Solid-State NMR Study of Poly(phenylacetylene) Synthesized with a Rhodium Complex Initiator

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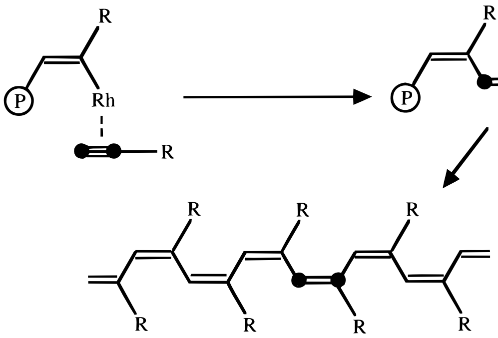
ABSTRACT: The polymerization mechanism and the structure of poly(phenylacetylene) synthesized using the Rh(C≡CC$_6$H$_5$)(2,5-norbornadiene)[P(C$_6$H$_5$)$_3$]$_2$ initiator were investigated by solid-state NMR. The ^{13}C Pake doublet of the poly(phenylacetylene) containing 5% [1,2-^{13}C]phenylacetylene was observed by effectively removing the chemical shift anisotropies using a composite inversion pulse sequence. The ^{13}C—^{13}C bond distance was determined to be 1.386 Å from the spectrum, which corresponds to a double bond length. This result clearly shows that the polymerization by the Rh initiator progresses by the cis-insertion mechanism. The ^{13}C isotropic chemical shifts of the protonated and nonprotonated olefin carbons were deduced to be 131.8 and 141.4 ppm, respectively, from differences between some overlapped CPMAS spectra. Two-dimensional ^{13}C CPMAS exchange experiments revealed conformational inhomogeneity of the main chain and the presence of slow π-flip motion of the phenyl ring.

Poly(acetylene) derivatives have interesting physical properties such as photoconductivity[1] and nonlinear response to light[2,3] and magnetic field.[4,5] These properties are influenced by the presence and type of substituent, configuration, and molecular weight. To control them, stereospecific living polymerization is highly desirable, and as a basis for understanding such a controlled synthesis, polymerization mechanisms and structures should be revealed. In this paper, we report a solid-state NMR study on the mechanism of phenylacetylene polymerization by the Rh(C≡CC$_6$H$_5$)(nbd)[P(C$_6$H$_5$)$_3$]$_2$ (nbd = 2,5-norbornadiene) initiator, which was recently found to initiate living stereospecific polymerization of phenylacetylene,[6,7] and on the structure of the synthesized polymer.

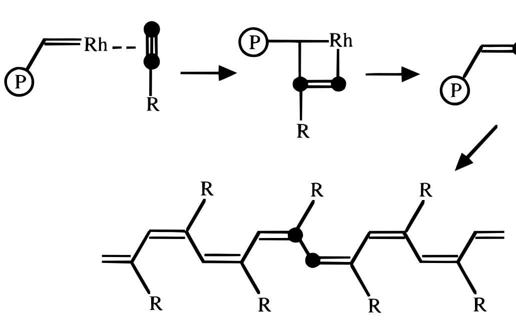
The polymerization of acetylene and its derivatives is expected to proceed according to either the insertion mechanism (Scheme 1) or the metathesis mechanism (Scheme 2). To determine the polymerization mechanism of acetylene, Clarke et al.[8] observed the ^{13}C—^{13}C Pake doublet of poly(acetylene) synthesized from acetylene containing 5% doubly ^{13}C-labeled acetylene using nutation NMR spectroscopy and obtained the ^{13}C—^{13}C bond distance.[9] If poly(acetylene) is formed via the insertion mechanism, the ^{13}C pair should be on the double bond (Scheme 1), and if formed via the metathesis mechanism, it should be on the single bond (Scheme 2). Therefore, it can be determined by measurement of the ^{13}C—^{13}C bond length whether the polymerization proceeds by the insertion mechanism or the metathesis mechanism. The mechanisms of phenylacetylene polymerization by molybdenum and titanium initiators were also investigated using this method.[10]

Scheme 1. Insertion Mechanism



Ⓟ: polymer chain R: phenyl Rh: rhodium

Scheme 2. Metathesis Mechanism



Ⓟ: polymer chain R: phenyl Rh: rhodium

To investigate the mechanism of polymerization by the Rh(C≡CC$_6$H$_5$)(nbd)[P(C$_6$H$_5$)$_3$]$_2$ initiator, we followed the same strategy. However, the nutation NMR method, which was applied in a low magnetic field of 1.41 T (60 MHz for ^{1}H) in the above experiments, does not work

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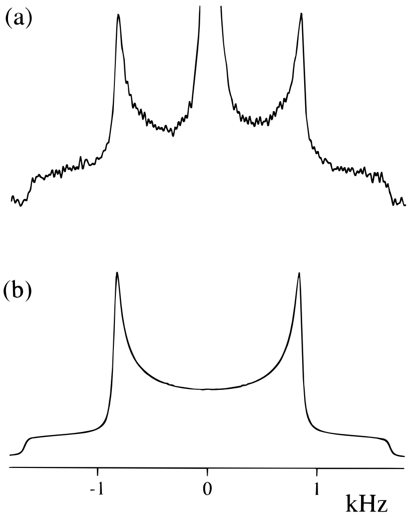

