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tion becomes most stable.[16] Then, a question arises regarding how sharp is the transition from a highly extended form to a coil. The D NMR method is sensitive only to short-range correlations. To answer the question, a combined use of some other technique such as the small-angle neutron diffraction[17] is needed.

Acknowledgment. This work was supported in part by a grant-in-aid for Scientific Research on Priority Areas, New Functionality Materials-Design, Preparation and Control, The Ministry of Education, Scientific and Culture (63604531).

Registry No. I-*n* (*n* = 9), 119908-59-7; I-*n* (*n* = 10), 119908-60-0; II-*n* (*n* = 9, SRU), 119908-61-1; II-*n* (*n* = 10, SRU), 119908-62-2; II-*n* (*n* = 9, copolymer), 119080-27-2; II-*n* (*n* = 10, copolymer), 119080-29-4.

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Addition of Difluorocarbene to Poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) and Poly(1,1-dimethyl-1-sila-*cis*-(and -*trans*)-pent-3-ene). Characterization of Microstructures by ^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR Spectroscopies

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ABSTRACT: Difluorocarbene, generated by the sodium iodide catalyzed decomposition of (trifluoromethyl)phenylmercury, adds stereospecifically to the carbon–carbon double bonds of poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) (I) as well as to those of poly(1,1-dimethyl-1-sila-*cis*-(and -*trans*)-pent-3-ene) (II) to yield product polymers of increased molecular weight. The microstructures of these difluorocarbene adduct polymers were characterized by ^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR spectroscopy. Their thermal stabilities were determined by thermogravimetric analysis. They were considerably less stable than the starting polymers I or II. Their molecular weight distributions were determined by gel permeation chromatography.

There is considerable interest in the chemical modification of polymers.[1-4] Dichloro-[5-8] and difluorocarbene[9] have been added stereospecifically to the carbon–carbon double bonds of *cis*- and *trans*-1,4-polybutadiene.

We were interested in the stability of the polymers formed by the addition of difluorocarbene to the carbon–carbon double bonds of poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) (I)[10] and to those of poly(1,1-dimethyl-1-sila-*cis*-(and *trans*)-pent-3-ene) (II),[11] since we have previously found that polymers formed by addition of dichlorocarbene to I and II undergo facile chain scission at low temperature (25 °C).[11] 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 a silyl-stabilized allylic cation. It is well-known that silicon has a profound stabilizing effect on β-carbocation centers.[12] This is followed by nucleophilic attack by the chloride anion on an adjacent dimethylsilyl center which results in scission of the polymer chain (see eq 1).

The difluorocarbene adduct polymers of I and II would be expected to be more stable than the corresponding dichlorocarbene adduct polymers, if the first step in this process were rate determining since ionization of a carbon–fluorine bond will occur less readily than that of a carbon–chlorine bond.[13] On the other hand, if nucleophilic attack on the dimethylsilyl center that is β to the allylic carbocation is rate limiting, then we might anticipate that the difluorocarbene adduct polymers would decompose more rapidly since a silicon–fluorine bond is much stronger than a silicon–chlorine bond.[14]

In addition, the difluorocarbene adducts of I and II are most interesting polymers in that their microstructures can be analyzed by ^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR spectroscopies.

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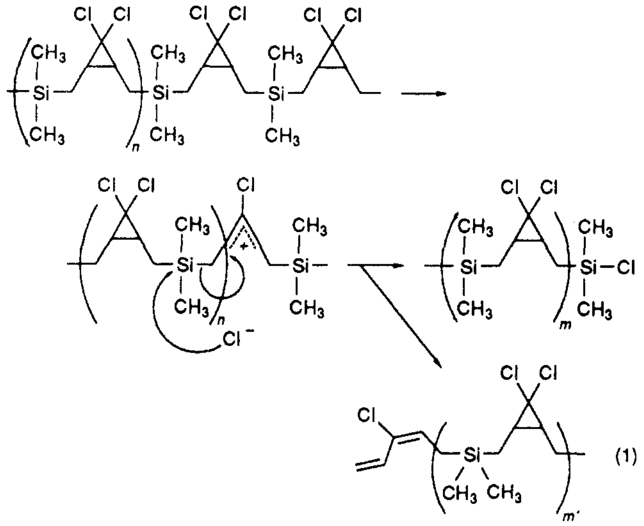
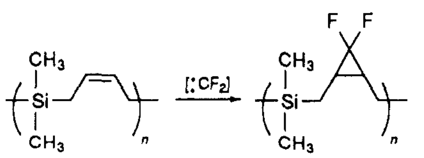


(1)

Finally, partially modified polymers may have properties that are intermediate between those of the starting polymer and the totally modified polymer. In this manner, we may be able to design polymers with specific desirable properties by controlling the extent of chemical modification.[15]

While there are several difluorocarbene precursors known,[16] we chose to utilize the sodium iodide catalyzed decomposition of (trifluoromethyl)phenylmercury developed by Seyferth,[17,18] since this reagent functions at a low temperature (80 °C) and under neutral conditions. These conditions were particularly attractive since we have previously found that addition of dichlorocarbene generated under basic phase-transfer catalysis (PTC) conditions to I or II results in dichlorocarbene adduct polymers of decreased molecular weight. Control experiments have shown that this chain scission process occurs on treatment of I with hydroxide under PTC conditions in the absence of chloroform (dichlorocarbene).[11] By comparison, when we have added difluorocarbene to either I or II, the molecular weight of the products polymers as determined by GPC increases with the extent of difluorocyclopropanation. While GPC data on two different polymers cannot be directly compared, nevertheless, these results suggest that polymer degradation is not a significant problem under the neutral difluorocyclopropanation reaction conditions. The extent of difluorocyclopropanation can be controlled by the molar ratio of (trifluoromethyl)phenylmercury to monomer units of I or II (see eq 2 and Table I). NMR analysis indicates that the addition of difluorocarbene to the carbon–carbon double bonds of I and II occurs in a completely stereospecific cis manner and that the addition is regiospecifically random. Thus the addition of difluorocarbene to the carbon–carbon double bonds of the polymer is not affected by neighboring groups. The extent of difluorocyclopropanation was determined by ^{1}H NMR integration.

