After evaluating the partial derivatives and substituting the assumed correct values of coordinates of atom 4, we obtain

$$\Delta l_4^2 = 2(x_4 - x_3)\Delta x_4 + 2(y_4 - y_3)\Delta y_4 + 2(z_4 - z_3)\Delta z_4$$

$$\Delta(\cos\theta_3) = \frac{(x_2 - x_3)}{l_3 l_4}\Delta x_4 + \frac{(y_2 - y_3)}{l_3 l_4}\Delta y_4 + \frac{(z_2 - z_3)}{l_3 l_4}\Delta z_4$$

$$\Delta(\cos\omega_3) = \frac{9}{8}\frac{(x_1 - x_2)}{l_2 l_4}\Delta x_4 + \frac{9}{8}\frac{(y_1 - y_2)}{l_2 l_4}\Delta y_4 + \frac{9}{8}\frac{(z_1 - z_2)}{l_2 l_4}\Delta z_4 \quad \text{(A-3)}$$

where $\Delta(\ )$ denotes the difference between the known metric and its value computed from coordinates so far generated. This constitutes a system of three linear equations in three unknowns, *viz.*, Δx_4, Δy_4, and Δz_4, which may be solved by any convenient method.[32]

The final step, after solution of eq A-3, is thus to form the corrected coordinates

$$x_{4\text{corr}} = x_{4\text{comp}} + \Delta x_4$$

$$y_{4\text{corr}} = y_{4\text{comp}} + \Delta y_4$$

$$z_{4\text{corr}} = z_{4\text{comp}} + \Delta z_4$$

^{13}C Nuclear Magnetic Resonance Spectra of *m*-Diethynylbenzene Polymers and Related Polyacetylenes[1a]

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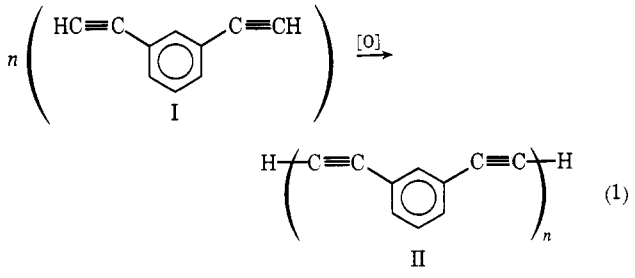
ABSTRACT: Pulsed Fourier transform (FT) ^{13}C nmr has been used to analyze low molecular weight trimethylsilyl-terminated polymers from the oxidative coupling of *m*-diethynylbenzene and also a number of model arylacetylenes. The FT spectra have sufficiently high resolution and signal-to-noise ratios to measure resonances for nuclei in the end groups and to rule out the occurrence of extensive side reactions during polymerization. Other analyses, including ^1H nmr and infrared spectroscopy support these findings.

Natural-abundance ^{13}C nuclear magnetic resonance has been shown to be a very powerful tool in the investigation of polymer microstructure.[2] The newly developing methods of pulsed Fourier transform (FT) ^{13}C nmr do much to overcome the well-known sensitivity limitations of natural-abundance carbon nmr studies.[2b] ^{13}C FT nmr is particularly suited for the analysis of the polymer II from the oxidative coupling of *m*-diethynylbenzene (I) (Reaction 1). Since ^{13}C



(1)

chemical shifts occur over a wide range (200 ppm), it should be possible to resolve nonequivalent carbons both in the aryl and acetylenic portions. With ^1H nmr, very little information is gained because of the relatively small number of protons and their similar chemical shifts. Utilization of Fourier ^{13}C nmr may allow detection of the end groups and uncover the presence of any abnormal groupings. To achieve similar ^{13}C spectra by the usual frequency sweep nmr methods (continuous wave, CW) would require experimental measurement times that exceed the sample's stability at the temperatures required for polymer dissolution. Another advantage is the high-resolution that can be attained, since ^{13}C spectra from FT experiments are not subject to the line broadening resulting from rapid sweeps in CW nmr.

The copper–amine-catalyzed oxidative coupling of *m*-diethynylbenzene (reaction 1) was reported by Hay.[3] Characterization by infrared spectroscopy, X-ray diffraction, and thermal analyses indicated that structure II was consistent with the properties of the polymer;[4] however, limited solubility prevented detailed characterization of the polymer. Recently, methods of polymerization have been found which permit polymerization under homogeneous conditions.[5] With these procedures, phenylethynyl-terminated polymers have been prepared with sufficient solubility to be characterized further.[5] The polymers, however, were either copolymers of *m*- and *p*-diethynylbenzene or terpolymers containing an additional diacetylene. The presence of repeating units other than the meta units tended to complicate the nmr spectra. Thus, a soluble all-meta polymer was desirable for a detailed examination by nmr.

This paper describes polymers with >99% *m*-diethynylenephenylene backbone units which are terminated with trimethylsilyl groups. The polymers are particularly suited for nmr analysis both by ^1H nmr (nine protons per trimethylsilyl group for end group analysis) and ^{13}C nmr, since the quantity of the monofunctional trimethylsilyl component can be varied to control the molecular weight. This permits the preparation of low molecular weight, more soluble polymers with high end group concentrations.

