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^{13}C NMR and ESR Studies on a Polydiacetylene Having Acetylenic Carbons in the Side Chains

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The ^{13}C NMR spin-lattice relaxation times and ESR spectra were measured for a polydiacetylene obtained by the solid-state polymerization of a tetrayne with n-$C_{14}H_{29}$ alkyl substituents (14-4A-14). Poly(14-4A-14) has two different side chains. One side chain contains two conjugated acetylenic bonds directly bound to the main backbone conjugated system; the other is an alkyl chain. Although the unpaired electron density of poly(14-4A-14) measured by ESR is less than that in *trans*-polyacetylene, paramagnetic effects may contribute to the long ^{13}C relaxation times of unsaturated carbons, which provides insight concerning the π-electron structure on the conjugated system.

Polydiacetylenes (PDA's) have received considerable attention due to the superior third-order nonlinear optical properties[1—5] and the special π-electron structures on the conjugated chain. PDA's having acetylenic moieties in the side chains directly bound to the backbone chain are a new class of PDA's,[6—8] and perfect π-conjugation between the main and side chains can be expected. We have reported that a triyne and tetraynes with long alkyl substituents are polymerized to produce PDA's, where one substituent contains an acetylenic moiety directly bound to the main chain; another is an alkyl chain. The solid-state polymerizations for these monomers always proceed in the scheme of 1,4-addition. Since these PDA's are insoluble, the structures were determined by solid-state high-resolution ^{13}C NMR spectroscopy. Among the PDA's, the PDA with a diacetylenic substituent obtained from the tetrayne with C_{14} alkyl chains (14-4A-14) could be reacted with the side-chain diacetylenic moieties by a thermal treatment.[7] The schematic representation of the two-step solid-state polymerization of 14-4A-14 and the structure of poly(14-4A-14) obtained by the first-step solid-state polymerization (polymer 1) are shown in Fig. 1. To investigate the molecular motions of polymer 1 and the reaction process from polymers 1 to 2, the ^{13}C spin-lattice relaxation times (T_1) of polymer 1 were measured and different T_1 values on the unsaturated carbons were found. The free radicals of polymer 1 were also observed by electron-spin-resonance (ESR) spectroscopy. The π-electron densities for a model compound were calculated so as to interpret the different values of ^{13}C relaxations. The results obtained in this study show interesting aspects concerning the π-electron structures which may be associated with the third-order nonlinear optical properties.

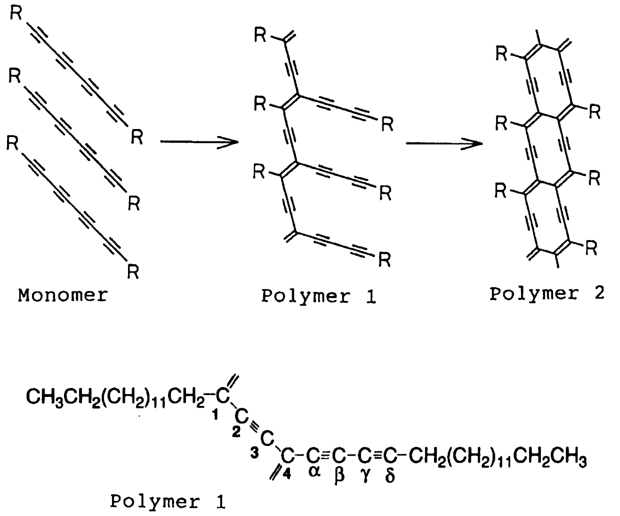

Fig. 1. Solid-state polymerization scheme of 14-4A-14 and the structures of polymers 1 and 2 of poly(14-4A-14).

Experimental

Poly(14-4A-14) was obtained by the solid-state polymerization from 15,17,19,21-hexatriacontatetrayne (14-4A-14, $C_{36}H_{58}$) stimulated by γ-ray irradiation. Syntheses of the monomer and polymers have been reported previously.[5—8]

The ESR spectra were measured at room temperature using a JEOL JES-RE1X spectrometer.

Solid-state high-resolution ^{13}C NMR spectra were recorded on a JEOL GSH-200 spectrometer operating at the resonance frequency of 50.23 MHz using a cross-polarization (CP) pulse sequence and dipolar decoupling (DD) in conjunction with magic-angle sample spinning (MAS). The MAS speed was about 4.5 kHz. About 0.2 g of poly(14-4A-14) in powder form was packed into a rotor of zirconium oxide with a Vespel (a polyimide) bottom and Kel-F[poly(chlorotrifluoroethylene)] cap. The CP time was set to be 5 ms, which was more favorable for observing quaternary carbons rather than carbons bonded to hydrogens. Under the CP condition, the ^{1}H 90° pulse was 4.2 μs. The ^{13}C shifts were referred to the CH_2 peak of external adamantane at 29.5 ppm.[9] The ^{13}C spin-lattice relaxation times were measured under the CP-condition.[10]