$$\mathrm{PhHgCF_3} \xrightarrow{\mathrm{NaI}} \mathrm{PhHgI} + \mathrm{NaI} + [\mathrm{:CF_2}]$$



(2)

Unlike the dichlorocarbene adducts of I or II, which decompose readily, the difluorocarbene adducts of I are quite stable. For example, a chloroform solution of the 98% difluorocyclopropanated I (98% CF$_2$–I) has an unchanged ^{1}H NMR 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 (see eq 1), is rate determining.

The thermal stability of the difluorocyclopropane adducts of I has also been determined by thermogravimetric

Table I
Effect of Molar Ratio of PhHgCF$_3$ to I or II on Percent Difluorocyclopropanation of I or II and M_w/M_n of Starting and Product Polymers

molar ratio PhHgCF$_3$/I	% difluorocyclopropanation	$10^{-3}M_w/M_n$ I	$10^{-3}M_w/M_n$ CF$_2$–I
0.3	5	193.0/82.5	259.0/82.5
1.0	58	193.0/82.5	273.0/96.8
3.0	75	116.0/19.4	167.0/24.7
7.0	98	193.0/82.5	227.9/104.0

molar ratio PhHgCF$_3$/II	% difluorocyclopropanation	$10^{-3}M_w/M_n$ II	$10^{-3}M_w/M_n$ CF$_2$–II
8.0	100	102.5/53.5	196.8/71.4

Table II
Effect of the Extent of Difluorocyclopropanation over I on Glass Transition Temperatures

% difluorocyclopropanation of I	T_g, °C	% difluorocyclopropanation of I	T_g, °C
0	-63	75	-39
5	-61	98	-25
58	-40		

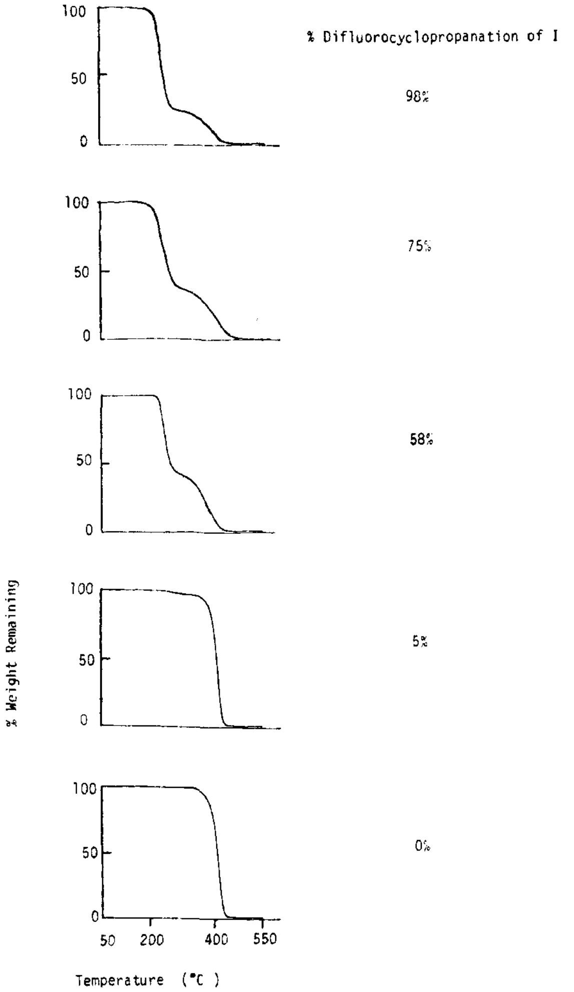


Figure 1. Effect of the extent of difluorocyclopropanation of I on thermostability by TGA.

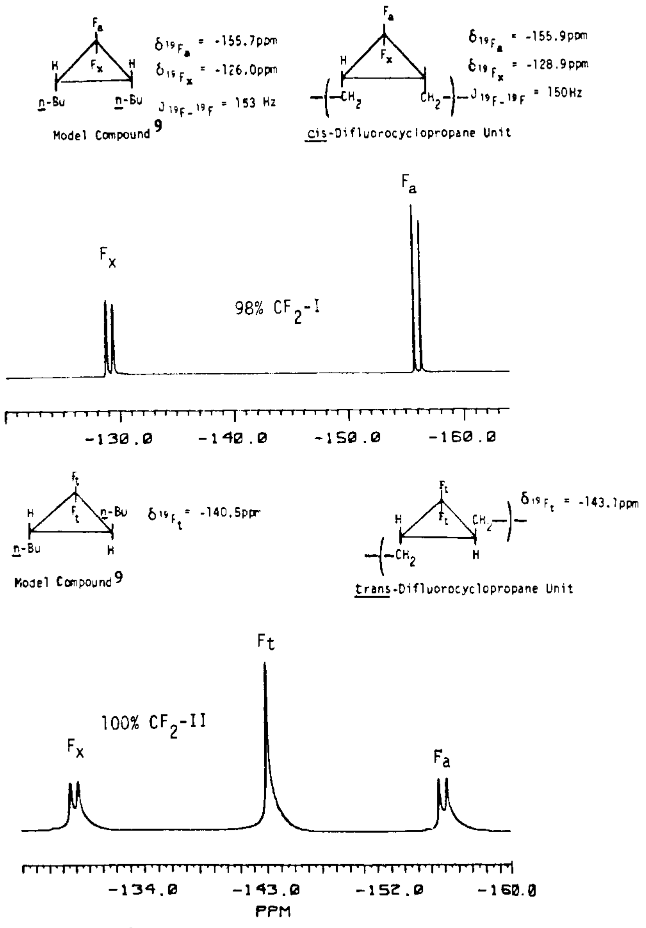


Figure 2. ^{19}F NMR spectra of 98% CF_2–I and 100% CF_2–II, comparison with model compounds.