(1) (a) Part III, Polymerization by Oxidative Coupling; part II, D. M. White, *J. Polym. Sci., Part A-1*, **9**, 663 (1971); (b) the publication of this paper was delayed owing to production difficulties.

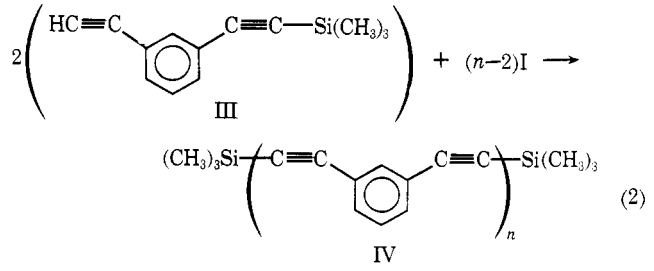
(2) (a) J. Schaefer, *Macromolecules*, **2**, 210 (1969); L. F. Johnson, F. Heatley, and F. A. Bovey, *ibid.*, **3**, 175 (1970); M. W. Duch and D. M. Grant, *ibid.*, **3**, 165 (1970); C. J. Carman, A. R. Tarpley, and J. H. Goldstein, *ibid.*, **4**, 445 (1971); (b) J. Schaefer, *ibid.*, **4**, 98, 105, 110 (1971).

(3) A. S. Hay, *J. Org. Chem.*, **25**, 1275 (1960).

(4) A. E. Newkirk, A. S. Hay, and R. S. McDonald, *J. Polym. Sci., Part A*, **2**, 2217 (1964).

(5) D. M. White, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **12** (1), 155 (1971).

The polymers were prepared by the cooxidation of 1-ethynyl-3-(trimethylsilylethynyl)benzene (III) with *m*-diethynylbenzene (reaction 2).

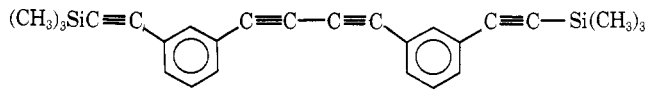


III

IV (2)

The oxidation of III alone produced compound V, the "dimeric" oligomer of polymer IV

III →



V

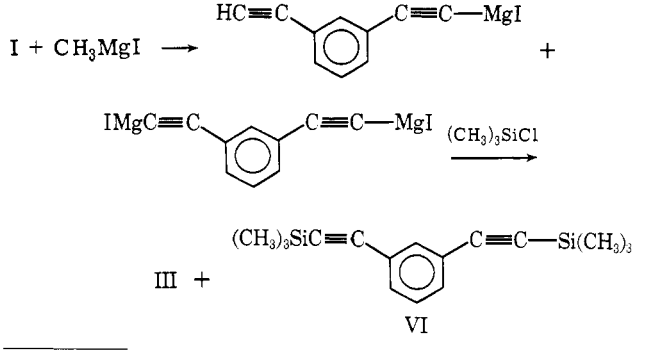
Compounds I, III, V, VI (see Experimental Section) and six unsilylated acetylenes were used as models to aid in structural assignments for the ¹³C spectrum of the polymer.

Experimental Section

Nmr Analysis. ¹³C nmr spectra were obtained at 25.2 MHz on a Varian XL-100-15 spectrometer equipped for both CW (frequency sweep) and FT (pulsed Fourier transform) operation. In all cases, pulse operation was utilized. Computer-controlled time averaging of between several hundred and 100,000 transient responses was used, depending on sample concentration. Specific and wide-band proton decoupling (100.0 MHz) was generated from the system Gyrocode® decoupler. Pseudonoise modulation was used to achieve complete ¹H decoupling in the wide-band experiments. In all cases, field-frequency control (lock) was effected by means of the solvent deuterium resonance. No resonance line broadening or line shifts from frequency instabilities resulted after overnight runs. The accumulated free-induction decays were processed[6] and transformed on the system computer (Varian 620-i); 30–40° pulses were generally used to allow rapid data acquisition. In each case, 4096 data points were acquired, yielding 2048 output points in the phase-corrected real spectrum. Partial spectra (1000, 1250, and 2000 Hz) were obtained in cases where resolution better than 3 Hz (5120 Hz, 2048 output points) was required.

Nmr spectral data are reported in parts per million downfield from internal tetramethylsilane (TMS) standard. Unless otherwise noted, chemical shift accuracy is 0.2 ppm. Probe temperature was *ca.* 40° except when sample insolubility required elevated temperatures. $CDCl_2CDCl_2$ solvent was used for experiments above 100° (bp 148°).