Results and Discussion

ESR: The ESR spectrum of poly(14-4A-14) shows a single line without a hyperfine structure. The *g*-

value was 2.0040 and the peak to peak line width was 0.48 mT. The concentration of the free radicals was 5.8×10^{17} spin/g, which corresponds to one unpaired electron for 2100 monomer units, 8400 unsaturated backbone carbons, or 16800 unsaturated carbons including the side chains. Previous ESR studies on PDA's have been made mainly from the viewpoints of polymerization reactions in diacetylene crystals, and the ESR spectra of the oligomer intermediates have been reported to split into fine and hyperfine structures.[11—15] To our knowledge, the ESR spectrum of poly(14-4A-14) in this study was the first measurement of the PDA in a stable polymer at room temperature.

It has been reported that the ESR spectra of undoped *trans*-polyacetylene (PA) film at room temperature is a single narrow line with a *g*-factor of 2.0026[16] or 2.0023[17] and a peak-to-peak linewidth of 0.143 mT[16] or 0.146 mT[17]. It has also been reported that there is one unpaired electron for 3200 carbon atoms, or 1.44×10^{19} spin/g.[16] The ESR signal of *trans*-PA was interpreted to arise from a highly mobile defect in the conjugated polymer chain arising from a neutral radical.

A comparison of the ESR results of poly(14-4A-14) with *trans*-PA indicates that the properties of the unpaired electrons are different. Although the unpaired electrons in poly(14-4A-14) can be assumed to be delocalized similar to *trans*-PA, the area of the delocalization is restricted, since the *g*-value of poly(14-4A-14) is quite different from that of free electrons (2.0023), and it has a broader line width than *trans*-PA. Furthermore, the spin density on the unsaturated carbons of poly(14-4A-14) is one-fifth that of *trans*-PA.

^{13}C NMR: The ^{13}C NMR spectra of PDA's have been studied in the solution state[18,19] as well as in the solid state,[20—26] where the two peaks of unsaturated carbons on the backbone were observed. On the other hand, as shown in Fig. 1, there are 8 inequivalent unsaturated carbons in poly(14-4A-14). The solid-state ^{13}C spectrum of poly(14-4A-14) is shown in Fig. 2 together with the spectral assignments determined in our previous paper.[6] The T_1 values are given in Table 1, where different values were obtained for each unsaturated carbon, except for the two overlapped acetylenic carbons in the backbone. Except for the methylene chain peak at 33.7 ppm, the relaxation could be simulated using a single exponential. The short relaxation times of the side-chain methylene and methyl carbons can be interpreted in terms of the chain mobility, especially for the terminal carbons.

Hitherto, the ^{13}C spin-lattice relaxation times in PDA's have been measured for poly(ETCD)[23] and poly(4BCMU)[25] in order to study the thermochromic phase transitions. In poly(ETCD) the T_1 values of the acetylenic and olefinic carbons on the conjugated backbone are 172 and 153 s, respectively, at room temperature before the thermal treatment. The corresponding values in poly(4BCMU) are 85 and 100 s. The T_1 values of the quaternary carbons in poly(14-4A-14) have a similar magnitude. Generally, the major relaxation mechanism for the ^{13}C resonance is via dipolar interactions with directly bonded hydrogens. Thus, quaternary carbons have longer T_1's than hydrogenated carbons. Since these quaternary carbons can be observed efficiently under the cross-polarization conditions, the dipolar interaction with protons must contribute to the ^{13}C relaxations. However, it would be difficult to find any relations between $1/T_1$ and the distances of the surrounding hydrogens for the quaternary carbons of PDA's hitherto obtained.

Table 1. ^{13}C Shifts, and T_1 of Poly(14-4A-14) and π-Electron Density of the Model Compound

Carbon Type		^{13}C shift	T_1	π-Electron
		ppm	s	density
1	C= backboen with C(saturated)	146.3	145	0.151
2	−C≡C− backbone	105	131	0.053
3		105	131	0.048
4	C= backbone with C≡	110.2	103	0.145
α	−C≡ side chain	72.6	113	0.019
β	−C≡ side chain	80.7	117	0.060
γ	−C≡ side chain	65.4	145	0.008
δ	−C≡ side chain	88.7	103	0.028
CH_2	$-CH_2-$C=	37.3	—	
CH_2	$-CH_2-$C≡	22.3	87	
CH_2	$(CH_2)_{11}$ chain	33.7, 31.3	70, 7	
CH_2	$-CH_2-CH_3$	24.4	12	
CH_3		14.8	3	

The T_1's of the quaternary carbons given in Table 1 vary slightly in magnitude, and show some alternate trends. Additional relaxation mechanisms may arise from the paramagnetic effect from the free radicals on the π-electron network.[27—30] Since the ESR line is a singlet, there may be delocalized unpaired electrons on the conjugated carbons. The alternate effect of the T_1 values on the side-chain acetylenic carbons suggests that the unpaired electrons distribute into the side-chain acetylenic carbons.