analysis (TGA). By TGA, the 100% dichlorocyclopropanated I begins to decompose at 110 °C while 98% CF_2–I does not start to decompose until 180 °C. Nevertheless, both are less thermally stable than I. The decomposition of difluorocyclopropane adducts of I occurs in two phases and leaves no residue. The extent of the decomposition in each phase is dependent on the percent difluorocyclopropanation of I. Thus 5% CF_2–I loses about 5% of its original weight in the first decomposition phase, while 98% CF_2–I loses 74% of its original weight in this temperature region (see Figure 1).

The glass transition temperatures of these polymers were determined by differential scanning calorimetry. These were also found to depend on the extent of difluorocyclopropanation (see Table II).

^{13}C, ^{19}F, and ^{29}Si NMR spectroscopies have proved particularly useful for the analysis of CF_2–I adduct polymer microstructures. ^{19}F NMR spectroscopy provides conclusive evidence that the addition of difluorocarbene to the carbon–carbon double bonds of I and II proceeds in a stereospecific cis manner. Thus the two fluorines of the *cis*-difluorocyclopropane units of CF_2–I are nonequivalent. This results in the observation of a doublet of doublets in the ^{19}F NMR spectrum at −128.9 and −155.9 ppm, $J_{^{19}F-^{19}F}$ = 150 Hz. On the other hand, in the ^{19}F NMR spectrum of CF_2–II a signal at −143.14 ppm is observed in addition to the ^{19}F signals assigned to cis units. This is assigned to the fluorines of the *trans*-difluorocyclopropane units, which are equivalent. These fluorine chemical shifts and coupling constants are consistent with those of model compounds[9] (see Figure 2). Neither the ^{19}F NMR spectrum of CF_2–I nor that of 100% CF_2–II is affected by the extent of difluorocyclopropanation. Apparently the ^{19}F NMR spectrum is sensitive only to the stereochemistry of the monomer unit. This is surprising since the ^{19}F NMR spectrum of partially difluorocyclopropanated adducts of *cis*-1,4-polybutadiene are sensitive to neighboring units.[9]

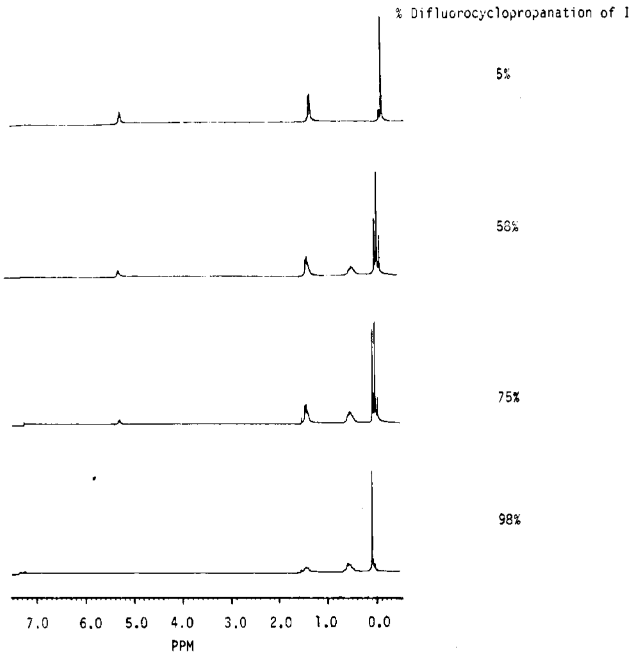


Figure 3. ^{1}H NMR spectra of difluorocyclopropanated I.

We will first discuss the ^{1}H, ^{13}C, and ^{29}Si NMR spectra of product polymers formed by difluorocyclopropanation of I since these are less complicated than the corresponding spectra of II.

^{1}H NMR spectroscopy provides a direct method for determining the extent of difluorocyclopropanation of I and II. Thus, although the resonances due to the cyclopropyl methine protons and the allylic protons of unreacted units in the polymer overlap to give a multiplet centered at 1.43 ppm, the signals from the vinyl protons at 5.29 ppm of the unreacted units of the polymer and the methylene protons at 0.49 ppm adjacent to the difluorocyclopropane rings are well resolved and can be integrated accurately (see Figure 3).

Three ^{1}H NMR signals are observed for the methyl groups bonded to silicon of CF_2–I. The fact that their intensities change with the extent of difluorocyclopropanation of I permits assignment. The first resonance results from dimethylsilyl groups located between two cis carbon–carbon double bonds (−0.02 ppm). The second signal (0.03 ppm) is produced by dimethylsilyl groups that have a cis carbon–carbon double bond on one side and a difluorocyclopropane group on the other. The final signal (0.08 ppm) results from dimethylsilyl groups that have difluorocyclopropane groups on both sides. Apparently, ^{1}H NMR spectroscopy is not sensitive to whether adjacent difluorocyclopropane rings are on the same or opposite sides of the polymer chain. Integration of these three signals provides confirmation of the extent of difluorocyclopropanation of I, although their small chemical shifts differences make this less accurate than the method above.