Synthesis of Trimethylsilyl Compounds. 1-Ethynyl-3-(trimethylsilylethynyl)benzene (III) was synthesized by the following sequence of reactions



VI

m-Diethynylbenzene[4,5,7] (I) (51.2 g, 0.4 mol) was added dropwise over a 30-min period to a solution of methylmagnesium iodide (from 12.5 g, 0.52 g-atom; magnesium ribbon, 75 g of methyl iodide, and 400 ml of ether) at 25° under dry nitrogen. Methane slowly evolved from the solution. After 24 hr a solution of trimethylsilyl chloride (81 g, 0.75 mol) in 300 ml of ether was added dropwise over a 60-min period. After standing overnight at 25°, the reaction mixture was filtered to remove magnesium salts and the filtrate was washed with cold 2 *N* hydrochloric acid (200 ml, which was added slowly at first) and two times with ice water. The ether layer was dried over magnesium sulfate, then filtered and concentrated to an oil which weighed 71 g. By distillation through a spinning band column, a fraction weighing 39 g (bp 66–70° (0.3 mm)) was obtained which consisted of 97% III, 1% I, and 2% VI by gas chromatographic analysis (retention times on a 6-ft Apiezon L column programmed from 100 to 300° at 10°/min were 8.7, 13.6, and 17.8 min for I, III, and VI, respectively). Redistillation gave a constant boiling fraction of III.

Anal. Calcd for $C_{13}H_{14}Si$: C, 78.7; H, 7.1; Si, 14.2. Found: C, 79.0; H, 7.1; Si, 14.0.

The infrared spectrum of the pure liquid showed absorptions at 3290 (s, ethynyl CH), 2960 (ms, methyl), 2154 (ms, C≡C), 1250 and 850 (vs, trimethylsilyl), and 898 and 795 cm^{-1} (s, meta substitution). The ultraviolet spectrum in 95% ethanol showed absorptions (mμ (ε)) at 308 (sh), 303 (183), 298 (396), 292 (464), 288 (435), 283 (793), 261 (16,500), 254 (16,300), 248 (18,200), 234 (44,700), and 224 (3020). The mass spectrum showed peaks at *m/e* 198 (relative abundance 5, parent ion), 184 (16), 168 (1), 153 (2), 58 (8), and 43 (100). The ¹H nmr spectrum showed peaks at δ 0.25 (s, 9 H, methyl), 3.14 (s, 1 H, ethynyl), and a complex aromatic pattern corresponding to four protons, a pair of doublets at 7.04 (J = 5) and 7.22 (J = 5), a doublet at 7.35 (J = 2), a quartet at 7.48 (J = 2), and a triplet at 7.64 (J = 2).

1,3-Bis(trimethylsilylethynyl)benzene (VI) was isolated by preparative scale gas chromatography of the reaction mixture for the preparation of compound III above, mp 56–57°.

Anal. Calcd for $C_{16}H_{22}Si_2$: C, 71.0; H, 8.2; Si, 20.3. Found: C, 71.1; H, 7.9; Si, 21.3.

The ¹H nmr spectrum in $CDCl_3$ (TMS reference) showed peaks at δ 0.25 (s, 18 H, methyl) and 7.0–7.7 (complex multiplet, 4 H, aryl). The mass spectrum showed peaks at *m/e* 284 (relative abundance 36, parent ion), 269 (100), 197 (6), 134 (21), and 87 (28). The uv spectrum (95% EtOH) showed maxima at 329 mμ (ε 190), 302 (563), 292 (1420), 278 (1030), 275 (1120), 263 (21,600), 250 (32,900), and 244 (47,700). The infrared spectrum showed characteristic absorptions at 2960, 1250, and 850 (trimethylsilyl), 2155 (C≡C), and 890 and 790 cm^{-1} (meta substitution).

Trimethylsilyl-terminated poly(*m*-diethynylenephenylene) (IV, $\overline{DP}_n$ *ca.* **9)** was prepared by adding a mixture of *m*-diethynylbenzene (6.00 g, 0.0476 mol) and 1-ethynyl-3-(trimethylsilylethynyl)benzene (4.72 g, 0.0238 mol) to a vigorously stirred (Vibromixer stirrer) oxygenated (1.0 ft^3/hr) solution of pyridine (3.4 ml), *N,N,N',N'*-tetramethylethylenediamine (0.39 ml, 2.64 mmol), and copper(I) chloride (0.261 g, 2.64 mmol) in 120 ml of *o*-dichlorobenzene in a 250-ml flask in a stirred oil bath at 80°. The temperature of the reaction mixture rose to 103.5° within 2 min, then generally decreased. After 58 min, the heating bath was removed and the reaction mixture was cooled. The polymer had already begun to precipitate from the solution at this time. The cooled slurry was added to 1000 ml of methanol containing 5 ml of concentrated hydrochloric acid and was stirred for 15 min. The polymer was washed twice by stirring with 1000 ml of methanol, then filtered, and dried at reduced pressure at 25°. The polymer weighed 7.85 g and had an intrinsic viscosity of 0.09 dl/g (in *o*-dichlorobenzene at 120°). The silicon analysis, 5.20%, corresponds to the molecular weight $\bar{M}_n$ = 1080. The calculated molecular weight based on stoichiometry and corrected for loss of dimer, trimer, and a portion of tetramer by fractionation during work-up is 1190. The ¹H nmr spectrum (in perdeuterio-*sym*-tetrachloroethane, TMS reference) showed

(6) *E.g.*, scaling of data, apodization, and exponential weighting of the free-induction decays (0.4–0.8 sec) for sensitivity improvement.

