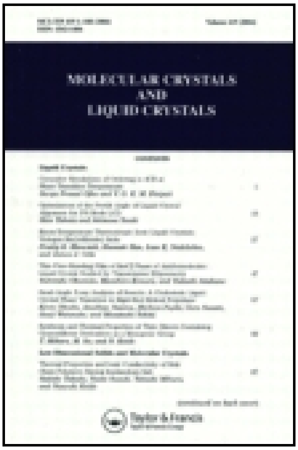

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Synthesis and characterization of bromine substituted polyacetylene, $[CH_{1-y}Br_y]_x$

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SYNTHESIS AND CHARACTERIZATION OF BROMINE SUBSTITUTED POLYACETYLENE, $[CH_{1-y}Br_y]_x$

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When ca. 85% cis films of the semiconducting polymer, polyacetylene, $(CH)_x$, are first doped with bromine and then partly dehydrobrominated at 150°C, substitution of H by Br occurs to yield new semiconducting polymers of general composition $[CH_{1-y}Br_y]_x$, where y=0.003-0.23. These films have been studied using electron paramagnetic resonance (EPR), dynamic nuclear polarization (DNP), and Raman spectroscopic techniques. EPR results indicate that with an increase in bromine substitution, the linewidth (ΔH_{pp}), g-value, and homogeneity of the samples increase. This is consistent with DNP results which suggest a decrease in the diffusion coefficient of unpaired spins as the bromine substitution level increases. Raman results are consistent with bromine substitution and indicate that essentially no change in conjugation length occurs when H is substituted by Br.

INTRODUCTION

Polyacetylene is the simplest possible organic polymer, and is therefore of special fundamental interest. We have shown previously that it can be prepared in either the cis- or trans-forms as silvery, flexible, high-quality films which can be treated with either n- or p-type dopants to yield a series of semiconductors, which at higher dopant levels are converted into organic metals.[1,2] In principle, the hydrogen atoms can be replaced either partially or completely by organic, inorganic, or organometallic groups to yield a wide range of substituted derivatives having the polyacetylene backbone. In addition, a large variety of organic metals and semiconductors having different chemical and physical properties should, in principle, be obtainable by doping these derivatives. In this way, chemical substitution should permit controlled modification of physical parameters such as band gap, conductivity, etc.

We have reported previously the successful synthesis of bromine substituted polyacetylene by thermal dehydrobromination of cis-$(CH)_x$ films doped with bromine to the metallic regime.[3] Up to ca. 20% of the hydrogen atoms in $(CH)_x$ were replaced by bromine by this procedure. These films were reported to be golden, relatively flexible p-type semiconductors of approximate composition $[CH_{1-y}Br_y]_x$, where $[(1-y)+y]\sim0.82-0.98$. It was believed that some cross-linking between chains and/or allene or alkyne formation within a chain had occurred during the dehydrobromination since the sum of (1-y) and y did not equal 1.00. These films could be doped with I_2 or AsF_5 vapor to give relatively flexible films conducting in the metallic regime.

RESULTS AND DISCUSSION

We report here a modified thermolysis procedure utilized in preparing films of $[CH_{1-y}Br_y]_x$. Ca. 85% cis-$(CH)_x$ films were treated with Br_2 vapor (≤10 Torr) at room temperature to yield bright lustrous purple to green films of metallic $[CHBr_z]_x$ ($z\sim0.02-0.46$), as determined by weight uptake of Br. These films, derived from 10-20 mg of $(CH)_x$, were then heated under static vacuum at 145-150°C in a ca. 100 ml Pyrex glass tube for a period of 3-3.5 minutes, and then cooled to room temperature for approximately five minutes. The evolved gases (mainly HBr with a trace of Br_2) were thus allowed to intimately mix with the film throughout the procedure.

The samples of $[CH_{1-y}Br_y]_x$ ($y\sim0.003-0.23$) thus obtained have values of $[(1-y)+y]\sim0.99\pm0.02$, indicative of essentially zero cross-linking and/or allene or alkyne formation within experimental accuracy, as can be seen in Table I.

