support was prepared in benzene and in contrast to the preparations by using toluene, and 2-methoxyethanol cracking of the solvent is not expected to occur. In this scheme, reaction of the adsorbed ethoxy groups would lead to ethanol production. Dehydration of coordinated ethanol or ethoxy groups would result in the formation of ethylene while dehydrogenation of ethanol produces acetaldehyde. Acetaldehyde is detected in the early phases of our experiments by GC and GC/MS. Ethylene is detected throughout the experiment as a minor byproduct. As shown in Figure 4, ethylene may then react with HCl to produce ethyl chloride which is the major product from the reaction of ethanol or ethoxy groups with HCl. Ethylene may be cracked over the alumina surface producing carbon species. Reaction of the carbon species with hydrogen and HCl would account for the methane and methyl chloride observed in our experiments with the ethoxy phosphino silane. All of these reactions are further complicated by reactions involving the intermediate species. Evidence for such a scheme is supported by reports in the literature. Several reports indicate that ethanol can be converted over inorganic oxides to ethylene,[10–12] ethane,[10] and acetaldehyde[13,14] all of which were observed as minor products in our reactions. It is generally recognized that olefins are an important source of carbon formation involved in catalytic cracking.[15] Reports indicate that over a metal surface ethylene may decompose to carbon atoms via an acetylene intermediate.[16,17] We believe similar chemistry is occurring whereby decomposition of ethoxy groups eventually lead to the formation of methyl chloride.

When alumina was functionalized with $(CH_3CH_2O)_3SiC_2H_4P(C_6H_5)_2$, we found that the adventitious carbon could be removed by passing HCl gas over the functionalized support at 150 °C until ethyl chloride was no longer observed in the exit gas. It was a concern that after this treatment the support would lead to the decomposition of metal carbonyls, but we were able to show that the tetrairidium cluster could be absorbed onto the alumina when $Ir_4(CO)_{12}$ is reacted with the solid in refluxing benzene. Infrared showed that the cluster remained intact. When this catalyst was then reacted with H_2, CO, and HCl at 70 °C, no products corresponding to those expected from the reduction of CO or from organic residues introduced during synthesis were observed.

Acknowledgment. We appreciate the generous support of this research by Dow Corning Corporation and thank Dr. R. King for his guidance with the GCMS.

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Solid-State Bromination of Poly(1,6-di-*N*-carbazolyl-2,4-hexadiyne): A ^{13}C CP–MAS NMR Study

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Abstract: ^{13}C cross-polarization/magic-angle spinning (CP–MAS) NMR experiments at 50.36 MHz reveal that the solid-state reaction of the crystalline polymer poly(*N*-dicarbazolyl-2,4-hexadiyne) (poly-DCH) with liquid bromine results in the formation of covalent C–Br bonds in the polymer. The presence of bromine in these compounds results in loss of the signals arising from those carbon atoms directly bonded to or adjacent to bromine due to broadening effects arising from dipolar coupling to the quadrupolar $^{79,81}Br$ isotopes. Nevertheless, ^{13}C CP–MAS NMR can identify carbon atoms more than two bonds removed from bromine and allows one to monitor semiquantitatively the course of the bromination. By comparison with model compounds it is shown that bromine effects selective electrophilic aromatic substitution at the 3,6 positions on the aromatic rings of the carbazole moiety, forming a polymer with four Br per repeat unit. At higher bromination levels addition to the multiple bonds in the backbone occurs. For the material of composition poly-DCH($Br_{6.0}$), the results indicate extensive conversion of the polydiacetylene structure to a mixed polyacetylene structure. The observation of additional weak absorptions corresponding to butatrienic units suggests that the bromine–backbone interaction leads to localization of conjugation defects.

The homogeneous topochemical polymerization of conjugated diacetylene monomers produces macroscopic polymer single crystals with a high degree of perfection.[1] The polydiacetylenes thus formed (see eq 1) have a fully conjugated planar backbone and are, as wide-band one-dimensional semiconductors, of fundamental theoretical interest from a solid-state physics viewpoint. In addition, they possess optical and electronic properties that are unusual for polymers and which suggest applications in electronic

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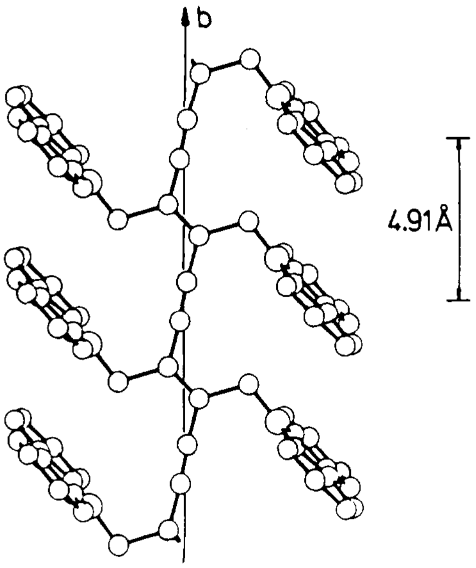
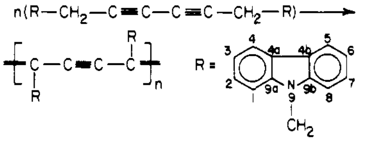


Figure 1. Molecular structure of poly-DCH. Reproduced with permission from ref 1. Copyright 1984, Springer-Verlag.

devices. Most polydiacetylenes are insoluble, although judicious choice of the side groups has produced derivatives with some limited solubility.



(1)

The polydiacetylenes differ from the polyacetylenes in several important respects. They are crystalline rather than semicrystalline or amorphous and they are more stable at ambient temperatures. Thus, they represent a simpler system in which to investigate optical and electronic properties of conjugated backbones. Unlike polyacetylenes, which can be doped readily with electron-donor or -acceptor molecules to produce conductive metallic polymers, the polydiacetylenes do not react in this fashion because of their high crystallinity. Thus, the opportunities for modifying the physicochemical properties of polydiacetylenes have been severely limited by their lack of chemical reactivity.