(7) R. Leuchat, *Ann. Chim (Paris)*, 11, **1**, 181 (1934); A. S. Hay, *J. Org. Chem.*, **25**, 637 (1960).

TABLE I
CHEMICAL SHIFTS *vs.* TMS AT POSITION INDICATED

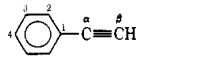
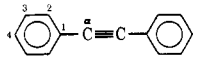
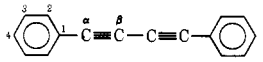
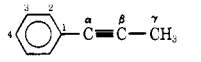
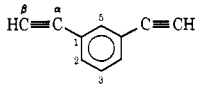
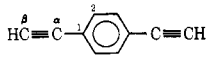
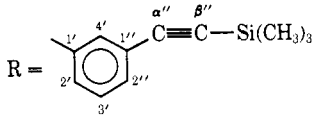
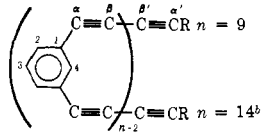
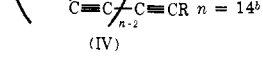
	1	2	3	4	5	α	β	γ
	121.9	131.9	128.1	128.4		83.3	77.7	
	123.7	131.9	128.9	128.8		89.9		
	121.3	132.5	128.7	129.5		81.7	74.0	
	124.1	131.5	128.1	127.3		85.7	79.8	4.0
	122.4	132.1	128.3		135.2	82.5	78.9	
	122.7	132.3				82.9	80.6	
Benzene			128.7					

TABLE II
^{13}C CHEMICAL SHIFTS AT POSITION INDICATED FOR COMPOUNDS CONTAINING THE MOIETY

R = 

	1	1′	1″	2	2′	2″	3	3′	4	4′	α″	β″	Other
R—H			122.8			131.4		127.5			104.4	92.5	2′ 127.3[a]
R—C(α′)≡C(β′)H (III)		121.7	122.9		131.4	131.3		127.6		134.7	102.9	94.1	α′ 82.0 β′ 77.5
R—C≡C—Si(CH₃)₃ (VI)			123.7			131.9		128.6		135.6	104.1	95.0	
(R—C(α′)≡C(β′))₂ (V)		121.9	123.8		132.7	132.4		128.7		135.7	103.4	95.3	α′ 80.8 β′ 74.2
 n = 9	122.3	121.9	124.1	133.2	132.5	132.0	128.8	128.3	136.2	135.8	103.4	95.5	α 80.8 β 74.9 α′ 80.4 β′ 74.7
 n = 14[b]	122.2	121.7	123.8	132.8	132.2	131.7	128.3	127.8	136.0	135.6			α 81.0 β 75.0

(IV)

[a] For this compound, C-2′ is not ortho to an ethynyl group, thus not comparable to the other 2′ carbon in Table II. [b] For this compound R = $-C_6H_4C{\equiv}CH$ (see text).

a trimethylsilyl singlet absorption at δ 0.08 and a complex aromatic multiplet between 7.0 and 7.6 in the intensity ratio 18:35.3 which corresponds to $\bar{M}_n$ = 1240. The infrared spectrum of a thin film cast on a silver chloride sheet showed absorption bands not present in normal high molecular weight polymer at 2950 (trimethylsilyl), 2150 (C≡C—Si), 1250 (trimethylsilyl), 840, and 760 cm^{-1}. No ethynyl C–H stretching frequency at 3300 cm^{-1} was detected.

Trimethylsilyl-terminated poly(*m*-diethynylenephenylene) (IV, $\overline{DP}_n$ *ca.* 14) was prepared by adding a mixture of *m*-diethynylbenzene (8.00 g, 0.0635 mol) and 1-ethynyl-3-(trimethylsilylethynyl)-benzene (2.52 g, 0.0127 mol) to a vigorously stirred oxygenated (1.0 ft^3/hr) solution of pyridine (3.4 ml), *N,N,N′,N′*-tetramethylethylenediamine (0.42 ml, 0.00282 mol), and copper(I) chloride (0.28 g, 0.00282 mol) in 120 ml of *o*-dichlorobenzene in a 250-ml flask in a stirred oil bath at 65°. The temperature of the reaction mixture rose to 94.5° within 2 min, then gradually decreased. After 48 min, the reaction mixture was cooled and worked up in an identical manner as for the $\overline{DP}_n$ 9 sample above. The product weighed 9.24 g, intrinsic viscosity 0.13 dl/g (in *o*-dichlorobenzene at 120°). The silicon analysis, 3.00%, corresponds to $\bar{M}_n$ = 2100; calculated value based on stoichiometry and corrected for fractionation on work-up, 2100. The ^1H nmr spectrum ($CDCl_2CDCl_2$) has a [trimethylsilyl H]:[aryl H] ratio of 18:55.9 corresponding to $\bar{M}_n$ 1880.