Stereospecific cis addition of difluorocarbene to the carbon–carbon double bonds of I produces polymers whose microstructures can be analyzed by ^{13}C NMR spectroscopy. ^{13}C NMR spectroscopy has been used to explore the microstructures of product polymers formed by addition of difluorocarbene[9] and dichlorocarbene[6,7] to *cis*- and *trans*-1,4-polybutadiene. Since ^{13}C NMR spectra were run without broad-band fluorine decoupling, ^{13}C–^{19}F coupling is observed for some ^{13}C resonances. The fluorine-substituted carbons of 98% CF_2–I appears as a doublet of doublets at 115.54 ppm, $J_{^{13}C-^{19}F}$ = 295.2 and 286.0 Hz. This results from the nonequivalence of the adjacent geminal fluorines. The ^{13}C NMR resonance due to the fluorine-substituted carbon is not appreciably sensitive to the extent of difluorocyclopropanation of I.

At low levels of difluorocyclopropanation (5% CF_2–I), a triad exists in which both nearest neighbors to the central difluorocyclopropane unit are *cis*-carbon–carbon double bonds units. The methine carbons of the difluorocyclopropane rings in this situation are split to a triplet by the two adjacent geminal fluorines whose two bond $J_{^{13}C-^{19}F}$ coupling constants are fortuitously identical (δ = 21.74 ppm, $J_{^{13}C-^{19}F}$ = 11.0 Hz). At high levels of difluorocyclopropanation (98% CF_2–I), triad analysis predicts three distinct microenvironments: one in which three adjacent difluorocyclopropanes are on the same side of the polymer chain (s,s,s), one in which two adjacent cyclopropanes are on the same side while the next is on the opposite side (s,s,o), and finally one in which one cyclopropane is on one side, the next on the opposite, and the third on the same side of the polymer chain as the first (s,o,s). Analysis of these situations leads to the prediction that the two symmetrical triads (s,s,s) and (s,o,s) will each give rise to distinct methine ^{13}C NMR resonances, while the unsymmetrical triad (s,s,o) will give rise to two unique methine carbon signals for a total of four distinct ^{13}C resonances. Each of these would be further split to a triplet by two adjacent geminal fluorine atoms. In fact, only two pairs of triplets are observed in the ^{13}C NMR spectrum for the methine carbons rather than the four sets of triplets predicted. This may be explained, if fortuitously the triplet resonances that result from one of methine of the unsymmetrical triad (s,s,o) is coincident with the triplet signal for the first symmetrical triad (s,s,s) while the other triplet signal of the unsymmetrical traid (s,s,o) is identical with that of the other symmetrical triad (s,o,s) (see Figure 4).

At intermediate levels of difluorocyclopropanation even more complicated patterns of ^{13}C resonances are observed for the methine carbons. These result from the occurrence of the triads described above, as well as those in which the central difluorocyclopropane units have as nearest neighbors an unsaturated unit on one side and a difluorocyclopropanated unit on the other. In these, the two methine carbons of the central difluorocyclopropane are nonequivalent and will result in two ^{13}C signals, each of which will be further split to triplets by the adjacent geminal fluorine atoms. In fact, at intermediate levels of difluorocyclopropanation the methine carbons result in 10 resolved resonances (see Figure 4).

At low levels of difluorocyclopropanation, the methylene carbons exist in a single environment. This results in a unique ^{13}C resonance at 6.36 ppm. At high levels of difluorocyclopropanation triad analysis predicts three microenvironments: (s,s,s), (s,o,s), and (s,s,o), which should result in four distinct ^{13}C methylene resonances. In fact, only two carbon resonances of equal intensity are observed at 6.29 and 6.13 ppm. This can be accounted for by fortuitous overlap of signals as discussed for the ^{13}C methine signals above. At intermediate levels of difluorocyclopropanation two broad signals are observed (see Figure 4).

At low levels (5%) of difluorocyclopropanation, two ^{13}C resonances are observed for the methyl carbons bonded to silicon (−3.42 and −3.55 ppm). The first results from the carbons of dimethylsilyl units in which both nearest neighbors are *cis*-carbon–carbon double bonds, while the second arises from such units in which one neighbor is a *cis*-carbon–carbon double bond and the other is a difluorocyclopropane. At intermediate degrees of difluorocyclopropanation three ^{13}C methyl resonances are observed. The first two result from the microstructures previously discussed, while the third result from a microenvironment in which a dimethylsilyl unit has a difluorocyclopropane as its neighbors on either side (−3.65 ppm). Finally, when the extent of difluorocyclopropanation is high (98%) only two ^{13}C signals are observed (−3.55 and −3.65 ppm). The relative intensities of these peaks is consistent with the extent and random nature of the difluorocyclopropanation process. Apparently, the methyl ^{13}C signals are not affected by the cis or trans stereochemical relationship of adjacent difluorocyclopropane rings to the polymer backbone.

As polymer I undergoes difluorocyclopropanation, the ^{13}C NMR signals due to the allylic and vinyl carbons of I decrease in intensity. At intermediate levels of difluorocyclopropanation, the vinylic and allylic ^{13}C resonances provide additional insight into the microstructures of these copolymers. The allylic carbon can be analyzed in terms of triads. At low conversion, two types of triads are predicted. The first is symmetrical in which all three adjacent units are unsaturated. This should lead to a ^{13}C resonance whose chemical shift (16.47 ppm) is essentially identical with that observed for I (16.47 ppm). In the second type of triad, the central unsaturated unit is bonded to an unsaturated unit on one side and to a difluorocyclopropane unit on the other. The allylic carbons of the central unsaturated unit of this latter triad are predicted to be nonequivalent and to lead to two distinct ^{13}C resonances. In fact, at low conversion two carbon resonances are observed at 16.47 and 16.32 ppm, rather than the three signals predicted. We believe the signal at 16.47 ppm results from the allylic carbons of triads that are completely unsaturated. Further, we propose that the allylic carbon adjacent to the difluorocyclopropane unit leads to the signal at 16.32 ppm, while the allylic carbon adjacent to an unsaturated unit may be coincident with the signal at 16.47 ppm. At higher levels of difluorocyclopropanation the signals centered at 16.32 ppm increases while multiple signals centered at 16.47 ppm of decreasing intensity are observed (see Figure 4).