TABLE I Composition[a] of Samples of $[CH_{1-y}Br_y]_x$ Having Various Degrees of Bromine Substitution

$[CH_{1-y}Br_y]_x$	(1-y)+y
$[CH_{0.81}Br_{0.25}]_x$	1.06
$[CH_{0.77}Br_{0.23}]_x$	1.00
$[CH_{0.81}Br_{0.19}]_x$	1.00
$[CH_{0.83}Br_{0.14}]_x$	0.97
$[CH_{0.87}Br_{0.14}]_x$	1.01
$[CH_{0.87}Br_{0.13}]_x$	1.00
$[CH_{0.85}Br_{0.12}]_x$	0.97
$[CH_{0.87}Br_{0.11}]_x$	0.98
$[CH_{0.86}Br_{0.11}]_x$	0.97
$[CH_{0.94}Br_{0.06}]_x$	1.00
$[CH_{0.94}Br_{0.05}]_x$	0.99

[a] Determined by initial weight uptake of Br and subsequent weight loss of HBr.

These films are somewhat more flexible than films obtained in earlier procedures. Raman and EPR studies show that they have the trans configuration. In addition, films of $[CH_{1-y}Br_y]_x$ prepared in this manner have similar conductivity and redoping properties to those described earlier.[3] For example, a dark golden film of composition $[CH_{0.94}Br_{0.05}]_x$ (as determined by initial weight uptake of Br and subsequent weight loss of HBr) shows a room temperature conductivity of 8.5×10^{-5} $ohm^{-1}cm^{-1}$, indicative of its semiconductor nature. Upon doping with I_2 vapor and subsequent pumping, a shiny silver-black film of composition $[CH_{0.94}Br_{0.05}I_{0.16}]_x$ (composition determined by weight uptake of I) is obtained. This has a conductivity (in the metallic regime) of 4.9 $ohm^{-1}cm^{-1}$ at room temperature.

Preliminary EPR studies performed on films of $[CH_{1-y}Br_y]_x$ prepared using earlier procedures indicated the existence of two superimposed signals. This was attributed to inhomogeneity in the polymer fibrils, in which some chains were believed to have undergone heavy bromine substitution, whereas others remained essentially pure $(CH)_x$.

The new procedure described above, however, yields a single, essentially symmetric EPR signal using an X-band spectrometer (10 GHz). Figure 1, for example, shows the EPR spectrum obtained for a film of composition $[CH_{0.77}Br_{0.23}]_x$, with trans-$(CH)_x$ as a reference. Comparison of these spectra indicate an increase in linewidth (ΔH_{pp}) from 0.73 G in

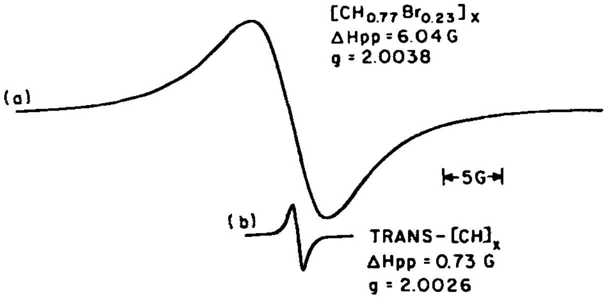

FIGURE 1 EPR spectra (room temperature) at 10 GHz of (a) bromine substituted $[CH_{0.77}Br_{0.23}]_x$; (b) trans-$(CH)_x$ reference

trans-$(CH)_x$ to 6.04 G in $[CH_{0.77}Br_{0.23}]_x$. In addition,[4] the g-value shifts, from 2.0026 in the case of trans-$(CH)_x$ to 2.0038 in the bromine substituted film. The shift in g-value is further verified in Figure 2, in which trans-$(CH)_x$ is taped on the outside of the EPR tube containing the $[CH_{0.77}Br_{0.23}]_x$, thus providing simultaneous measurement of both materials. The spectrum obtained is consistent with an overlap of two signals having different g-values. Samples of $[CH_{1-y}Br_y]_x$ with lower bromine substitution yield linewidths and g-values intermediate in value, as can be seen in Table II.

Two conclusions can be drawn from the results in Table II: (1) as the bromine content increases, the g-value increases in a direction away from that of the free-electron spin-only value of 2.0023. Spin-orbit coupling between the odd electron and covalently bound bromine, which has a relatively large spin-orbit coupling constant as compared to hydrogen, is consistent with this shift in g-value;[5] and (2) there is an overall tendency for the linewidth to broaden with increasing bromine substitution. This is consistent with strong spin-orbit coupling due to the Br atoms, which results in a strong decrease of the electronic relaxation time with a consequent increase in linewidth.[6] It is also consistent with a decreased electron mobility in $[CH_{1-y}Br_y]_x$, as compared to trans-$(CH)_x$. This could be caused by an increased localization of spin on a bromine $2p\pi$ orbital. Which of these two sources of broadening of the linewidth is more important is not yet clear.