1,4-Bis[3-(trimethylsilylethynyl)phenyl]-1,3-butadiyne (V) was prepared by adding 1-ethynyl-3-(trimethylsilylethynyl)benzene (5.00 g, 25.7 mmol) to a vigorously stirred, oxygenated (0.5 ft^3/hr) mixture of 0.85 ml of pyridine, *N,N,N′,N′*-tetramethylethylenediamine (0.135 ml, 0.92 mmol), copper(I) chloride (0.091 g, 0.92 mmol), and anhydrous magnesium sulfate (2 g) in 60 ml of benzene in a wide-mouth tube in a stirred oil bath at 40°. After 2 hr, the mixture was filtered to remove the magnesium sulfate. The filtrate was washed with 2 *N* hydrochloric acid, then with water, and dried over anhydrous magnesium sulfate. Evaporation of the benzene left white crystals, 4.90 g, which were recrystallized from *n*-hexane, 3.80 g, mp 126–128°. The ^1H nmr spectrum in deuteriochloroform (TMS reference) showed absorptions at δ 0.27 (s, 18 H, trimethylsilyl), 7.3–7.7 (complex multiplet, 6 H, aryl), and 7.7–7.9 (complex multiplet, 2 H, aryl). The infrared spectrum (KBr disk)

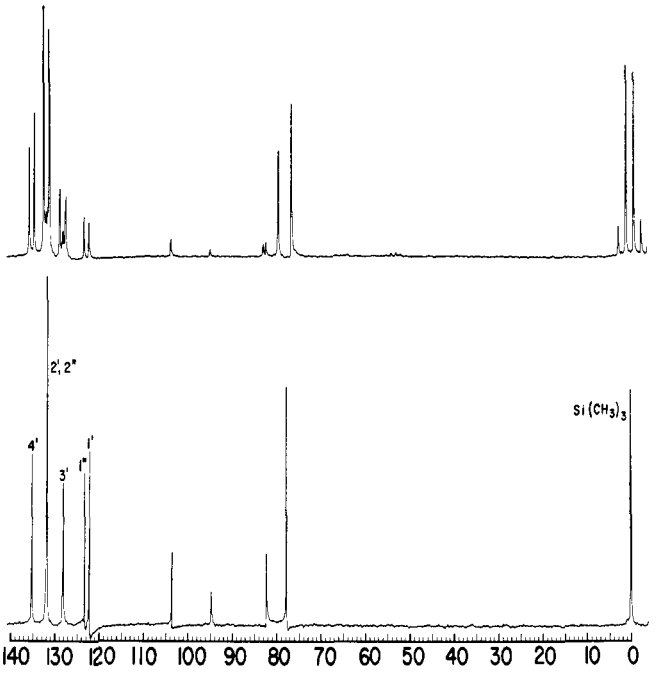


Figure 1. ^{13}C FT spectra of compound III in acetone-d_6, with partial proton decoupling (top) and completely decoupled (bottom). In each case, several thousand transients were accumulated at a pulse interval of 0.4 sec. Chemical shifts are relative to TMS (not present for these spectra but added later).

showed characteristic absorptions at 2160 (C≡C), 1245, 840, 758 (trimethylsilyl), and 890 and 790 cm^{-1} (1,3-disubstituted benzene). The uv spectrum (95% ethanol) showed maxima at 329 mμ (ε 190), 302 (563), 292 (1420), 278 (1030), 275 (1120), 263 (21,600), 258 (32,900), and 244 (47,700).

^{13}C nmr spectra were run on various related but unsilylated model compounds: phenylacetylene, 1-phenylpropyne,[8] 1,4-diphenylbutadiyne,[9] *p*-diethynylbenzene,[7] *m*-diethynylbenzene,[7] and tolane (Table I) and on the following trimethylsilyl compounds: phenyltrimethylsilylacetylene[10] and compounds III, IV, V, and VI (Table II).

Results and Discussion

Interpretation of Spectra. The spectra of several model compounds and of the polymer illustrate the utility of ^{13}C Fourier transform nmr for the analysis of highly unsaturated systems. The spectra of compound III (Figure 1) when completely proton decoupled and partially proton decoupled, allow one to distinguish between the carbon nuclei bearing protons and those without protons. Longer range coupling to hydrogen is also noted for the carbon adjacent to the C–H ethynyl carbon. The spectrum of compound V (Figure 2) illustrates complete resolution of the 11 types of carbon atoms in the molecule. The spectrum of the polymer, compound IV (n = 9) (Figure 3), not only allows differentiation of the atoms comprising the basic repeating unit but also permits end group characterization. The high resolution and high signal-to-noise ratios were attainable even for the sparingly soluble polymer under conditions which did not lead to sample degradation.

The spectral data for five model systems are listed in Table I. Comparison of the chemical shifts of these spectra, along with the information gained from partial proton decoupling and peak intensities, permits complete assignment of the spectra.

(8) M. S. Kharasch, *et al.*, *J. Org. Chem.*, **10**, 298 (1945).
(9) A. S. Hay, *ibid.*, **27**, 3320 (1962).
(10) C. Eaborn and D. R. M. Walton, *J. Organometal. Chem.*, **2**, 95 (1964).