The ^{13}C resonances of the vinyl carbons of partially difluorocyclopropanated I can be explained by application of a pentad analysis. Thus at low levels of difluorocyclopropanation three types of pentads are expected. The first is symmetrical, made up of five unsaturated units in a row. This results in a single carbon resonance at 123.22 ppm, which is coincident to that observed for the vinyl carbons in I. The second type of pentad has a single difluorocyclopropane unit adjacent to the central *cis*-carbon–carbon double bond unit. There are two types of vinyl carbons in such a pentad: one is adjacent to the difluorocyclopropane unit, while the other has an unsaturated unit as its nearest neighbor. These might be expected to be quite different from those of I (123.61 and 122.73 ppm). The third type has a difluorocyclopropane unit as the next nearest neighbor to the central *cis*-carbon–carbon double bond unit. It is anticipated that the ^{13}C chemical shift of these vinyl carbons will be closer to those observed for I (123.38 and 123.15 ppm). At higher levels of difluorocyclopropanation three more complex groups of vinyl resonances are observed. These are centered at 123.58, 123.14, and 122.73 ppm (see Figure 4). These can be accounted for by application of a pentad analysis. Their intensities decrease as the extent of difluorocyclopropanation increases as expected.

The ^{29}Si NMR spectrum of the difluorocyclopropane adducts of I is also sensitive to microstructure. Analysis

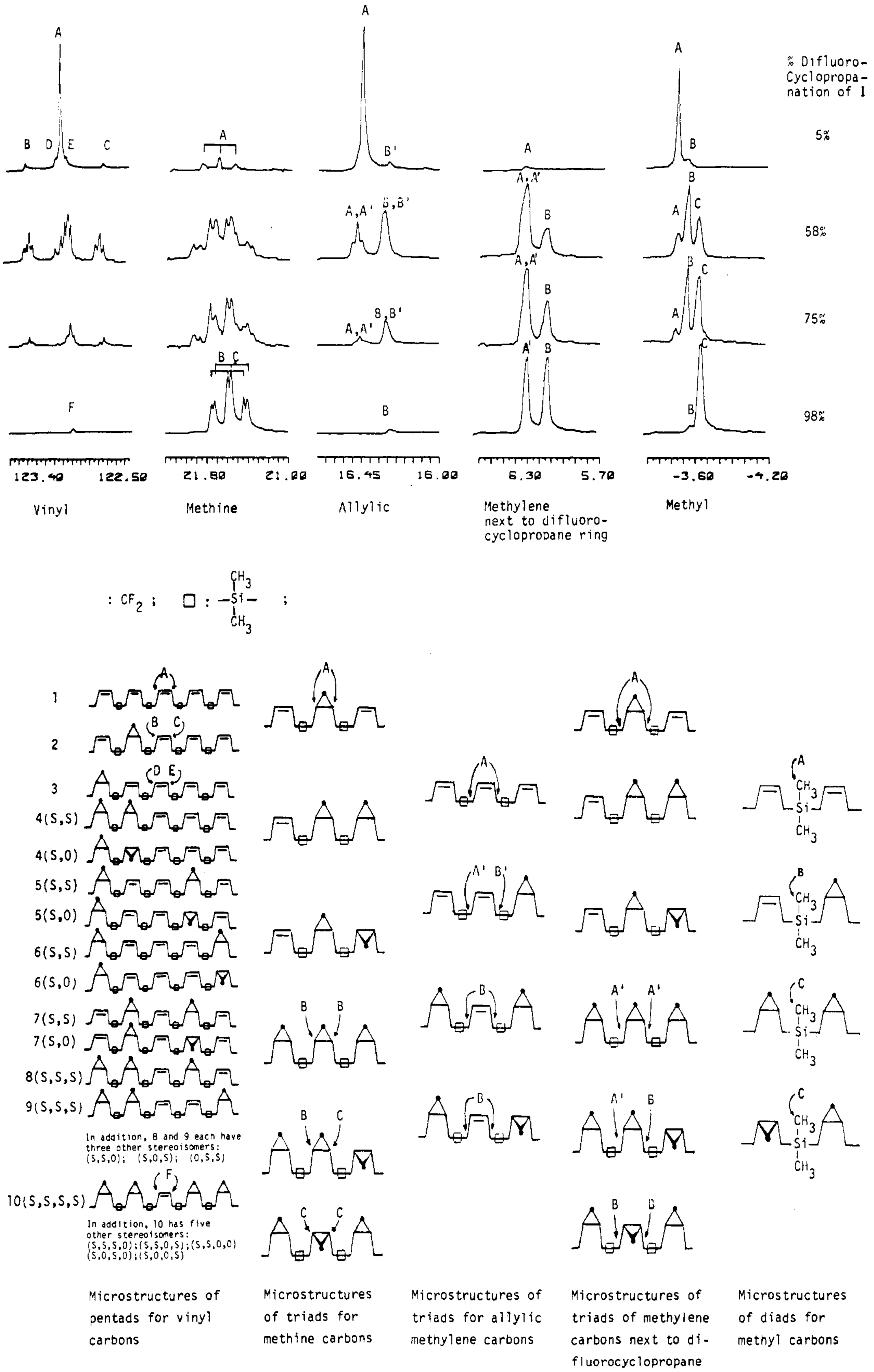
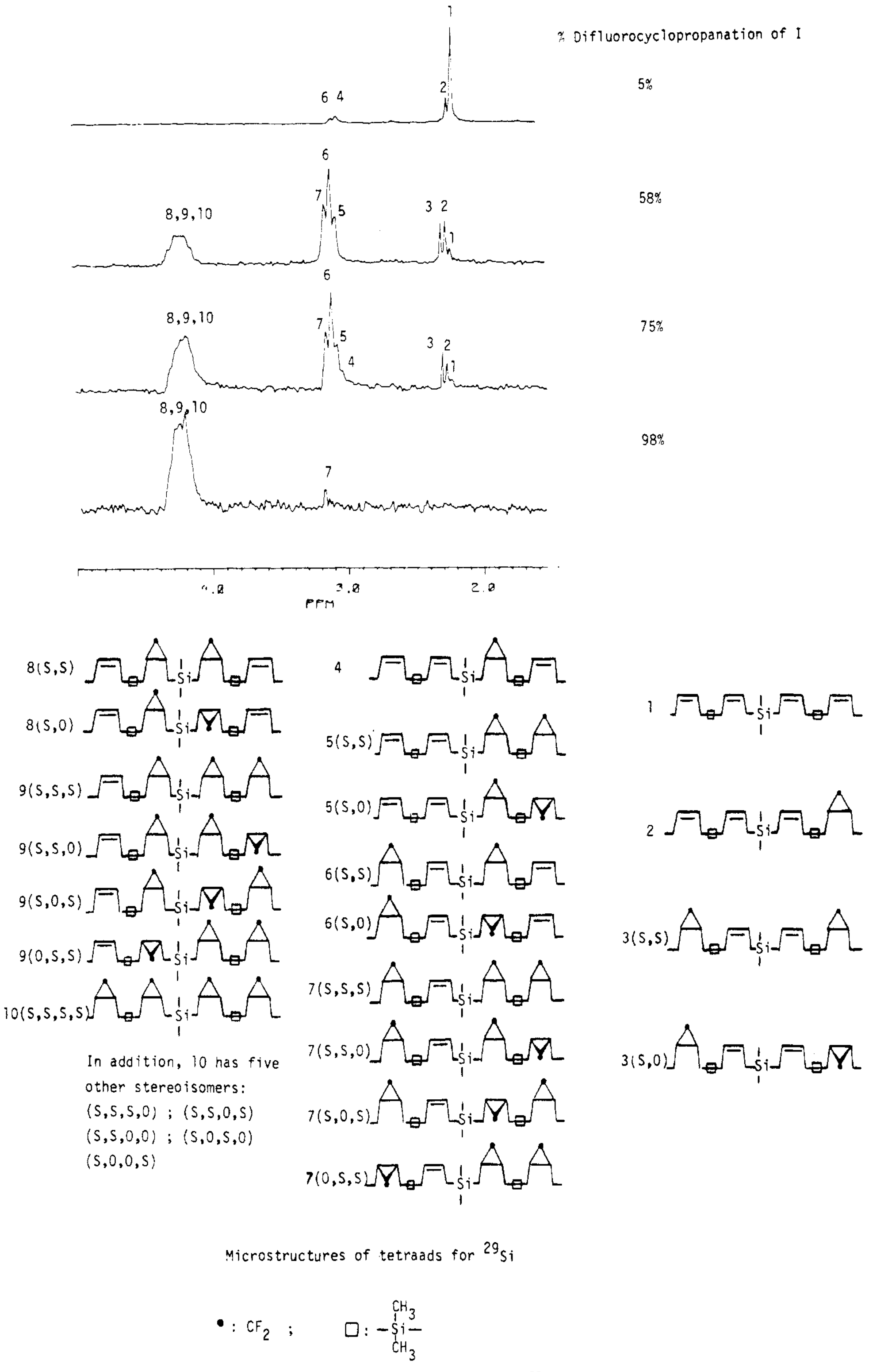