Recently two of us have found[2] that exposure of single crystals of poly(*N*-dicarbazolyl-2,4-hexadiyne) (poly-DCH, Figure 1, for the crystal structure, see ref 3) to liquid bromine produces highly crystalline materials with reproducible bromine contents ranging from 3 to 8 Br per repeat unit, with a concomitant color change from the brassy appearance of the starting polymer to a coppery-bronze and ultimately straw-colored product. While the reaction of halogens with polyacetylene can be discussed in terms of ionic intercalation ("doping"), the significantly higher halogen uptake encountered with poly-DCH, as well as the non-metallic character of both starting material and products, suggests a different mode of reaction involving formation of covalent C–Br bonds.[4] Potential bromination sites are the double and triple bonds, the allylic methylene group, and the aromatic carbazole moiety. However, the products cannot be predicted simply on the basis of the relative reactivities of the groups toward bromination, since anisotropic solid-state diffusion of bromine must be a major factor in governing the course of reaction.[2]

Detailed experimental identification of the products has proven elusive. Single-crystal X-ray diffraction methods have been hindered by crystallographic disorder. FT-IR methods indicate carbazole substitution, but are not unequivocal.[2] In addition, the insolubility of all of the brominated products precludes the use of traditional solution-state characterization methods. However, techniques which have been developed for obtaining high-resolution nuclear magnetic resonance (NMR) spectra of solids[5] appear well-suited to address this problem. In particular, high-resolution solid-state ^{13}C NMR with use of cross-polarization and magic-angle spinning (CP–MAS) has proven a valuable means for characterizing organic polymers in the solid state,[6] including various polydiacetylenes.[7,8]

In this study we have used ^{13}C CP–MAS NMR to clarify the course of bromination of poly-DCH. Information about the chemical structure of the reaction products has been obtained by utilizing CP–MAS NMR data on model compounds as well as solution NMR data to aid in the assignments. Through the combined use of different CP–MAS NMR experiments, assignments have been obtained and the conditions for semiquantitation established. The presence of quadrupolar bromine nuclei leads to broadening of peaks in the ^{13}C CP–MAS NMR spectra and must be taken into account in the interpretation of results.

Experimental Section

Sample Preparation and Characterization. DCH monomer was synthesized and polymerized with ^{60}Co γ radiation as previously described.[9] Exposure of the large, rod-like crystals of poly-DCH to liquid bromine for 2 h at −5 °C resulted in uptake of 3 Br per polymer repeat unit, exposure for 4 h at −5 °C led to uptake of 3.8 Br, and exposure for 24 h at 20 °C resulted in uptake of 6 Br per polymer repeat. Compositions of the brominated polymer inferred by weight gain are in good agreement with those found by complete chemical analysis. The initial brassy color of the pristine polymer becomes coppery bronze upon bromination. The deeply colored metallic appearance of all of these materials indicates the preservation of a conjugated backbone (see below). Polymers with higher Br content (7.4 and 8.2 Br per repeat) were prepared by refluxing poly-DCH with a 75:25 w/w mixture of Br_2 and CCl_4 or pure liquid bromine, respectively. The non-metallic straw-like color of these materials suggests that extensive disruption of conjugation has occurred. All products appear homogeneous by both scanning and transmission electron microscopy. X-ray diffraction studies of crystals which have gained ca. 6 Br atoms per repeat reveal a slight decrease of the chain repeat distance from 490 (in the pristine material) to 475 ± 5 pm, as well as new reflections which are more diffuse than those of poly-DCH. Corresponding zero-level Weissenberg photographs of this material reveal that the crystallites are well aligned in the chain direction but poorly correlated perpendicular to it.[2]

Samples of the new monomer model compounds bis(3′,6′-dibromo-*N*-carbazolyl)-2,4-hexadiyne ($DCHBr_4$ monomer) and bis(1′,3′,6′,8′-tetrabromo-*N*-carbazolyl)-2,4-hexadiyne ($DCHBr_8$ monomer) were synthesized by coupling of the relevant propargyl compound, in analogy to the synthesis of DCH.[9] The procedures are as follows.

Synthesis of 1-(3′,6′-Dibromocarbazolyl)-2-propyne. Sodium amide (7.73 g, 0.198 mol) was carefully added to a suspension of 3,6-dibromocarbazole (54.7 g, 0.168 mol) in liquid ammonia (ca. 600 mL), under an argon atmosphere. After dissolution, propargyl bromide (20.2 g, 0.170 mol) in toluene was added dropwise over 25 min. The reaction mixture was stirred for an additional 100 min, and the ammonia was allowed to evaporate. The resultant solid was washed with water and recrystallized from ethanol to give 39 g (63% yield) of tan needles, mp 193–194 °C. This solid gave an infrared spectrum with significant features at 3290, 2120, 870, 830, 800, and 790 cm^{-1}. Anal. Calcd (in wt %) for $C_{15}H_9NBr_2$: C, 49.62; H, 2.50; N, 3.86; Br, 44.02. Found: C, 49.47; H, 2.65; N, 3.88; Br, 43.78.

Synthesis of Bis(3′,6′-dibromo-*N*-carbazolyl)-2,4-hexadiyne ($DCHBr_4$ Monomer). To a solution of *N*-propargyl-3,6-dibromocarbazole in dioxane (150 mL) was added *N,N,N′,N′*-tetramethylethylenediamine (0.6 g) and CuCl (0.5 g). The mixture was stirred and oxygen was bubbled through the solution for 3.5 h. The reaction mixture was poured into 0.6 M hydrochloric acid, and a greenish precipitate was collected and vac-

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uum dried to give a 72% yield. The solid was further purified by Soxhlet extraction with toluene. Anal. Calcd (in wt %) for $C_{30}H_{16}N_2Br_4$: C, 49.76; H, 2.23; N, 3.87; Br, 44.14. Found: C, 49.89; H, 2.47; N, 3.89, Br, 44.11. Crystals of this compound are light tan in color and decompose (polymerize) at temperatures above 200 °C. For example, at 210 °C the crystals turn pink in about an hour, subsequently becoming purple on further heating. The monomer is far less reactive to ^{60}Co γ radiation polymerization than DCH.

Synthesis of 1-(1′,3′,6′,8′-Tetrabromocarbazolyl)-2-propyne. 1,3,6,8-Tetrabromocarbazole was prepared as described in the literature.[10] A solution of this compound (5.02 g, 0.01 mol) in 80 mL of acetone was brought to a boil. Finely ground NaOH (0.6 g, 0.015 mol) was added to the solution and refluxed for 1 h. 2-Propynyl-1-*p*-toluenesulfonate (8.1 g, 0.04 mol) was added dropwise to the solution over 15 min, resulting in a yellow precipitate. The mixture was heated for 15 min more and then cooled to room temperature. The solid was filtered off and washed with 250 mL of ethanol and vacuum dried to constant weight. The material was recrystallized from 400 mL of ethyl acetate. A white crystalline solid was collected, mp 222–223 °C, 2.75 g (50% yield). The IR spectrum (Nujol mull) revealed the absence of an N–H absorption at 3400 cm^{-1} and showed significant absorptions at 3290, 1550, 1445, 1280, 1185, 855, 795, 720, 715, 685, 670, 645, 635 cm^{-1}. Anal. Calcd (in wt %) for $C_{15}H_7NBr_4$: C, 34.59; H, 1.35; N, 2.69; Br, 61.37. Found: C, 34.67; H, 1.39; N, 2.99; Br, 60.40.