The ^{1}H and ^{13}C spin-lattice relaxation times of *trans*-PA have been reported to be about 40 ms and 1.2 s at room temperature, respectively.[31,32] It was assumed that the main part of the relaxation arose from the neutral soliton present on the chains. However, the ^{13}C relaxations of the conjugated carbons in PDA's are very slow compared with that of *trans*-PA. Even though free radicals exist in poly(14-4A-14), as shown by ESR, the distribution of the unpaired electrons on the conjugated system of PDA should be quite different from that of *trans*-PA.

MO Calculation: To confirm the conjugation effect, a preliminary calculation was made by the AMI method[33] to obtain the electron densities of the highest occupied molecular orbital. The very simple model

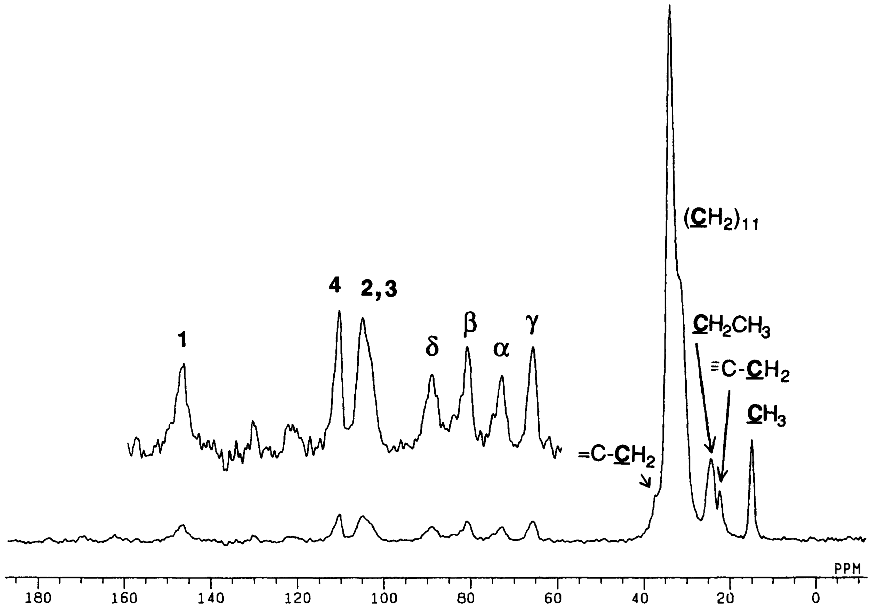

Fig. 2. Solid-state high-resolution ^{13}C NMR spectrum of poly(14-4A-14).

compound shown below (Chart 1) was used for the calculation. The geometry was fully optimized by imposing C_s symmetry restrictions. The molecular orbital calculation by the AMI method was performed with MOPAC Ver. 5.01.[34] The molecular orbital calculation of the model compound used in this study indicates that about 80% of the π-electron density distributes on the main chain conjugated system. The spin density of free radical was assumed to be proportional to the π-electron density and also to contribute to the ^{13}C relaxation of the conjugated unsaturated carbons. Although the shorter T_1 of C_4 may be correlated with the higher π-electron density, and the longer T_1 of C_γ may be interpreted by a smaller π-electron density, it is difficult to find a general relationship between the spin densities of the unpaired electrons and the relaxation times. Since the present calculation is limited to the model compound without a chain structure, the discrepancy may be due to neglecting the conjugated chain structure.

As reported in our previous paper,[7] additional polymerization takes place by a thermal treatment, as shown in Fig. 1. The reaction scheme is a 1,4-addition at the side chains with acetylenic carbons, i.e. the C_α and C_δ positions. That these two reactive carbons have short T_1 values is very indicative concerning the π-electron structure.

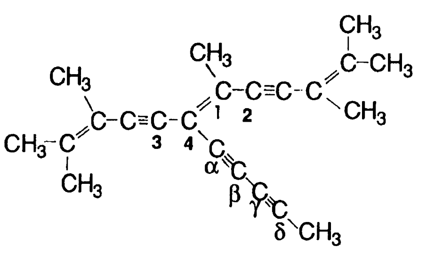

Chart 1.

In summary, the ^{13}C resonances for the unsaturated carbons of poly(14-4A-14) partially relax due to the paramagnetic effect of the unpaired electrons distributed on the π-electron network of the conjugated system, which includes the main backbone chain as well as the side-chain acetylenic carbons.

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