Figure 4. ^{13}C NMR spectra of difluorocyclopropanated I. Assignment of ^{13}C resonances to CF_2–I microstructures.

of neighbors as well as next nearest neighbors is necessary to account for the complexity of the ^{29}Si resonances observed. Three groups of ^{29}Si signals are observed. The first centered at 2.20 ppm is due to dimethylsilyl groups that have unsaturated groups as nearest neighbors on both sides. The second centered at 3.10 ppm results from dimethylsilyl groups adjacent to an unsaturated group on one side and a difluorocyclopropane group on the other. The third is centered at 4.12 ppm. This arises from dimethylsilyl groups that have difluorocyclopropane groups as nearest neighbors on either side. At low and intermediate levels of difluorocyclopropanation, three resonances are observed in the region centered at 2.20 ppm. On the other hand, at low and moderate levels of difluorocyclo-



In addition, 10 has five other stereoisomers: (S,S,S,O) ; (S,S,O,S) (S,S,O,O) ; (S,O,S,O) (S,O,O,S)

Microstructures of tetraads for ^{29}Si

Figure 5. ^{29}Si NMR spectra of difluorocyclopropanated I. Assignment of ^{29}Si resonances to CF$_2$–I microstructures.

propanation four resonances centered at 3.10 ppm are observed. These can be assigned to the microstructures below (see Figure 5). At high levels of difluorocyclopropanation a broad resonance is observed centered at 4.20 ppm. This peak probably results from the overlap of signals that result from the 12 microstructures below.

We have not carried out partial difluorocyclopropanation of II. Hence our discussion of this system will be limited to ^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR spectra of completely difluorocyclopropanated II (CF$_2$–II). The cis-to-trans ratio of II utilized was essentially 1:1. We have previously discussed the ^{19}F NMR spectrum of II; see above.