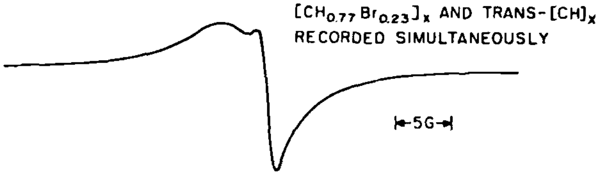

FIGURE 2 EPR spectra at 10 GHz of bromine substituted $[CH_{0.77}Br_{0.23}]_x$ and trans-$(CH)_x$ recorded simultaneously at room temperature

TABLE II Summary of X-Band EPR Spectra for $[CH_{1-y}Br_y]_x$

$[CH_{1-y}Br_y]_x$	ΔH_{pp}	g-Value
$[CH_{0.77}Br_{0.23}]_x$	6.04G	2.0038
$[CH_{0.81}Br_{0.19}]_x$	6.32G	2.0035
$[CH_{0.83}Br_{0.14}]_x$	3.54G	2.0033
$[CH_{0.87}Br_{0.14}]_x$	2.30G	2.0030
$[CH_{0.87}Br_{0.13}]$	2.89G	2.0030
$[CH_{0.87}Br_{0.11}]_x$	2.67G	2.0028
$[CH_{0.86}Br_{0.11}]_x$	2.15G	2.0028
$[CH_{0.94}Br_{0.05}]$	1.53G	2.0027
trans-$(CH)_x$	0.73G	2.0026

In order to gain further information concerning the homogeneity of bromine substitution, the EPR spectra were further examined at a Zeeman frequency of 35 GHz (Q-band), where the resolution is significantly better than at 10 GHz. The shape and symmetry of spectra at this higher frequency are particularly useful diagnostic means for detecting even small degrees of non-homogeneity. Figure 3 shows the EPR spectra at 35 GHz of $[CH_{1-y}Br_y]_x$ with (a) y=0.06 and (b) y=0.25. For the lightly substituted sample, the lineshape is not symmetric and the peak to peak linewidth of the spectrum (2.5G) is considerably greater than the width (1.7G) obtained at 10 GHz (Table III).This could be caused by a g anisotropy with an axial symmetry or by the superposition of many lines with different widths and g values due to non-homogeneous substitution. It is not possible to find an axial anisotropic g-value from which spectra may be derived which fit both the 35 GHz and 10 GHz experimental spectra. Hence, the lineshape and width are not caused by anisotropy of g and must be caused by some non-homogeneity of bromine substitution.

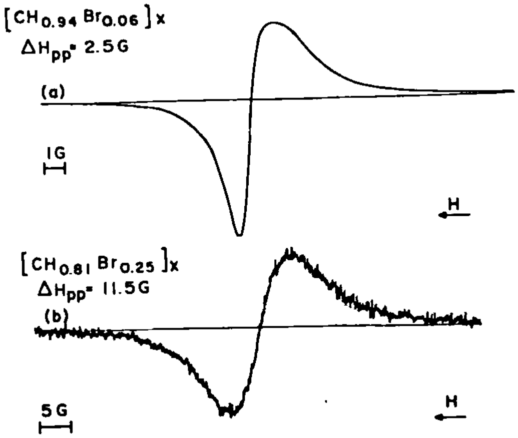

FIGURE 3 EPR spectra at 35 GHz of (a) bromine substituted $[CH_{0.94}Br_{0.06}]_x$; (b) bromine substituted $[CH_{0.81}Br_{0.25}]_x$

TABLE III Comparison of X-Band and Q-Band EPR Spectra for $[CH_{1-y}Br_y]_x$

$[CH_{1-y}Br_y]_x$	ΔH_{pp}	
	X-Band	Q-Band
$[CH_{0.94}Br_{0.06}]_x$	1.7G	2.5G
$[CH_{0.85}Br_{0.12}]_x$	3.0G	4.7G
$[CH_{0.81}Br_{0.25}]$	6.9G	11.5G

The greater symmetry of the line in the more highly substituted sample (y=0.25) shows that this material is more homogeneous; however, the broadeneing of the line makes it difficult to determine precisely the degree of homogeneity. This conclusion is consistent with the fact that highly substituted samples, which are obtained from highly doped films, are expected to be more homogeneous than lightly substituted ones which require shorter doping times with a consequent inhomogeneous distribution of the dopant.