Synthesis of Bis(1′,3′,6′,8′-tetrabromocarbazolyl)-2,4-hexadiyne (DCHBr$_8$ Monomer). A solution of 1-(1′,3′,6′,8′-tetrabromocarbazolyl)-2-propyne (2.26 g, 4 mmol) and *N,N*-dimethylformamide (75 ml) was brought to 70 °C. Copper(I) chloride (0.20 g, 1.5 mmol) and *N,N,N′,N′*-tetramethylethylenediamine (0.20 g, 1.2 mmol) were added and stirred for 70 min, forming an olive-green precipitate. The entire reaction mixture was poured into 50 mL of 0.6 N HCl. A yellow-green solid was filtered off and washed with 50 mL of 0.6 N HCl, 200 mL of water, and 50 mL of ethanol. The compound was recrystallized from 700 mL of chlorobenzene, yielding 1.19 g of white solid (50% yield), mp 270 °C dec. Except for the disappearance of the absorption at 3290 and 685 cm^{-1}, the IR spectrum (Nujol mull) is indistinguishable from that of the precursor. Anal. Calcd (in wt %) for $C_{30}H_{12}N_2Br_8$: C, 34.66; H, 1.16; N, 2.69; Br, 61.49. Found: C, 34.60; H, 1.25; N, 2.85; Br, 60.87.

Nuclear Magnetic Resonance Studies. The ^{13}C CP–MAS NMR data were obtained at room temperature on a home-built double-resonance high-power spectrometer controlled by a Nicolet 1280 data system and a 293B pulse programmer and operating at a ^{13}C frequency of 50.36 MHz. Measurements were carried out with a CP–MAS probe from Doty Scientific Inc. The 7 mm o.d. sapphire rotors were spun at the maximum speed for each sample. At lower spinning speeds some loss in relative intensity of the centerbands with respect to the spinning sidebands occurs, especially for those peaks with large chemical shift anisotropies. However, critical comparisons were made on samples run with similar spinning speeds (3.2 to 3.8 kHz). The transmitters, Amplifier Research Models 200L (for ^{13}C) and 500L (for ^{1}H), were equipped and operated with blanking pulses. ^{1}H 90° pulse lengths of 5 μs were used, corresponding to a radio frequency field strength of 1.2 mT. Cross-polarization contact times were typically 3 to 5 ms, and the Hartmann–Hahn matching condition was set with use of an adamantane standard, whose methylene peak also provided a secondary chemical shift reference at 38.56 ppm from Me_4Si.[11] High-power decoupling was applied during the acquisition period of 20 ms. The cross-polarization pulse program incorporated spin temperature inversion[12] to suppress artifacts and "flipback" of the ^{1}H magnetization into the z direction by an additional $90°_{-x}$ pulse at the end of the acquisition period. The latter procedure was helpful because of the rather long ^{1}H spin–lattice relaxation times in these apparently rather rigid samples. Further experiments were carried out in order to discriminate between protonated and nonprotonated carbon atoms, utilizing the large differences in the ^{1}H–^{13}C dipolar interactions. Adding a 60-μs delay time without decoupling after the cross-polarization period, prior to acquisition with decoupling, leads to a dephasing of the signals arising from protonated carbon atoms and thus enables the selective observation of unprotonated carbon atoms.[13] On the other hand, protonated carbon atoms can be selectively identified by using short contact times (100 μs or less), since the proton–carbon cross-relaxation times T_{C-H} for these carbon atoms are greatly reduced due to the stronger dipolar coupling. Indirect ^{1}H $T_{1\rho}$ rotating frame relaxation time measurements were made by spin-locking the protons for a variable delay time before cross-polarizing with a constant contact time of 3 ms[14] and measuring the integrated areas of the peaks (no changes in the relative intensities of peaks were observed).

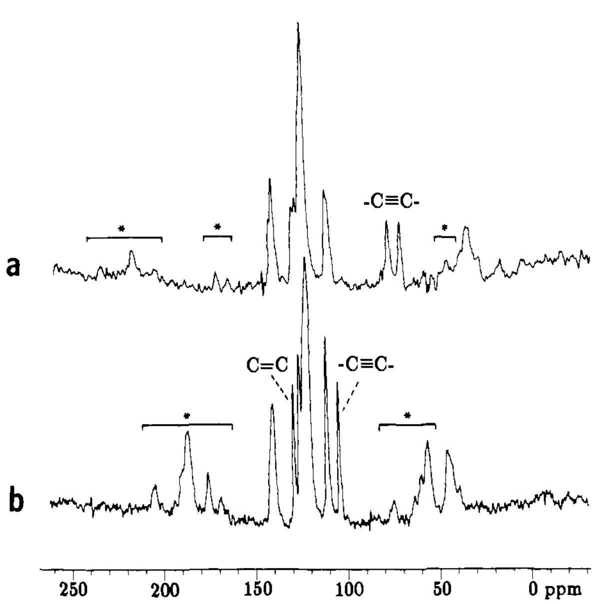

Figure 2. (a) ^{13}C CP–MAS spectrum at 50.363 MHz of DCH monomer. Spinning side bands are indicated by asterisks. The spectrum was obtained under the following conditions: spinning speed 5.0 kHz, 3 ms contact time, recycle delay 6 s (with magnetization flipback), 1108 scans. (b) ^{13}C CP–MAS spectrum at 50.363 MHz of poly-DCH. Spinning side bands are indicated by asterisks. The spectrum was obtained under the following conditions: spinning speed 3.2 kHz, 10 ms contact time, recycle delay 60 s (no magnetization flipback), 292 scans.

The free induction decays were multiplied by an exponential apodization function, equivalent to a Lorentzian line-broadening of 10–20 Hz, and were zero-filled from 1K to 4K data points prior to Fourier transformation. A "rolling base line" in some spectra was eliminated by left-shifting the free induction decay by 0–100 μs or by using a base line fit routine in the Nicolet NMC software. Integration of peak intensities was carried out using the same software. Because the needle-like crystals may have been partially oriented during packing into the rotor, we did not attempt to calculate chemical shift anisotropies from the relative intensities of spinning sidebands.