The ^{1}H NMR spectrum of CF$_2$–II is characterized by a multiplet at 1.45 ppm assigned to the methine protons of *cis*-difluorocyclopropane units and a multiple centered at 0.94 ppm assigned to methine protons of *trans*-difluorocyclopropane units. The methylene proton resonances adjacent to *cis*- and *trans*-difluorocyclopropane units overlap resulting in a multiplet centered at 0.50 ppm. Three signals at 0.08, 0.07, and 0.06 ppm result from methyl groups bonded to silicon. The first is assigned to the dimethylsilyl groups whose nearest neighbors are both *cis*-difluorocyclopropane groups, the second to dimethylsilyl groups one of whose neighbors is a *cis*- and the other

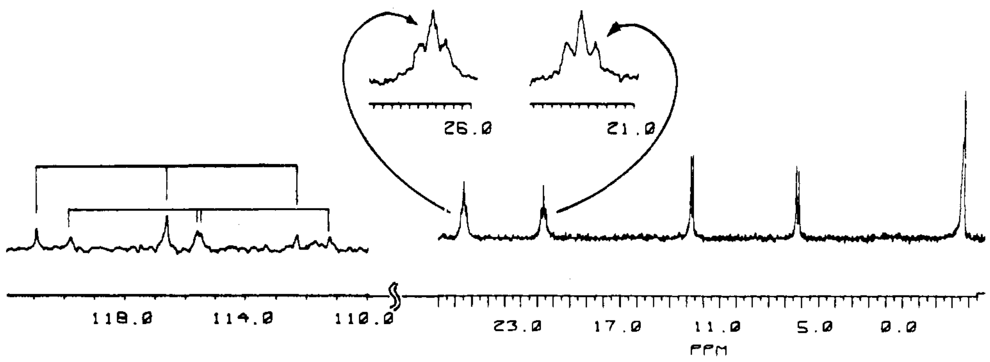


Figure 6. ^{13}C NMR spectrum of 100% CF_2–II.

a *trans*-difluorocyclopropane group and the third to dimethylsilyl groups both of whose nearest neighbors are both *trans*-difluorocyclopropane groups. The intensity ratio of these peaks is 1:2:1 as expected.

The ^{13}C NMR spectrum of CF_2–II provides considerable insight into the microstructure of the polymer. The carbon atom substituted with two fluorine atoms in *trans*-difluorocyclopropane units has a chemical shift of 116.6 ppm and is split to a triplet by the equivalent fluorine atoms $J_{^{13}C-^{19}F}$ = 292.8 Hz. The chemical shift for the fluorine-substituted carbon in *cis*-difluorocyclopropane units is 115.5 ppm, which is split to a doublet of doublets $J_{^{13}C-^{19}F}$ = 286.0 Hz and $J_{^{13}C-^{19}F}$ = 295.0 Hz as previously discussed. The chemical shifts of the fluorine-substituted carbons of CF_2–II are not affected by nearest neighbors. The resonance due to methine carbons of *cis*-difluorocyclopropane rings is found at 21.59 ppm and is split to a triplet by the two fluorines whose two bond coupling constants are fortuitously equivalent, $J_{^{13}C-^{19}F}$ = 10.9 Hz, while the signal from methine carbons of *trans*-difluorocyclopropane rings comes at 26.45 ppm. This signal is also split to a triplet by the two equivalent adjacent geminal fluorines $J_{^{13}C-^{19}F}$ = 9.5 Hz. Both of these triplets display small further splitting. This may result from the effect of neighboring units whose stereochemistry is different. Two signals at 6.29 and 6.13 ppm are observed for methylene groups adjacent to *cis*-difluorocyclopropane rings. These have been previously accounted for by a triad analysis; see above. Likewise, two signals are observed for methylene groups adjacent to *trans*-difluorocyclopropane rings at 12.72 and 12.56 ppm. The methyl groups bonded to silicon lead to a broad peak centered at −3.60 ppm (see Figure 6).

Finally, the ^{29}Si NMR spectrum for CF_2–II provides significant information concerning the polymer microstructure. Three broad resonances are observed: 4.24, 3.53, and 2.81 ppm (see Figure 7). The first is assigned to silyl groups whose nearest neighbors are both *cis*-difluorocyclopropane groups, the second to silyl group surrounded on one side by a *cis*- and on the other by a *trans*-difluorocyclopropane group, while the third is assigned to silyl groups both of whose neighbors are *trans*-difluorocyclopropane group. The broadness of these peaks results from differences in stereochemical orientation of neighboring difluorocyclopropane rings as previously discussed.

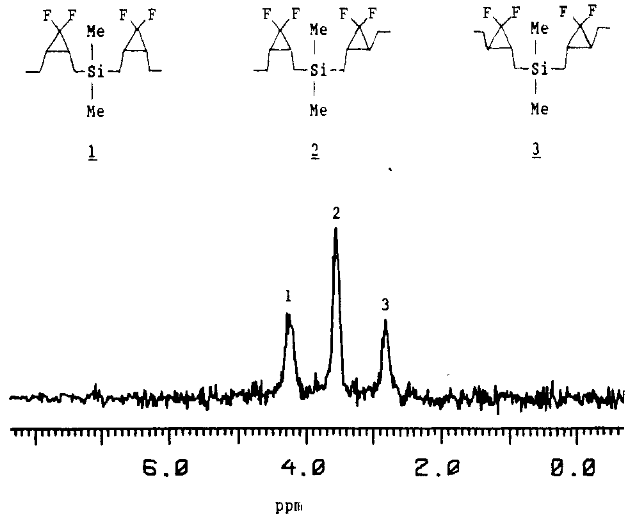


Figure 7. ^{29}Si NMR spectrum of CF_2–I and assignments to microstructures.

