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APPENDIX IV

ADDITION OF DIFLUOROCARBENE TO POLY(1-METHYL-1-PHENYL-1-SILA-CIS-PENT-3-ENE). CHARACTERIZATION OF MICROSTRUCTURES BY ^1H , ^{13}C , ^{19}F AND ^{29}Si NMR

by
Howard Shih-Jen Lee and William P. Weber*
Department of Chemistry, D.P. and K. B. Loker
Hydrocarbon Research Institute, University of
Southern California, Los Angeles, CA 90089-1661

INTRODUCTION

There is considerable interest in the chemical modification of polymers (1-3). Dichloro-(4-7) and difluorocarbene (8) add stereospecifically to the C-C double bonds of cis- and trans-1,4-polybutadiene.

We were interested in the polymers formed by the addition of difluorocarbene to the C-C double bonds of poly(1-methyl-1-phenyl-1-sila-cis-pent-3-ene) (9). We have previously added dichloro(10) and difluorocarbene (11) to poly(1,1-dimethyl-1-sila-cis-pent-3-ene).

EXPERIMENTAL

^1H , ^{13}C , ^{19}F and ^{29}Si NMR spectra were obtained either on a Bruker AM-360 or an IBM-Bruker WP-270-SY spectrometer operating in the FT mode. Polymer solutions (5% w/v) in CDCl_3 were utilized for ^1H and ^{19}F NMR spectra. For ^{29}Si and ^{13}C NMR spectra (20% w/v) solutions were used. ^{13}C NMR spectra were run with broad band proton decoupling. Chloroform was used as an internal standard for ^1H and ^{13}C NMR spectra. A DEPT pulse sequence (12) or a NOE with a pulse delay of 20 sec (13) was used to obtain ^{29}Si NMR spectra. These were externally referenced to TMS. ^{19}F NMR spectra were run with broad band proton decoupling to eliminate ^1H - ^{19}F scalar coupling. CCl_3F was used as an external standard for ^{19}F NMR spectra.

FT IR spectra were obtained on an IBM FT IR/30S, DTGS/CSI spectrometer. These were taken on films on NaCl plates. GPC analysis of the molecular weight distribution of the polymers were performed on a Waters system, comprised of a 7000 injector, 510 HPLC solvent delivery system, 8001 refractive index detector, and a model 820 Maxima Control system. A Waters 7.8 mm x 30 cm, 10 μm particle size, mixed pore size, crosslinked polystyrene gel column was used for the separation. The eluting solvent was reagent THF at a flow rate of 0.6 mL/min. The retention times were calibrated against known monodisperse polystyrene standards: M_p 212,400; 110,000; 20,400; 4,800; 1,350 whose M_w/M_n are less than 1.09.

TGA of 97% $\text{F}_2\text{C-I}$ 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 4°C/min to 750°C. T_g 's of the polymers were measured on a Perkin-Elmer DSC-7 differential scanning calorimeter. Temperature scans were begun at -100°C. This was increased at a heating rate of 20°C/min to 200°C.

THF was distilled from sodium benzophenone ketyl immediately prior to use. All reactions were conducted under an atmosphere of purified nitrogen.

(Trifluoromethyl)phenylmercury (II) was prepared by an exchange reaction between diphenylmercury and (trifluoromethyl)mercuric trifluoroacetate. The crude product was recrystallized from hexane, mp 141-143°C (14,15).

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. I was stored at 0°C under Argon (10).

Addition of Difluorocarbene to I

In a 50 mL rb flask equipped with a reflux

condenser and a Teflon covered magnetic stirring bar was placed I (60 mg), II (see Table 1) and a three fold molar excess of sodium iodide with respect to II. To this mixture was added 15 mL of degassed benzene. The solution was heat to reflux with vigorous stirring for 40 h. The mixture was cooled to rt and filtered. The solvent was removed by evaporation under reduced pressure. The polymer was dissolved in 3 mL of THF and was precipitated from CH_3OH , twice. The polymer was then dried under vacuum for 24 h. Yields between 80 and 86% of $\text{F}_2\text{C-I}$ were obtained. IR : 3071, 3050, 3011, 2961, 2929, 2892, 1461, 1428, 1411, 1297, 1259, 1214, 1113, 1084, 978, 849, 821, 734, 699 cm^{-1} .