In order to gain information about the variation of the diffusion coefficient (D_{11}) of the spins along the chains, dynamic nuclear polarization (DNP) experiments were performed. In 1-D systems, the increase of the nuclear signal (A) of protons obtained by saturating the electronic levels (Overhauser effect) depends on D_{11}. Thus,

$$A = K \frac{(A-B)R(\omega_e)}{(A+B)R(\omega_e)+CR(\omega_n)} \qquad (1)$$

where A, B, and C are related to the scalar and dipolar hyperfine constants, ω_n and ω_e are the nuclear and electronic Zeeman frequencies, respectively, and $R(\omega)$ is the spectral density function of the electronic spins. In such systems,

$$R(\omega) = k \frac{1}{\sqrt{D_{11}\omega}}. \qquad (2)$$

In the present (room temperature) study, DNP measurements were made at

$$\omega_e/2\pi = 9.6 \text{ GHz} \qquad (3)$$

corresponding to

$$\omega_n/2\pi = 14.574 \text{ MHz} \quad (4)$$

using the apparatus previously described.[7] The variation of A as a function of the bromine substitution level is given in Figure 4. We observe a strong decrease of the Overhauser

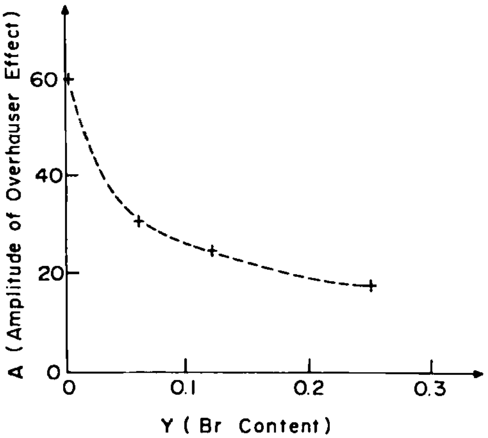

FIGURE 4 Amplitude of the Overhauser effect as a function of bromine content y

effect as compared to that observed in $(CH)_x$, even at low levels of substitution. It was found that $A \approx 60$ for $(CH)_x$ and $A \approx 30$ for $[CH_{0.94}Br_{0.06}]_x$. For small values of y, we can assume that the constants A, B, and C of equation (1) are essentially the same as in $(CH)_x$. Therefore, the DNP results suggest that in bromine substituted polyacetylene, D_{11} decreases as y increases. Additional experiments involving the proton nuclear spin lattice relaxation time (T_1) as a function of frequency are currently in progress. It appears that the decrease in D_{11} is due to the bromine substitution *per se* and not to any decrease in conjugation length during the substitution process since the Raman studies described below show that no significant change in conjugation length occurs during bromine substitution.

Raman scattering experiments were performed on thermally isomerized trans-$(CH)_x$, bromine doped cis-$(CH)_x$ (i.e., $[CHBr_z]_x$), and bromine substituted $(CH)_x$ (i.e., $[CH_{1-y}Br_y]_x$). Raman studies are useful in determining the extent of conjugation in a $(CH)_x$ chain. The extent of conjugation should not be confused with the length of a $(CH)_x$ chain. Thus, defect sites in a given $(CH)_x$ chain, caused by, for example, an unpaired spin on a carbon atom can cause a break in the conjugation without causing a break in the chain, in which all carbon atoms are joined by σ bonds.

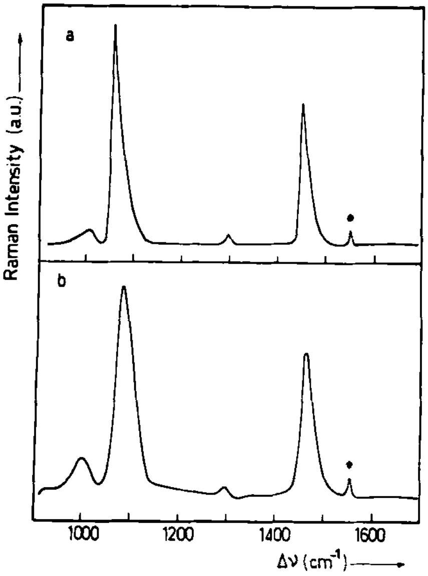

FIGURE 5 Raman spectra for $\lambda_{exc.}$=676.4nm taken at T=78 K of (a) trans-$(CH)_x$ thermally isomerized for 1 hour at 140°C under vacuum; (b) bromine doped $[CHBr_{0.17}]_x$.
(*) line originating from liquid nitrogen coolant

Figure 5 shows Raman spectra of both trans-$(CH)_x$ and $[CHBr_{0.17}]_x$. The latter sample (doped to the metallic regime) shows a spectrum very similar to trans-$(CH)_x$ (bands at 1064 cm^{-1} and 1457 cm^{-1}) with two main bands at 1084 cm^{-1} and 1464 cm^{-1} [8,9] for the excitation wavelength λ=676.4 nm. In doping the sample, we have achieved complete isomerization with a decrease in the relative number of long sequences of conjugated CH groups as compared to the trans reference. The lines characteristic of the cis isomer are no longer observable. This can be deduced from the change in shape and frequency of the two bands.[10,11] The very close similarity between the spectra of trans-$(CH)_x$ and $[CHBr_{0.17}]_x$ may be due to resonance enhancement of small amounts of trans sequences which are doped to only an insignificant extent.