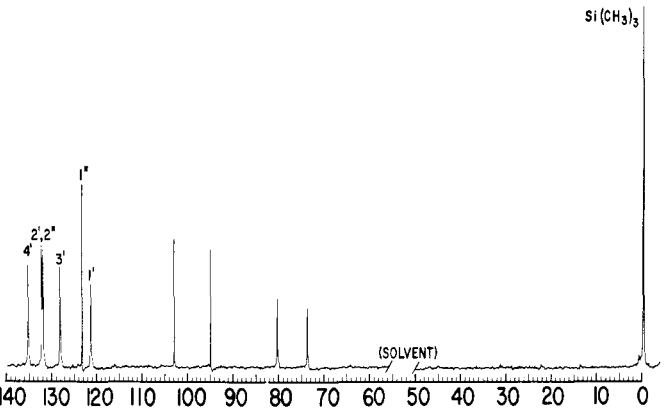


Figure 2. ^{13}C FT spectrum of compound V in acetone-d_6 (400 transients; 100-sec pulse interval). Chemical shifts relative to TMS (added later).

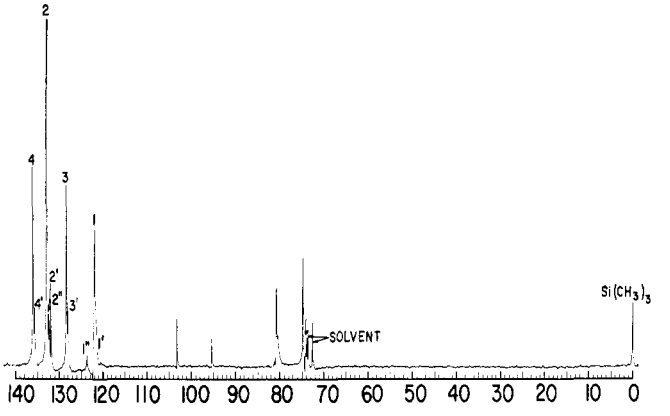


Figure 3. ^{13}C FT spectrum of polyacetylene IV (n = 9) in 1,1,2,2-tetrachloroethane-d_2 (75,000 transients; 0.4-sec pulse interval). Chemical shifts relative to TMS (added later).

The assignment for C-1 is based on the lack of splitting with partial ^{1}H decoupling (C-1 is the only aryl carbon in the first three compounds that does not have directly attached protons). The chemical shift of C-1 is always upfield from the unsubstituted ^{13}C resonance of benzene. The magnitude is dependent on the nature of the substitutent on the β carbon, *i.e.*, the electron-donating methyl group results in the largest upfield shift, the electron-withdrawing ethynyl group results in the smallest upfield shift. The C-4 assignment is based on the splitting to a doublet with partial decoupling and on the peak area when compared with the larger C-2 and C-3 peaks in the first three compounds. The chemical shift for C-4 is very similar to the benzene shift. Based on the correlations of chemical shift with $\sigma+$ constants,[11] this indicates that the *p*-ethynyl group has a $\sigma+$ value near zero.[12] The C-3 assignment is based on the decoupled spectrum and on the well-established observation that meta substitution has little effect on the ^{13}C chemical shift in substituted benzenes.[13] The assignment at C-2 is in accord with the partial proton decoupling spectrum and is the only unassigned position remaining in the first three compounds in Table I. For all the C-2's in Table I, the shift is upfield from benzene approximately 4 ppm. The assignment at C-5 is based on partial proton decoupling, peak intensity, the prior assignment of all remaining

(11) G. C. Levy, G. L. Nelson, and J. D. Cargioli, *J. Chem. Soc. D*, 506 (1971).
(12) Chemical evidence indicates the value for a *p*-ethynyl group to be 0.179: J. A. Landgrebe and R. H. Rynbrandt, *J. Org. Chem.*, **31**, 2585 (1966).
(13) G. E. Maciel and J. J. Natterstad, *J. Chem. Phys.*, **42**, 2427 (1965).

aryl carbons, and the approximate doubling of the downfield shift from benzene of the C-2 resonance due to the presence of two *o*-ethynyl substituents.

The C-β resonance for monosubstituted acetylenes in Table I occurs at 79 ppm and is characterized by formation of a doublet when the adjacent proton is partially decoupled. The C-α resonance, the only other ethynyl peak, is downfield from the C-β at *ca.* 83 ppm. When the β-carbon is further conjugated as in 1,4-diphenylbutadiyne, it is shifted upfield several ppm (to 74 ppm). The C-α peak is also shifted upfield slightly, but only *ca.* 1 ppm. An opposite shift occurs with the electron-donating methyl substituent; in 1-phenylpropyne, both the C-α and C-β resonances are *ca.* 2 ppm downfield from the corresponding peaks in phenyl acetylene. Considerably larger shifts due to the trimethylsilyl substituent are described below for the compounds in Table II.