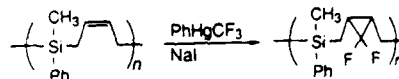


Table 1. Effect of Molar Ratio of PhHgCF_3 to I on Percent Difluorocyclopropanation of I (% $\text{F}_2\text{C-I}$). M_w/M_n of I and $\text{F}_2\text{C-I}$. Glass Transition Temperature (T_g)

Ratio PhHgCF_3	% $\text{F}_2\text{C-I}$	$M_w/M_n \times 10^{-3}$		T_g (°C)
		I	$\text{F}_2\text{C-I}$	
0.0	0	249/93		-38.6
0.5	16	249/93	194/100	-26.8
1.0	34	44/22	10/7	-24.4
3.0	55	44/22	10/6	-11.0
7.0	80	44/22	30/15	-3.1
12.0	97	44/22	11/7	+1.4

RESULTS AND DISCUSSION

We have utilized the NaI catalyzed decomposition of II to generate difluorocarbene, since this reagent functions at low temperature (80°C) under neutral conditions (14,15). These conditions were chosen to minimize polymer degradation, which was nevertheless a problem.

By TGA 97% $\text{F}_2\text{C-I}$ is less thermally stable than I (9). It is stable to 190°C. Rapid loss of 50% of its initial weight occurs between 210 and 265°C. Slower weight loss occurs between 270 and 430°C. Approximately a five percent residue is observed.

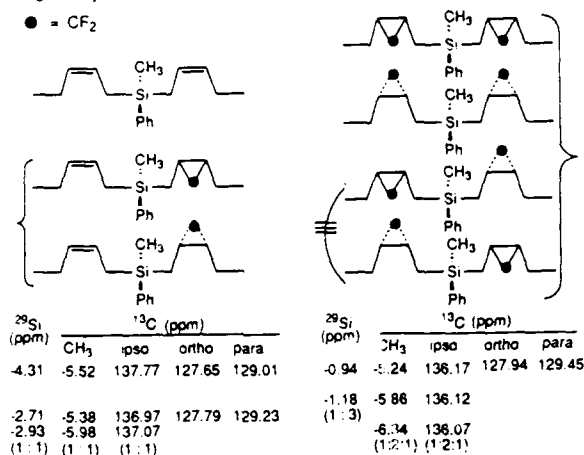
The microstructure of the difluorocarbene adducts of I can be analyzed by ^1H , ^{13}C , ^{19}F and ^{29}Si NMR spectroscopies. Partially difluorocyclopropanated polymers have T_g 's intermediate between those of I and 97% $\text{F}_2\text{C-I}$ (Table 1).

The extent of difluorocyclopropanation can be easily determined from the ^1H NMR data by comparison of the integrals of the resonances due to the phenyl groups at 7.46(s,2H) and 7.34(s,3H) ppm with the signal for the vinyl hydrogens at 5.25(s) ppm. The allyl hydrogens result in a signal at 1.64 ppm whose intensity is consistently twice that of the signal at 5.25 ppm. A broad singlet at 1.36 ppm is assigned to the methine hydrogens of the difluorocyclopropane (CF_2) rings while a singlet at 0.74 ppm results from the methylene hydrogens adjacent to the CF_2 groups. The methyl groups bonded to silicon give rise to three resonances whose intensities depend on the extent of difluorocyclopropanation. These can be assigned on the basis of a dyad analysis. The signal at 0.22 ppm is due to methylphenylsilylene (III) units whose nearest neighbors are C-C double bonds, while that at 0.29 is due to III units which have a C-C double bond on one side and a CF_2 unit on the other. Finally, the singlet at 0.36 ppm is due to III units which have CF_2 units on both sides.