Results

Figure 2 shows the ^{13}C CP–MAS NMR spectra of the starting *N*-dicarbazolyl-2,4-hexadiyne monomer and of the polymerized material. The appearance of a new peak at 129 ppm in the spectrum of poly-DCH, resulting from the formation of a double bond, is evident from the spectra. In addition, the polymerization causes a marked downfield shift of the triple bond resonances from 68.3 and 75.0 ppm in the diacetylenic monomer to 104.3 ppm in poly-DCH. This effect is well-documented for many polyconjugated systems containing triple bonds[8,15] and has been attributed to an increasing cumulene contribution to the original "enyne" electronic structure of such systems.[8]

The above changes in the spectra are very distinct, demonstrating that ^{13}C CP–MAS NMR is a sensitive means of monitoring the solid-state polymerization of DCH. In contrast, the peak patterns in the aromatic region are very similar for monomer and polymer as well as for solid carbazole itself. Detailed assignments (see Table I) were obtained by comparison with solution state spectra[16,17] and by delayed-decoupling experiments. For carbazole, close agreement (within ±1 ppm) between the solution and solid-state chemical shifts is observed. In addition, measurements as a function of contact time (shown in Figure 3 for

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Table I. Chemical Shift Assignments (ppm) to the Individual Carbon Atoms of the Compounds under Study (See Equation 1 for Numbering)[a]

sample	C-9a,b	C-1	C-2	C-3	C-4	C-4a,b	$C=C$	$C\equiv C$	CH_2
poly-DCH	141.3	110.7	125.4	119.9	121.0	122.9	129.0	104.3	44
poly-DCH($Br_{3.0}$)	139.6	111.1	125.2	peak around 121		123.7	128.7	102.4	44
poly-DCH($Br_{3.8}$)	139.4	111.7	broad envelope around 122–123			123.9	128.5	102.2	44
poly-DCH($Br_{4.5}$)	138.7	111.4	broad envelope around 122–123			123.6	127.8	96 to 102	44
poly-DCH($Br_{6.0}$)	139	113	broad envelope around 122–123			123	128	95 to 102	44
poly-DCH($Br_{7.4}$)	139	113	broad envelope around 122–123			123			44
poly-DCH($Br_{8.2}$)	139	114	broad envelope around 122–123			123			43
carbazole	139.8	111.5	126.4	peak around 120		121.5			
3,6-dibromocarbazole	138	116	broad envelope around 122–123			122.9			
1,3,6,8-tetrabromocarbazole	very broad spectrum, assignments uncertain								
di-*N*-carbazolyl-2,4-hexadiyne	139.0	108.8 107.6	127.6 125.7	peak around 120.6		122.5		75.0 68.3	32
bis(3′,6′-dibromo-*N*-carbazolyl)-2,4-hexadiyne	137.4	109.9 106.8	broad features at 122 and 128			122.4		73.2 71.9	32
bis(1′,3′,6′,8′-tetrabromo-*N*-carbazolyl)-2,4-hexadiyne	135	broad pattern around 130				124		74	39

[a] Error limits (unless indicated otherwise by the number of significant digits) are ±0.2 ppm for unbrominated compounds, ±0.5 ppm for poly-DCH($Br_{3.0}$), poly-DCH($Br_{3.8}$), and bis(3′,6′-dibromo-*N*-carbazolyl)-2,4-hexadiyne, and ±1 ppm for the remaining compounds.

Table II. Values of T_{C-H} Measured for Various C Atoms in Poly-DCH

carbon atom	T_{C-H}/ms
triple bond	1250 ± 80
double bond	570 ± 110
C-9a,b	890 ± 60
C-1, C-8	180 ± 20
other ring-C atoms	240 ± 20

both poly-DCH and poly-DCH($Br_{3.0}$)) serve to enhance the resolution in the crowded region around 119–124 ppm. The T_{C-H} values extracted from this series of measurements are shown in Table II and conform with the expectation that the triple bond carbon atoms, being most remote from protons, cross-polarize most slowly. If, however, contact times in excess of 3 ms are used, the peak area ratios observed in poly-DCH agree reasonably well (within 10%) with those predicted from the molecular structure. An attempt to obtain a ^{13}C MAS NMR spectrum of poly-DCH using 5 μs carbon 90° pulses, high-power proton decoupling, a recycle delay of 120 s, and 12 h accumulation time was unsuccessful. This demonstrates that the ^{13}C spin–lattice relaxation times are very long and underscores the absolute necessity of using the cross-polarization technique for obtaining spectra.

The effects of bromination upon the ^{13}C CP–MAS NMR spectrum of poly-DCH are shown in Figures 4 and 6, the latter of which displays an expansion of the triple bond chemical shift region. Figure 5 shows the ^{13}C CP–MAS NMR spectra of model compounds: both carbazole and DCH monomer, and their brominated derivatives, containing either two or four Br per carbazole ring. Table I summarizes the ^{13}C chemical shift data for all of the compounds in the present study.

In order to clarify the course of this reaction, special care was taken to obtain peak areas which are approximately representative of the relative numbers of carbon atoms of a given type. To this end, we considered several potential sources of error arising from possibly unequal proton T_1, $T_{1\rho}$ relaxation times and from the different T_{C-H} cross-relaxation times[18] by performing experiments on the samples poly-DCH, poly-DCH($Br_{3.0}$), poly-DCH($Br_{6.0}$), and bis(3′,6′-dibromo-*N*-carbazolyl)-2,4-hexadiyne. The relative peak intensities in the spectrum of poly-DCH($Br_{3.0}$) did not change significantly upon increasing the recycle delay in the flipback experiment from 5 to 240 s, indicating that proton T_1's do not affect the relative quantitation under the conditions used. This result agrees with the expectation that rapid proton spin-diffusion in these samples equalizes the spin–lattice relaxation times. Likewise, the ^1H $T_{1\rho}$ values as measured by monitoring each ^{13}C peak were found to be uniform, amounting to ca. 30 ms in poly-DCH. Thus ^1H relaxation during the cross-polarization process does not contribute to any distortions of the relative intensities of the ^{13}C peaks. Contact times of 3 ms or longer were found to be necessary to obtain constant peak area ratios. Although direct measurements of ^{13}C $T_{1\rho}$ were not carried out, the values must be substantially longer than the 3 or 5 ms contact times used, since the absolute signal intensities in these samples increase up to a contact time of approximately 5 ms before beginning to decrease. The above studies confirm that, under the conditions employed, the ^{13}C CP–MAS NMR experiment can be used to monitor the course of bromination in a reasonably quantitative manner.