Experimental Section

^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR spectra were obtained on an IBM Brucker WP-270-SY spectrometer operating in the FT mode. Polymer solutions (5–10% w/v) in chloroform-*d* were used to obtain ^{1}H and ^{19}F spectra, whereas 10–15% solutions were utilized for ^{29}Si and ^{13}C spectra. ^{13}C NMR spectra were recorded with broad-band proton decoupling. Chloroform was used as an internal standard for ^{1}H and ^{13}C spectra. ^{19}F spectra were run with broad-band proton decoupling to eliminate ^{1}H–^{19}F scalar coupling. CCl_3F was used as an internal standard for ^{19}F NMR measurements. A DEPT pulse sequence was used to obtain ^{29}Si NMR spectra. This was effective since all the silicon atoms have at least two methyl groups bonded to them.[19] All ^{1}H, ^{13}C, and ^{29}Si chemical shifts reported were externally referenced to tetramethylsilane.

IR spectra were recorded on a Perkin-Elmer PE-281 spectrometer. These were taken on films on NaCl plates: 3000, 2950, 2700, 1460, 1280, 1240, 1100, 990, 970, 870 (br) cm^{-1}.

GPC analysis of the molecular weight distribution of the polymers was performed on a Perkin-Elmer series 10 liquid chromatograph equipped with an LC-25 refractive index detector (maintained at 25 °C), a 3600 data station, and a 660 printer. A 32 cm × 77 mm Perkin-Elmer PL 10-μm particle size, mixed pore size cross-linked polystyrene gel column was used for the separation. The eluting solvent was HPLC grade tetrahydrofuran at a flow rate of 0.7 mL/min. The retention times were calibrated against known monodisperse polystyrene standards: M_p 3600000, 194000, 28000, 7600, and 2550 whose M_w/M_n are less than 1.09.

The TGA of the polymers was carried out on a Perkin-Elmer TGS-2 instrument at a nitrogen flow rate of 40 cm^3/min. The temperature program for the analysis was 50 °C for 10 min followed by an increase of 5 °C/min to 550 °C.

Glass transition temperatures of the polymers CF_2–I were performed on a Perkin-Elmer DSC-4 differential scanning calorimeter. Temperature scans were begun at −100 °C. The temperature was increased at a heating rate of 20 °C/min to 20 °C.

Elemental analysis of 98% CF_2–I was performed by Galbraith Laboratories, Knoxville, TN. Calcd: C, 52.06%; H, 7.52%. Found: 52.38%; H, 7.68%.

(Trifluoromethyl)phenylmercury was prepared by an exchange reaction between diphenylmercury and (trifluoromethyl)mercuric trifluoroacetate. The crude product was recrystallized from hexane, mp 141–143 °C.[20]

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

Poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) (I)[10] and **poly(1,1-dimethyl-1-sila-*cis*-(and -*trans*)-pent-3-ene) (II)**[11] were prepared following literature procedures.

Addition of Difluorocarbene to I. Under an atmosphere of purified nitrogen, 0.1 g of I,[10] CF$_3$HgPh (see Table I), and a 3-fold molar excess with respect to CF$_3$HgPh of NaI were placed in a 50-mL round-bottom flask equipped with a reflux condenser and a Teflon-covered magnetic bar. To this mixture was added 25 mL of degassed benzene. The solution was vigorously stirred and heated at reflux for 25-30 h. The mixture was cooled to room temperature and filtered. The solvent was removed by evaporation under reduced pressure. The polymer, dissolved in 3 mL of THF, was precipitated from a large excess of methanol. This purification process was repeated. The polymer was dried under vacuum for 24 h. Yields between 89 and 95% of difluorocyclopropanated polymers were obtained.

Addition of difluorocarbene to II was carried out as above. The product polymer was obtained in 90% yield after the methanol precipitation.

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Vinylidene Chloride-Methyl Methacrylate Random Copolymers: Sequence Length Effects on IR Spectra and Thermal Stability

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ABSTRACT: Two series of vinylidene chloride-methyl methacrylate (VDC/MMA) random copolymers, prepared by batch free radical polymerization in solution, were examined by DSC for thermal transitions, T_g and T_{ll}, as reported elsewhere. The thermal analysis was accompanied by thermal decomposition with lactone formation and foaming, both known from prior literature. Quantification of the decomposition reaction is reported here. In one series, the initial monomer ratio was kept equimolar and the percent conversion varied; in the other, the initial VDC/MMA monomer ratio was varied. FTIR studies have shown that, in the solid state, the observed C=O frequency of the MMA units is a function of sequence length and distribution in the copolymers. The TGA studies show that the thermal stability of the copolymers is also a function of sequence length and distribution. The thermal degradation is maximized when the number of adjacent MMA and VDC units is at a maximum and the primary mode of thermal decomposition involves intramolecular cyclization via loss of both methyl chloride and HCl to form an unsaturated lactone. The structure of the resultant lactone has been characterized by FTIR analysis.

Introduction

We have previously reported[1] the synthesis, characterization, and differential scanning calorimetry (DSC) studies of two series of vinylidene chloride-methyl methacrylate (VDC/MMA) random copolymers. In one series, the initial VDC/MMA monomer ratio was varied; in the other, the initial monomer ratio was kept equimolar, and the percent conversion for the polymerization was varied. It was shown that both the glass transition (T_g) and the liquid-liquid transition (T_{ll}), as detected by DSC, varied linearly as a function of copolymer composition in both series.

In an attempt to gain additional insight into the types of interaction (both inter- and intrachain) occurring in this copolymer series, we have examined the variation of the carbonyl stretching frequency in both copolymer series. Also, because of foaming and/or decomposition problems, which complicated the earlier DSC analyses,[1] we have examined the thermal stability of these samples by thermogravimetric analysis (TGA).[2]

Experimental Section

Synthesis and Characterization. Synthesis and characterization data for both VDC/MMA copolymer series have been previously reported.[1]

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