Four different bromine substituted samples (i.e., $[CH_{1-y}Br_y]_x$) have been studied with y=0.003, 0.05, 0.11, and 0.23. Raman spectra were recorded for several excitation wavelengths in the range 457.9 nm to 676.4 nm. The most significant results were obtained for λ=676.4 nm, as shown in Figure 6. For y=0.003, the two Raman bands are observed at

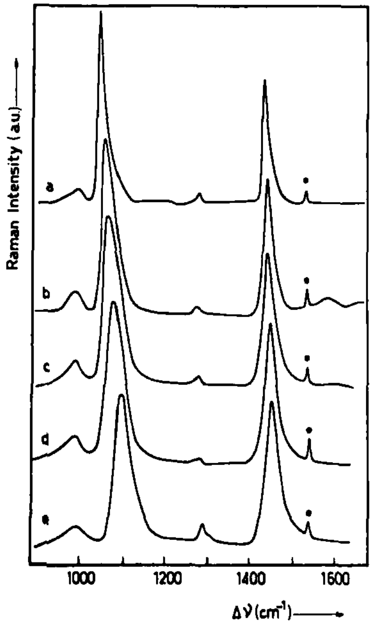

FIGURE 6 Raman spectra for λ_{exc}=676.4 nm taken at T=78 K of (a) trans-$(CH)_x$ as in Figure 5(a); (b) bromine substituted $[CH_{0.982}Br_{0.003}]_x$; (c) bromine substituted $[CH_{0.94}Br_{0.05}]_x$; (d) bromine substituted $[CH_{0.87}Br_{0.11}]_x$; (e) bromine substituted $[CH_{0.77}Br_{0.23}]_x$
(*) line originating from liquid nitrogen coolant

1076 cm^{-1} and 1460 cm^{-1}. It can be seen that the low frequency side of each band rises quite sharply as compared to the bromine doped $[CHBr_{0.17}]_x$ described above (see Figure 5). This result indicates a large concentration of long sequences of conjugated CH groups in the bromine substituted $[CH_{0.982}Br_{0.003}]_x$. As the substitution level y increases from 0.003 to 0.23, the high frequency band (1460 cm^{-1}) does not change in frequency. At the same time, however, the low frequency band shifts gradually from 1076 cm^{-1} to 1104 cm^{-1}. For smaller excitation wavelengths (457.9 nm and 514.5 nm), which give information about short sequences of conjugated CH groups, insignificant changes are observed as the substitution level varies.

The high frequency (1460 cm^{-1}) Raman band is mainly assigned to the carbon-carbon double bond (C=C) stretching vibration, while the low frequency band (1076 cm^{-1}) is a mixture of the C=C and C-C stretching modes, and the carbon-hydrogen (C-H) bending mode.[11] The fact that no change in frequency occurs for the high frequency (1460 cm^{-1}) Raman band as we increase the substitution level from y=0.003 to 0.23 indicates that no significant change in conjugation length or introduction of cross-linking involving sp^3 hybridized C atoms has occurred during replacement of H by Br. In addition, the observation that the low frequency (1076 cm^{-1}) Raman band moves to higher frequencies on Br substitution with increasing Br content, as shown in Figure 6, is believed to be due to a relatively long range effect of the C-Br bond upon the C-H bending mode.

CONCLUSION

In conclusion, EPR, DNP, and Raman results provide supportive evidence for bromine substitution of hydrogen in $(CH)_x$. The shape of the EPR spectra at 10 GHz suggest that bromine substitution is homogeneous at all substitution levels; however, studies at 35 GHz indicate non-homogeneity, particularly at lower levels of substitution. DNP studies suggest that the diffusion coefficient of unpaired spins in $[CH_{1-y}Br_y]_x$ decreases as bromine substitution increases. The Raman studies show that the modified thermolysis procedure described in this paper produces films of Br-substituted $(CH)_x$ with essentially no change in conjugation length. Detailed spectral and electronic studies of this new polyacetylene derivative are underway.

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