Figure 4 reveals a progressive marked broadening of all resonances as well as relative intensity losses for certain peaks of the polymer as the bromine content is increased. These observations are not attributable to a distribution of chemical shifts since the same behavior is seen for the brominated derivatives of carbazole and those of the DCH monomer (Figure 5). Rather, this broadening arises from the dipolar coupling of the ^{13}C nuclei to nearby bromine nuclei (^{79}Br and ^{81}Br, the only naturally occurring isotopes of bromine, both have spin $^3/_2$). Because of the large nuclear quadrupole coupling constants (which are of the order of 300 MHz in brominated aromatic compounds[19]) the dipolar coupling is not averaged to zero by magic-angle spinning, since the spins of the quadrupolar bromine nuclei are quantized primarily along the axis of the electric field gradient rather than the external magnetic field. As has been previously discussed,[20,21] a complicated powder pattern results, the actual appearance of which is determined by the dipolar and scalar coupling constants and by the ratio of the quadrupolar coupling constant relative to the Zeeman interaction. Although such powder patterns have actually been detected in favorable cases,[20] the resonance of the atom

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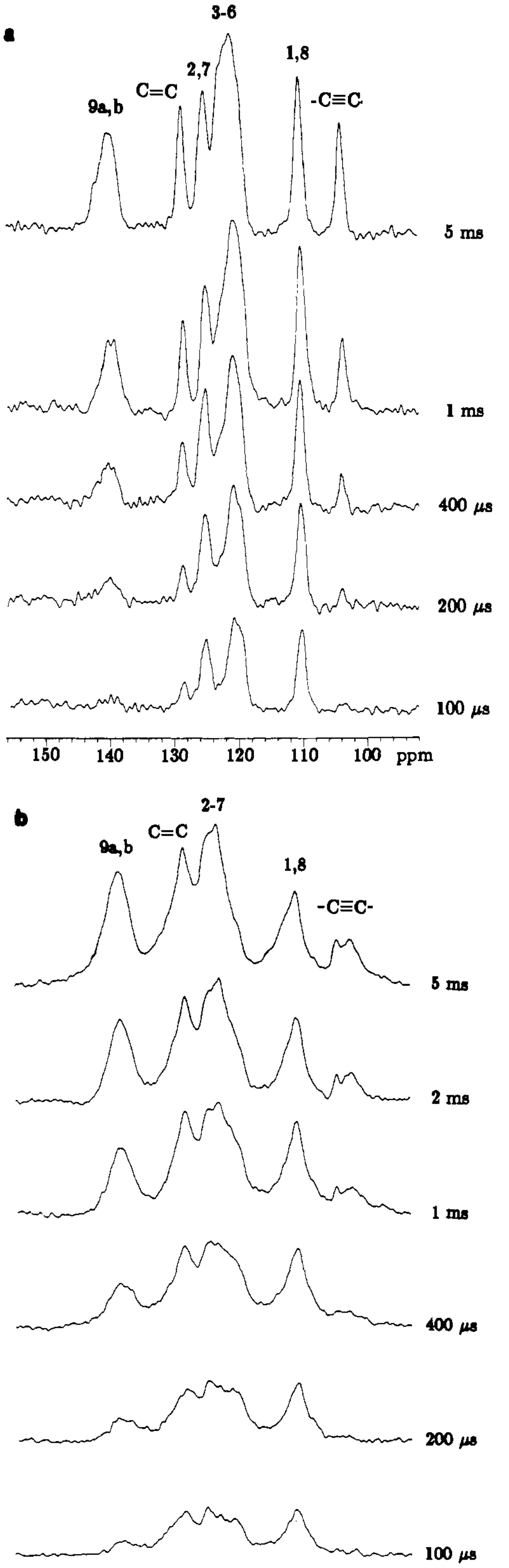

Figure 3. Expanded view of the aromatic and multiple-bond region as a function of contact time (indicated on figure) in the ^{13}C CP–MAS spectra at 50.363 MHz of (a) poly-DCH and (b) poly-DCH($Br_{3.0}$).

directly bonded to a quadrupolar nucleus may be broadened beyond detection, as has been observed for ^{13}C in a polymer containing quadrupolar chlorine nuclei.[22] For brominated compounds this effect is expected to be more severe than that for chlorinated ones because of the stronger dipolar coupling and the larger nuclear electric quadrupolar coupling constants associated with the $^{79,81}Br$ isotopes. We note that this effect would persist at the highest magnetic field strengths currently available, since the quadrupolar interaction is dominant. The experimental results obtained with the brominated model compounds (Figure 5) indicate that resonances from carbon atoms directly bonded to bromine as well as from adjacent carbon atoms are broadened to such an extent that they do not yield identifiable peaks in the spectrum. The broadening effects are found to be more severe in the brominated carbazoles than in the brominated DCH monomers, presumably because of the stronger *inter*molecular dipolar interactions in the former compounds. For this reason we believe that the brominated DCH monomers represent better model compounds for identifying the chemical changes taking place upon bromination of poly-DCH.

Finally, it should be noted that the CH_2 group and the carbon atom of the carbazole moiety bonded to nitrogen are subject to the same effect, arising from the dipolar coupling to the quadrupolar ^{14}N nucleus. However, in this case the quadrupole coupling constant is much smaller (2.16 MHz for *N*-methylpyrrole[19]), and only a moderate, asymmetric broadening of the peaks results. For these asymmetric resonances, the chemical shift was measured at the center of gravity.

Discussion

We will now discuss the changes observed in the ^{13}C CP–MAS NMR spectra in terms of the chemical reactions taking place upon bromination. Our descriptions of the bromination products imply average structures; we cannot rule out the occurrence of low levels of bromine at positions other than those specified below. Conceivable chemical reactions include electrophilic substitution on the aromatic carbazole rings, substitution at the allylic methylene group, addition to the double or triple bonds, or carbocation formation concomitant with intercalation of a bromine species without direct formation of a C–Br bond. The last possibility can be ruled out, since in contrast to studies of doped polyacetylenes[23-25] the ^{13}C spectra obtained with the present materials show no resonances at downfield positions typical of carbocationic species. We note incidentally that in the studies of polyacetylene doped with iodine[23] and bromine,[24] significant broadening effects were observed which were ascribed to a broad range of chemical shifts. We believe that our present results demonstrate that the dipolar coupling to the quadrupolar halogen nuclei may be a source of much of the resonance broadening observed in these cases.

Our results prove furthermore that bromination of the allylic methylene group does not take place, since the methylene peak remains unaffected by the reaction at all levels. Comparison of Figure 4 with the spectra of the model compounds (Figure 5) reveals that the spectral pattern in the aromatic region observed in the brominated samples closely resembles that of the 3,3′,6,6′-tetrabrominated monomer. This close resemblance is also observed in additional experiments involving delayed decoupling and variable contact times. The peaks corresponding to the 1,8-positions show only moderate broadening and are observable up to the highest bromination levels. Likewise, the observed spectra are incompatible with bromination at the 2-, 4-, 5-, or 7-positions, which are known to be chemically less reactive. These data provide strong evidence for selective bromination of the aromatic rings at the 3,6-positions.

