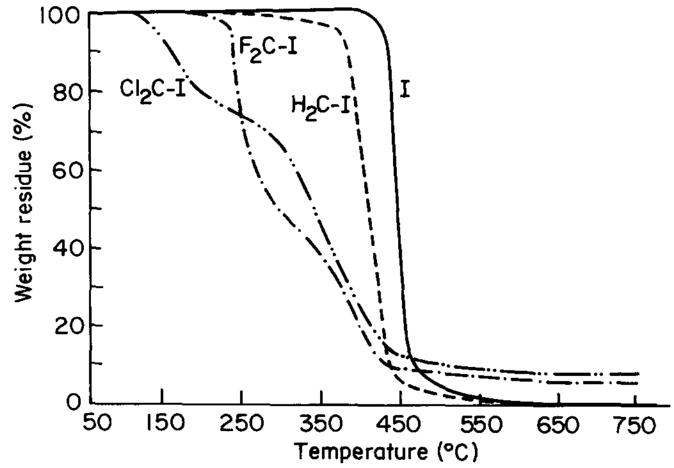


**Figure 6** Thermogravimetry of I, $H_2C$-I, 97%$F_2C$-I and $Cl_2C$-I

stereochemical (*cis* or *trans*) relationship of adjacent difluorocyclopropanes to the polymer chain (*Figure 5*). The agreement between the observed $^{13}C$ n.m.r. and that predicted from the triad model is quite remarkable.

Unlike the dichlorocarbene adducts of I which decompose readily[10], the difluorocarbene adducts of I are quite stable. For example, a chloroform solution of the 97% difluorocyclopropanated I (97% $F_2C$-I) has an unchanged $^1H$ n.m.r. spectrum after 1 month at room temperature. On this basis, we conclude that ionization of the carbon–fluorine bond (step one in the mechanism discussed above) is rate determining.

The thermal stability of 97% $F_2C$-I was determined by thermogravimetric analysis (t.g.a.). It is less stable than I or $H_2C$-I, but significantly more stable than $Cl_2C$-I (*Figure 6*). Specifically, 97% $F_2C$-I is stable to 190°C. Thermal decomposition of $F_2C$-I occurs in two stages. Rapid loss of 50% of the initial sample weight occurs between 210 and 265°C. Slower loss of 45% of the initial weight occurs between 270 and 450°C. A residue amounting to approximately 5% is observed.

The glass transition temperatures ($T_g$) of these difluorocarbene adduct copolymers have been determined by d.s.c. Partially difluorocyclopropanated polymers have $T_g$s intermediate between those of I and 97% $F_2C$-I (*Table 1*). The $T_g$s are found to increase linearly with the extent of difluorocyclopropanation. Such linear relationships between properties and percentage composition of essentially random copolymers have frequently been observed[25,26].

## ACKNOWLEDGEMENT

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