The ^{29}Si NMR can likewise be understood by application of a dyad analysis. Three groups of

resonances are observed whose intensities vary with the extent of difluorocyclopropanation. The signal at -4.31 ppm is due to the silicon of III units which have C-C double bonds on either side. Two signals are observed at -2.71 and -2.93 ppm in a 1:1 ratio. These result from III units which have a C-C double bond on one side and a CF₂ unit on the other. Consideration of molecular models (Fig. 1) predict three ²⁹Si NMR resonances in a 1:2:1 ratio due to III units which have CF₂ units on either side. In fact, two signals assigned to such units are observed: -0.94, -1.18 ppm in a 1:3 ratio.

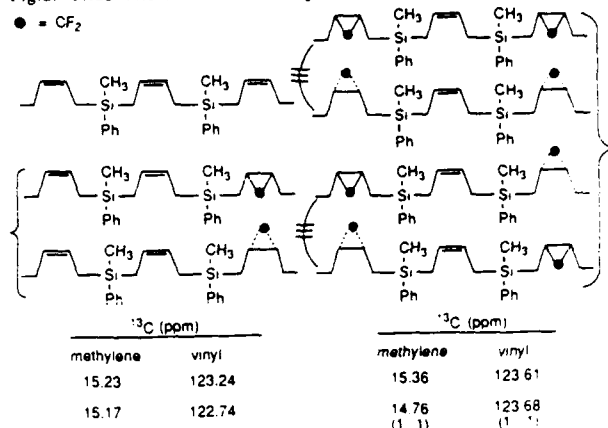
Fig. 1. Dyad microstructures of F₂C-I



The ¹³C NMR data can also be explained in terms of both the extent of difluorocyclopropanation as well as on the basis of microenvironments which are determined by neighboring groups. The ¹³C NMR resonances of the III groups can be understood on the basis of a dyad analysis. Thus the methyl carbons of these give rise to six distinct signals. They have been assigned on the basis of the variation of their intensities with the extent of difluorocyclopropanation of I (Figure 1). Similarly the ipso carbon of the phenyl group gives rise to six resonances. On the other hand, the ortho and para carbons each give rise to three signals: 127.65, 127.79, 127.94 and 129.01, 129.23, 129.45 ppm. The one in each group at highest field is assigned to III units which have C-C double bonds as its nearest neighbors. The next results to those units which have a C-C double bond on one side and a CF₂ unit on the other, while the resonances at lowest field in each group arise from III units which have CF₂ units on both sides. The meta carbons are not sensitive to microstructure and give rise to a single resonance at 133.78 ppm.

The ¹³C NMR signals due to 1,4-cis-but-2-ene can be assigned on the basis of a triad analysis. For example, the vinyl carbons give rise to four signals at 122.74, 123.24, 123.61, 123.68 ppm. The resonance at 123.24 ppm is assigned to the vinyl carbons of 1,4-cis-but-2-ene units which have C-C double bonds on either side. The high field signal may result from vinyl carbons which have a C-C double bond on one side and a CF₂ on the other. Finally, the two low field resonances may result from vinyl carbons which have CF₂ units on either side. Two lines are observed. These can have a cis or trans relationship to one another (Fig. 2).

Fig. 2. Triad microstructures of F₂C-I



The resonance for the difluoromethylene carbon is found at 115.27 ppm. It is split to a triplet by the two geminal fluorine atoms which fortuitously have identical coupling constants of 208 Hz. The ¹³C NMR resonance due to the fluorine substituted carbon is not appreciably sensitive to the extent of difluorocyclopropanation of I. cis-2,3-Difluoromethylene-1,4-butene units can be assigned on the basis of a triad analysis as in Fig. 2 by replacement of the central 1,4-cis-but-2-ene groups by a cis-2,3-difluoromethylene-1,4-butene unit. The allyl, methine carbons of the CF₂ rings and the methylene bonded to Si can be assigned.

¹⁹F NMR spectroscopy provides conclusive evidence that the addition of difluorocarbene to the C-C double bonds of I proceeds in a stereospecific cis manner. Thus the two fluorines of the CF₂ units of F₂C-I are nonequivalent. This results in the observation of a doublet of doublets in the ¹⁹F NMR spectrum at -124.9 and -151.3 ppm, J = 150 Hz.

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