Bromination of the carbazole group in the poly-DCH($Br_{3.8}$) sample results in a small (2 ppm) upfield shift of the acetylenic carbon resonance. As suggested by Wenz et al.,[8] the chemical shift of the triple bond resonance may be a very sensitive measure of the number of conjugated carbon bonds. Thus, the slight upfield shift observed in the brominated polymer could possibly reflect

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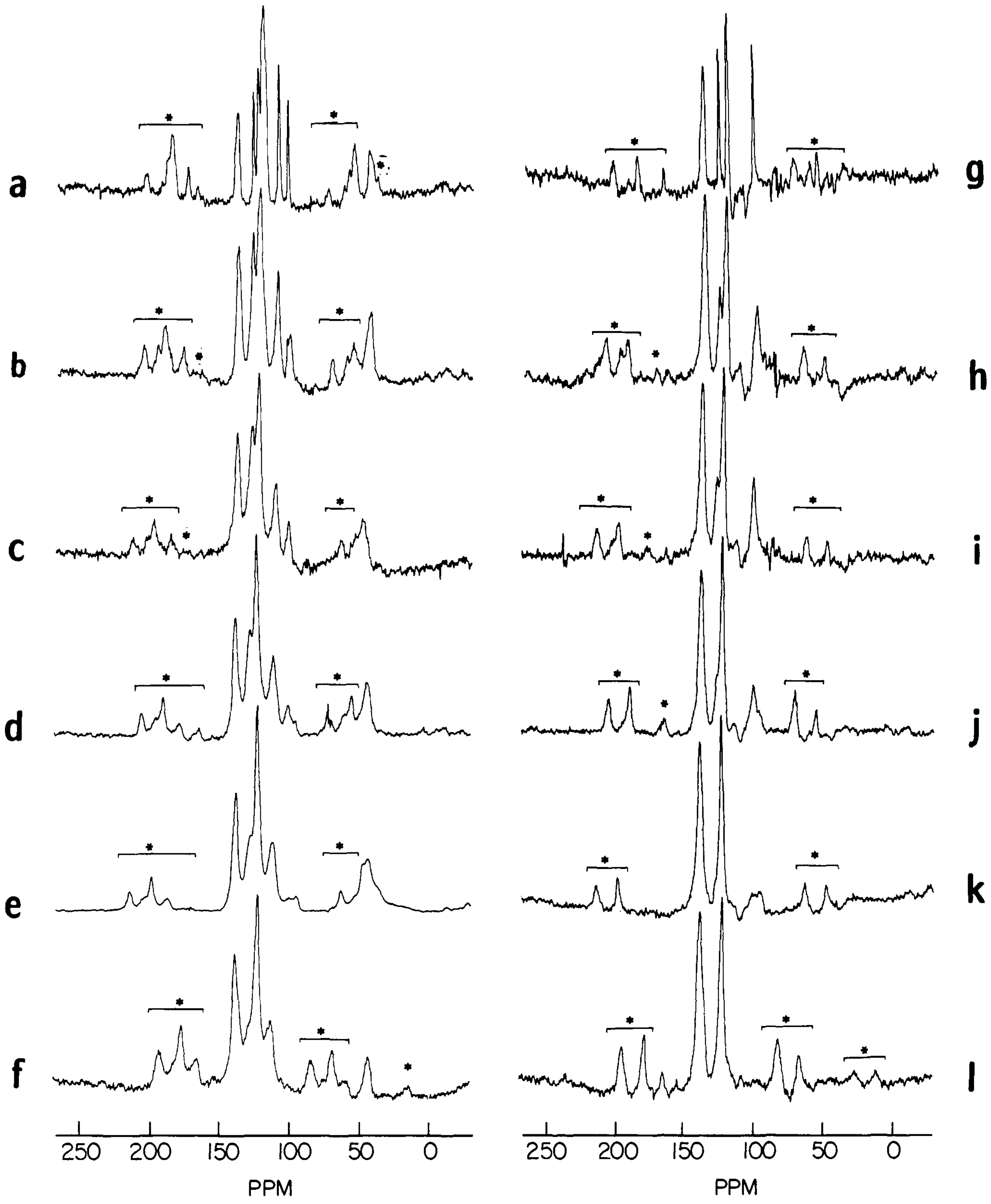

Figure 4. ^{13}C CP–MAS spectra at 50.363 MHz of poly-DCH and its brominated reaction products. Spinning side bands are indicated by an asterisk. (a) Pristine poly-DCH: spinning speed 3.2 kHz, 10 ms contact time, recycle delay 60 s (no magnetization flipback), 292 scans. (b) Poly-DCH($Br_{3.0}$): spinning speed 3.4 kHz, 5 ms contact time, recycle delay 5 s (with magnetization flipback), 1444 scans. (c) Poly-DCH($Br_{3.8}$): spinning speed 3.9 kHz, 5 ms contact time, recycle delay 20 s (no magnetization flipback), 230 scans. (d) Poly-DCH($Br_{4.5}$): spinning speed 3.4 kHz, 3 ms contact time, recycle delay 5 s (with magnetization flipback), 1280 scans. (e) Poly-DCH($Br_{6.0}$): spinning speed 3.8 kHz, 5 ms contact time, recycle delay 5 s (with magnetization flipback), 8220 scans. (f) Poly-DCH($Br_{8.2}$): spinning speed 2.8 kHz, 5 ms contact time, recycle delay 5 s (with magnetization flipback), 567 scans. (g) Pristine poly-DCH: spinning speed 3.3 kHz, 10 ms contact time, delayed decoupling interval 60 μs, recycle delay 60 s (no magnetization flipback), 252 scans. (h) Poly-DCH($Br_{3.0}$): spinning speed 3.5 kHz, 3 ms contact time, delayed decoupling interval 60 μs, recycle delay 5 s (with magnetization flipback), 1000 scans. (i) Poly-DCH($Br_{3.8}$): spinning speed 3.9 kHz, 5 ms contact time, delayed decoupling interval 60 μs, recycle delay 60 s (no magnetization flipback), 228 scans. (j) Poly-DCH($Br_{4.5}$): spinning speed 3.4 kHz, 3 ms contact time, delayed decoupling interval 60 μs, recycle delay 5 s (with magnetization flipback), 1718 scans. (k) Poly-DCH($Br_{6.0}$): spinning speed 3.8 kHz, 5 ms contact time, delayed decoupling interval 60 μs, recycle delay 5 s (with magnetization flipback), 1224 scans. (l) Poly-DCH($Br_{8.2}$): spinning speed 2.8 kHz, 5 ms contact time, delayed decoupling interval 60 μs, recycle delay 5 s (with magnetization flipback), 1092 scans.