The assignments in Table I have been applied in Table II to aid in the assignment of the peaks in the spectra of the silylated model compounds. Thus, ethynyl carbons in compound III and the conjugated diyne carbons in IV are directly assignable. The C≡C—Si carbons for structures III–VI in Table II can be assigned based on the spectrum of the first compound in Table II, phenyltrimethylsilylacetylene. In this material, C-α'' and C-β'' are assigned on the basis of side bands which flank the 92.5-ppm peak. These are due to a doublet arising from the ^{13}C–^{29}Si coupling between C-β'' and the adjacent silicon atoms (J = 83.6 Hz). The carbon at 104.4 ppm shows long-range coupling to ^{29}Si, J = 16.1 Hz. One-bond carbon–silicon coupling observed in several compounds appears roughly proportional to the s character of the carbon atom.[14] The one-bond coupling in phenyltrimethylsilylacetylene is consistent with these results. The large downfield shift of approximately 21 ppm for both acetylenic carbons in this compound may be an effect of $(p\text{–}d)_\pi$ bonding between the silicon and acetylenic orbitals.[14,15] The same deshielding of trimethylsilylated acetylenic carbons can be observed in compounds III–VI (see Table II).

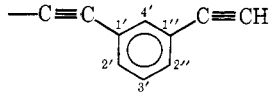
In the polymer, the carbon resonances for the terminal acetylenes are clearly identified due to the large downfield chemical shift caused by trimethylsilyl substitution. The diyne carbons of the internal repeating units can be assigned due to the peak size (large, because of the high concentration) and location. The resonances of carbons C-α' and C-β' in the diyne links between the terminal and penultimate ring also appear to have discrete absorption bands (chemical shifts that differ from the other internal diyne shifts) and tend to complicate this region. Thus, a weak peak adjoins the 80.8-ppm peak and is probably due to the C-α' nucleus. Similarly, near the 74.9 ppm C-β peak is a shoulder at 74.7 ppm, corresponding to the C-β nucleus.

The assignments of the aryl carbons of the model compounds in Table II are based primarily on the results in Table I and in part on the spectrum of the polymer. The analogy in Table I permits the general assignment of the various isolated peaks; however, it does not resolve the more subtle difference between the almost overlapping pairs of peaks such as the resonances of the C-1′ and C-1″ carbons in compound V. Distinction between the very similar carbons can be made from the assignments for the spectrum of the polymers which are discussed below. It is found that the C-1′ and C-1″ assignments for compounds IV and V match well with those of the polymer. This is also the case at C-2′ and C-2″. The chemical shifts at C-1″ and C-2″ for compound VI and for phenyltrimethylsilylacetylene are also in accord with the C-1″ assignment in the polymer.

The aryl carbon assignments in the spectrum of the polymer can be made partly on the basis of peak area, since the concentrations of end group atoms are lower than atoms in internal units (see Figure 3). This permits specific identification of C-1, C-2, C-3, C-3′, C-4, and C-4′, since these occur either as a large peak or as a single small peak paired with a large peak. The assignments for the two small peaks due to C-2′ and C-2″ are based on the C-2′ being intermediate in nature between C-2 and C-2″, but this is not established with certainty. The C-1″ chemical shift appears to differ from the other end group carbons, since the peak is shifted downfield from the internal C-1 resonances. That it is the C-1″ peak is indicated by a comparison of the model compounds; *e.g.*, for VI (Table II) *vs.* 1,4-diphenylbutadiyne (Table I), the C-1 atoms are shifted *ca.* 1 ppm downfield when the adjacent ethynyl group bears a trimethylsilyl group instead of another ethynyl group. The assignment at C-1″ is also in accord with the spectrum of 1-phenylpropyne (Table I) in which the presence of the electron-donating methyl group on the ethynyl group causes a downfield shift of several parts per million at C-1 when compared to the effect of the electron-withdrawing phenylethynyl group in 1,4-diphenylbutadiyne.

Comparison of Low and Higher Molecular Weight Polymers. The ^{13}C nmr spectrum of a higher molecular weight polymer, IV (n = 14), is also described in Table II. The measurement was carried out at a higher temperature (115°) and for a longer time (150,000 transients) since the solubility was poorer than for the lower molecular weight polymer. The spectrum resembled the spectrum of the lower polymer (Figure 3), particularly in the aryl carbon region; however, there were several notable differences mainly in the nonaryl regions. The principal difference was the lack of both a trimethylsilyl peak and also peaks corresponding to the α''- and β''-ethynyl carbons. The presence of the ethynylsilylane groups in the original sample of polymer was confirmed by elemental analysis, the ^1H nmr spectrum, and the infrared spectrum. These spectra, however, were obtained with only brief exposures of the polymer to high temperatures. Thus, the trimethylsilyl groups appear to be cleaved at the high temperatures and long measurement times of the ^{13}C nmr experiment. This higher polymer may represent a borderline case for obtaining usable ^{13}C spectra on diethynylbenzene polymers with high meta contents. Attempts to keep samples of higher molecular weight homopolymers in solution without discoloration and gelation were unsuccessful.