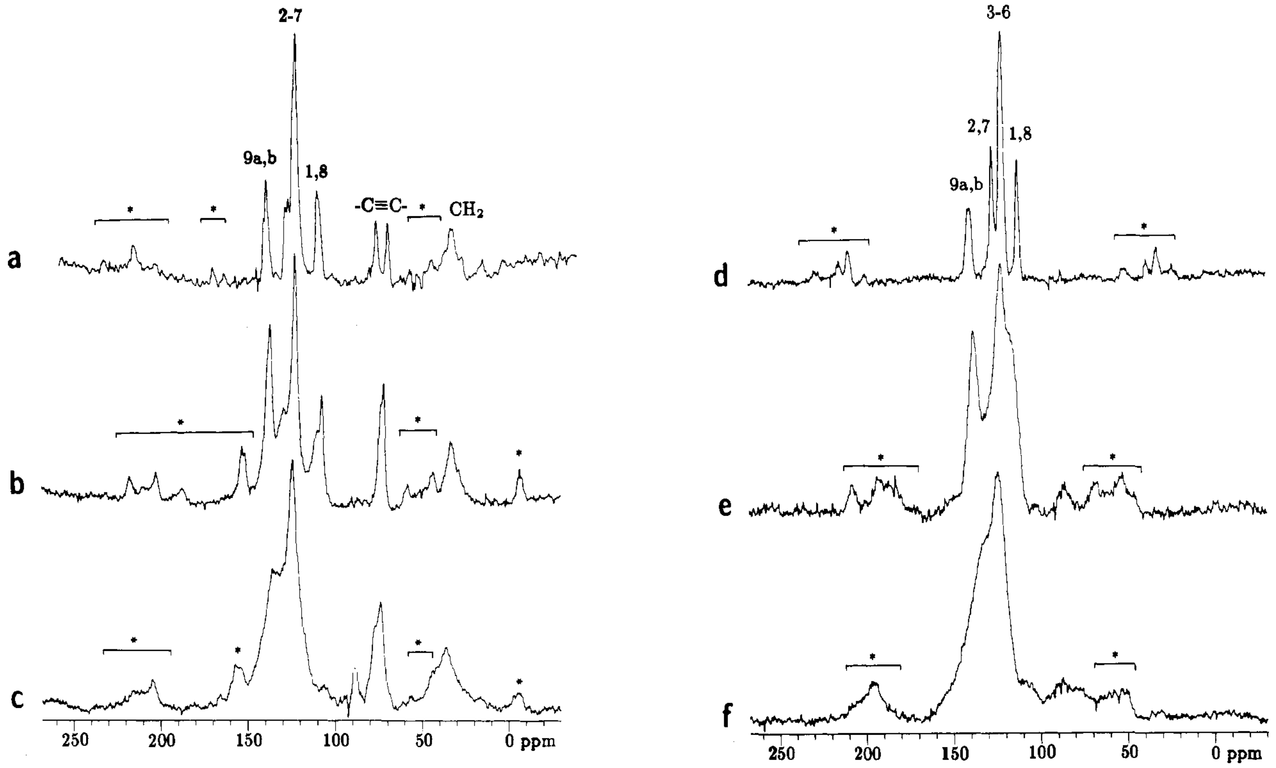

Figure 5. ^{13}C CP-MAS spectra at 50.363 MHz of monomeric model compounds. Spinning side bands are indicated by an asterisk. (a) *N*-Carbazolyl-2,4-hexadiyne: spinning speed 5 kHz, 3 ms contact time, recycle delay 6 s (with magnetization flipback), 1108 scans. (b) Bis(3′,6′-dibromo-*N*-carbazolyl)-2,4-hexadiyne: spinning speed 4.0 kHz, 10 ms contact time, recycle delay 60 s (without magnetization flipback), 172 scans. (c) Bis(1′,3′,6′,8′-tetrabromo-*N*-carbazolyl)-2,4-hexadiyne: spinning speed 4.2 kHz, 3 ms contact time, recycle delay 5 s (with magnetization flipback), 1120 scans. (d) Carbazole: spinning speed 4.4 kHz, 5 ms contact time, recycle delay 4 s (with magnetization flipback), 227 scans. (e) 3,6-Dibromocarbazole: spinning speed 3.5 kHz, 10 ms contact time, recycle delay 20 s (without magnetization flipback), 60 scans. (f) 1,3,6,8-Tetrabromocarbazole: spinning speed 3.6 kHz, 10 ms contact time, recycle delay 20 s (without magnetization flipback), 440 scans.

a decrease in the average conjugation length, as a result of some minor degree of attack on the backbone even at low bromination levels. Alternative explanations cannot be ruled out, however. The acetylenic region of the DCH($Br_{3.0}$) spectrum contains peaks in both the original position and the upfield-shifted position with an area ratio of roughly 1:3 (see Figure 6). This result suggests that the reaction does not produce a polymer with a statistical distribution of carbazole rings containing zero, one, and two bromine substituents but rather results in a heterogeneous mixture of unbrominated polymer and polymer containing completely dibrominated carbazole rings.

Up to a level of 4 Br per repeat unit, bromination appears to be confined to the carbazole moiety, occurring selectively at the 3,6-positions. Four Br per repeat unit are required to completely brominate these sites. Above this level the absorption pattern assigned to the carbazole moiety remains unchanged, indicating that no further ring bromination takes place. Instead, the peaks associated with the double and triple bonds are observed to weaken significantly. Although the olefinic and especially the acetylenic carbon atoms are remote from protons, and hence cross-polarize rather slowly, the experiments discussed in the previous section establish that the spectra obtained should be reasonably quantitative. It is worth noting that these unsaturated carbons are most likely cross-polarized by the methylene protons, which are two and three bonds distant from the double and triple bonds, respectively. Since the NMR results show that these protons are retained during bromination, cross-polarization should occur even at the highest bromination levels. The weakened intensity of these resonances observed at a bromination level of 6 Br per repeat unit (Figure 4) is therefore likely due to the addition of Br_2 to the multiple bonds. Since the results on the model compounds show that bromination renders the ^{13}C resonances of both the directly bonded as well as of the adjacent carbon atoms unobservable, these results are consistent with addition to either double or triple bonds or a combination of both. The resonances could also disappear as a result of the dispersion of chemical shift arising from any disruption of the backbone conjugation. However, the coppery-bronze color of this material indicates the preservation of a conjugated backbone, and the observation of additional features in the region of double bond stretching in the resonance Raman spectrum[26] is most compatible with extensive conversion of the triple bond to a Br—C=C—Br moiety. This addition process would retain the polyconjugation, thus converting the polydiacetylene structure to a mixed polyacetylene structure. This reaction would consume two Br atoms per repeat in addition to the four Br consumed by carbazole substitution, in agreement with the experimentally observed stoichiometry poly-DCH($Br_{6.0}$). While this seems to be the preferred reaction, Figure 4e,k and 6 do reveal some absorption in the triple bond region. The upfield character of this broadened resonance may indicate some decrease in the average conjugation length, caused by the formation of single bonds along the backbone.

Levels of bromination above six Br per repeat unit have only been achieved under more vigorous conditions (refluxing). Other results to be published[26] indicate that reaction under these conditions proceeds in a different manner, since these highly brominated products cannot be obtained by further reaction of polymers containing 3–6 Br per repeat. The carbazole region in the CP–MAS spectrum closely resembles that of $DCHBr_4$ monomer rather than that of $DCHBr_8$ monomer, indicating that even at this high bromination level the attack upon the carbazole moiety in this polymer has been limited to the 3,6-positions (4 Br/repeat unit). Since only two additional Br can be added to (the triple bond of) the backbone while preserving polyconjugation, the stoichiometry of 7–8 Br per repeat implies that extensive disruption of polyconjugation in the backbone must have occurred. (In addition to the 4 Br per repeat which react with the carbazole ring, total saturation of the backbone would consume an additional 6 Br per repeat.) The straw-colored appearance of the products

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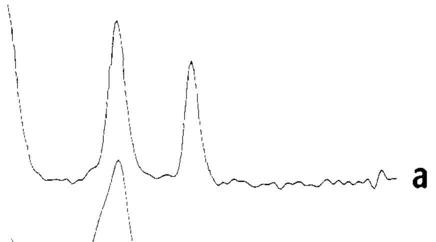
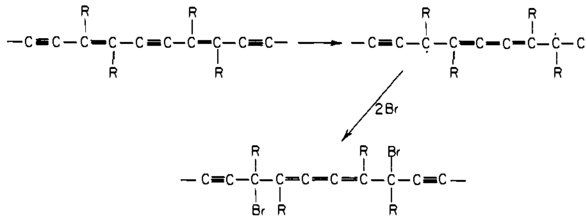


Figure 6. Expanded view of the triple bond region in the spectra of (a) poly-DCH, (b) poly-DCH($Br_{3.0}$), (c) poly-DCH($Br_{3.8}$), (d) poly-DCH($Br_{4.5}$), (e) poly-DCH($Br_{6.0}$), and (f) poly-DCH($Br_{8.2}$). Each of these plots was scaled separately with the respective peak height of the C-1,8 resonance.

is indeed indicative of a loss of conjugation. Another interesting feature, especially prominent in these highly brominated samples, is the presence of two additional weak peaks at 165.5 and 154.5 ppm.[27] These chemical shifts are typical of the values found for β-carbon atoms in liquid[28] and solid[29] butatriene samples. This finding is interesting in view of a possible representation of the polydiacetylene backbone structure which involves butatriene units associated with conjugation defects.[29] The solid-state NMR spectrum of the parent poly-DCH does not show butatriene peaks, implying that any conjugation defects are delocalized. In contrast, interaction between bromine and the backbone may lead to a localization of these conjugation defects which can then act as traps for the halogen reagent (see eq 2).[30]

The resulting butatriene structures could account for the two peaks at 165.5 and 154.5 ppm in the CP–MAS spectra mentioned above.



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Conclusions

The reaction of poly-DCH crystals with liquid bromine represents the rare case of a solid-state transformation of a polydiacetylene. Cross-polarization/magic-angle spinning ^{13}C NMR techniques can identify carbon atoms which are further than two bonds away from bromine atoms and allow one to monitor the course of this reaction under approximately quantitative conditions. Utilizing studies of model compounds and liquid state spectra we conclude that the bromine reagent selectively attacks the 3,6-positions on the aromatic rings of the carbazole moiety, forming a polymer with 4 Br/repeat unit. Further bromination of the ring does not take place even at the highest bromination levels. Instead, the results indicate that addition to acetylenic and/or olefinic carbon atoms takes place. For the material of composition poly-DCH($Br_{6.0}$), the results are consistent with preferred conversion of the polydiacetylene structure to a mixed polyacetylene structure having significant crystalline order. Further NMR evidence concerning the bromination of multiple bonds in the polyconjugated polymer backbone could be obtained by monitoring the carbon–carbon bond lengths with use of ^{13}C nutation NMR in a manner similar to that described recently for polyacetylenes.[31]

We attribute the unusual solid-state reactivity of poly-DCH compared to other polydiacetylenes to crystal morphology and to the fact that the highest filled level (HOMO) of carbazole is closer to the top of the polydiacetylene valence band than is the case in corresponding materials with other side chains. The observation that the carbazole group is completely brominated at the 3,6-positions prior to the reaction with the multiple bonds of the backbone underscores the control of this reaction by anisotropic diffusion: bromine likely diffuses parallel to the polymer chains via defects, and at least initially only between the columns of the polymer. The initial reaction takes place at the carbazole groups, which are exposed to these diffusion pathways. In contrast, the backbone is well-shielded due to the bulkiness of the carbazole side chains, and it appears to be attacked by bromine only after the crystalline order has been perturbed during the initial ring bromination. Finally, we note that with one exception[32] it has not proven possible to obtain highly crystalline polyacetylenes by solid-state polymerization. Hence, the above reactions provide an intriguing approach to the preparation of novel, highly crystalline polyacetylene materials.

Acknowledgment. The NMR data were obtained at the Southern California Regional NMR Facility, supported by NSF Grant CHE84-40137.

Registry No. DCH (homopolymer), 65461-63-4; DCH (SRU), 74977-07-4; $DCHBr_4$, 102036-44-2; $DCHBr_8$, 105729-56-4; 4-$H_3CC_6H_4SO_2CH_2C{\equiv}CH$, 14790-33-1; 1-(3′,6′-dibromocarbazolyl)-2-propyne, 105729-54-2; 3,6-dibromocarbazole, 6825-20-3; *N*-propargyl-3,6-dibromocarbazole, 106-96-7; 1-(1′3′,6′,8′-tetrabromocarbazolyl)-2-propyne, 55119-09-0; 1,3,6,8-tetrabromocarbazole, 105729-55-3.

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[27] In addition, a weak resonance around 108 ppm is observed in the delayed decoupling spectra. This chemical shift is typical for the α-C atom of butatrienes.

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