Two other differences between the higher and lower molecular weight polymers are in the aryl region. The first is the lower intensity of the peaks for the terminal rings and, as expected, is proportional to the lower end group concentration. The second difference probably results from the cleavage of the trimethylsilyl groups (see above). The differences in chemical shifts of the end group peaks relative to the nearby large peaks, however, differed from those of the lower polymer. It is likely that the aryl carbons in the end group which resulted from trimethylsilyl cleavage, *i.e.*, the moiety

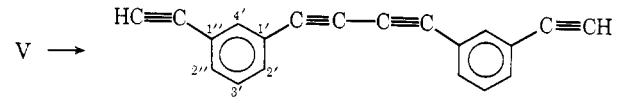


would have chemical shifts which would differ from the analogous carbons in the silylated end groups. The nonequivalence caused by ethynyl *vs.* diynyl substitution was

(14) G. C. Levy, J. D. Cargioli, and D. M. White, *J. Magn. Resonance*, in press.

(15) M. E. Freeburger and L. Spialter, *J. Amer. Chem. Soc.*, **93**, 1894 (1971).

demonstrated by conversion of compound V to the bis-monsubstituted acetylene VII by an alkali cleavage reaction. The ^{13}C spectrum of VII did display two sets of equally intense



VII

peaks. One pair corresponding to C-1′ and C-1″ differed in chemical shifts by 0.24 ppm while the C-2′ and C-2″ pair differed by 0.20 ppm. This further confirmed the spectral data for the higher polymer.

Polymer Characterization. The ratio of trimethylsilyl protons to aromatic protons in the ^1H nmr spectrum of the lower molecular weight polymer corresponded to a number-average molecular weight (M_n) for the polymer of 1110. This value is in agreement with elemental silicon analysis for which $\overline{M}_n = 1080$ and with the initial stoichiometric ratios of monofunctional to difunctional acetylenes after correcting for fractionation of the lowest oligomers during isolation. In addition, both the gel permeation chromatographic behavior and the intrinsic viscosity are in accord with a molecular weight near 1000 when compared with phenylethynyl-terminated polymers which were prepared predominantly from *m*-diethynylbenzene.[5] For the higher molecular weight polymer the spectral, elemental, and solution analyses were also consistent with the calculated molecular weight.

All of the peaks in the ^{13}C nmr spectrum of the lower polymer can be assigned to the carbon atoms in structure IV. Weak peaks due to end group nuclei are present at approximately the intensities which are suggested by the molecular weight. Variations in the observed intensities can be accounted for by relaxation phenomena and the Overhauser effect which can cause up to a threefold enhancement in signal where a proton is attached to or near the carbon undergoing resonance. Since all of the observed peaks can be assigned to structure IV, there is no evidence for abnormal linkages or moieties in the polymer. This is also the case for the ^1H spectrum where vinyl protons, for example, would be discernible. Thus, the polymer does not appear to be highly branched or to have undergone reactions other than the normal oxidative coupling. Additional reactions as the "Strauss coupling" reaction[16]

$$2R{-}C{\equiv}CH \longrightarrow R{-}C{\equiv}C{-}CH{=}CH{-}R$$

are copper catalyzed and can occur at elevated temperatures, but normally require acidic conditions. This reaction would lead to disubstituted vinyl groups in the backbone, but would not result in branching. Not only is there no evidence for these groups in the ^{13}C and ^1H spectra, but also there are no characteristic olefinic absorptions in the infrared spectra of either polymer.

(16) F. Strauss, *Justus Liebigs Ann. Chem.*, **342**, 190 (1905).

Shear Creep Studies of Narrow-Distribution Poly(*cis*-isoprene). II. Extension to Low Molecular Weights[1]

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ABSTRACT: Shear creep measurements have been made on six poly(*cis*-isoprene) samples of narrow molecular weight distribution with the molecular weights ranging from 3100 to 43,000. The viscosity η, the steady-state compliance J_e, and the maximum relaxation time τ_m are calculated from the creep curves. The critical molecular weight M_c at which the logarithmic plot of η against M exhibits an abrupt change in slope from 1.0 to 3.7 is found to be about 10,000. The molecular weight dependence of J_e also undergoes a rapid change near $M_b = 50{,}000$. At low molecular weights, J_e is approximately linearly dependent on M, in agreement with the prediction of the Rouse theory, while at high molecular weights, it is nearly independent of M. The maximum relaxation time τ_m varies as the 3.7 power of M over a wide range of molecular weight, from 6000 to 1,120,000. The entanglement compliance J_{eN} is found to be about 1.6×10^{-7} cm²/dyn for samples having $M > M_b$, which is merely one-eighth to one-tenth of J_e. The average molecular weight M_e between entanglement coupling points is about 3000, as evaluated from J_{eN}.

In a previous paper,[2] the shear creep behavior of undiluted poly(*cis*-isoprene) of narrow molecular weight distribution (MWD) was studied with samples of molecular weight ranging from 57,000 to 1,120,000. It was found that the steady-state compliance J_e was nearly independent of molecular weight M and that the viscosity η, as well as the maximum relaxation time τ_m, varied as the 3.4 power of M. These properties of the viscoelastic functions agreed with those observed for other species of narrow MWD polymer, polystyrene,[3-10] poly(α-methylstyrene),[11-12] and poly(dimethyl-

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