Figure 1. ^{13}C Pake doublet for poly(phenylacetylene) polymerized from 5% [1,2-^{13}C]phenylacetylene using the Rh-(C≡CC$_6$H$_5$)(2,5-norbornadiene)[P(C$_6$H$_5$)$_3$]$_2$ initiator: (a) observed using the MLEV4−4′ sequence.[13] The scaling factor is 0.3957. (b) Simulated. The ^{13}C—^{13}C bond length was assumed to be 1.386 Å.

well in high fields of commonly used superconducting magnets, because the nutation method is very sensitive to chemical shift offset effects. Namely, the ^{13}C rf field intensity must be much stronger than the chemical shift anisotropies as well as the shift difference to remove effectively the line broadening due to the chemical shifts.[9] It is exceedingly difficult to satisfy this condition in high fields. The Carr−Purcell Meiboom−Gill sequence (CPMG)[11] can also be used to measure dipolar coupling constants.[12] In a high field, however, the CPMG method cannot effectively remove chemical shifts, causing large distortions in the Pake doublet. In this study, we used a newly developed MLEV4−4′ pulse sequence for measurements of ^{13}C—^{13}C dipolar couplings.[13] In this sequence, two different MLEV-4 sequences[14] are combined as (τ-R-2τ-R-2τ-R*-2τ-R*-2τ-S-2τ-S-2τ-S*-2τ-S*-τ), where R, R*, S, and S* are composite inversion pulses: R = $(\pi/2)_y(4\pi/3)_x(\pi/2)_y$, R* = $(\pi/2)_{-y}(4\pi/3)_{-x}(\pi/2)_{-y}$, S = $(\pi/2)_y(4\pi/3)_{-x}(\pi/2)_y$, and S* = $(\pi/2)_{-y}(4\pi/3)_x(\pi/2)_{-y}$. The MLEV4−4′ sequence works well even in high fields, effectively removing chemical shifts and compensating various nonideal pulse effects. We have reported a similar composite inversion sequence MLEV8/8$^{\mathrm{R}}$ for accurate determination of ^{13}C—^{15}N dipolar couplings.[15]

Figure 1a shows the experimental ^{13}C spectrum observed using the MLEV4−4′ pulse sequence for poly(phenylacetylene) (PPA) polymerized from 5% [1,2-^{13}C]phenylacetylene by the Rh initiator. A clear Pake doublet was successfully obtained in a high field of 7 T. The center peak is due to the isolated ^{13}C spins. If the product contains both single and double ^{13}C—^{13}C bonds, the spectrum must exhibit an overlap of two Pake doublets.[16] Hence, the observation of a single Pake doublet demonstrates that the product contains either only single or only double ^{13}C—^{13}C bonds. Figure 1b shows the best-simulated spectrum; from the simulation, the ^{13}C—^{13}C bond length was determined to be 1.386 ± 0.009 Å.

The PPA polymerized by the molybdenum or titanium initiator has been reported to contain both single and double ^{13}C—^{13}C bonds, and the single and double bond lengths have been determined to be 1.48 and 1.36 Å, respectively, by nutation NMR at 77 K.[10] The above length of 1.386 Å for the PPA polymerized by the Rh initiator is much closer to the double bond length than the single bond one. Therefore, the observed length is ascribed to the double bond, although the cause of the difference between 1.386 and 1.36 Å is not clear at present. Thus, we can conclude that the Rh complex initiator promotes the insertion polymerization, and hence the present PPA is necessarily of cis configuration as the usual insertion polymerization.

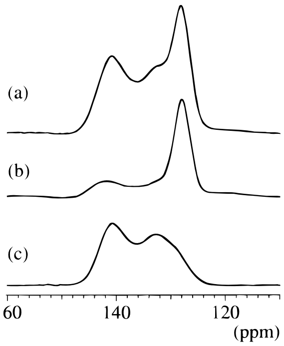

Figure 2. ^{13}C CPMAS spectra of poly(phenylacetylene) polymerized from (a) 5% [1,2-^{13}C]phenylacetylene and from (b) natural abundant poly(phenylacetylene) using the Rh-(C≡CC$_6$H$_5$)(2,5-norbornadiene)[P(C$_6$H$_5$)$_3$]$_2$ initiator, and (c) the CPMAS spectrum [A] due only to the ^{13}C-labeled olefin sites. The bottom spectrum [A] was obtained by subtracting spectrum (b) from spectrum (a).

Next, we deduce the ^{13}C chemical shifts of the olefin carbons from overlapped CPMAS lines and compare these in the solution state. Parts a and b of Figure 2 show ^{13}C CPMAS spectra for 5% doubly ^{13}C-labeled PPA and nonlabeled PPA, respectively. Both spectra were acquired under the same experimental conditions so that their amplitudes can directly be compared. Three lines can be seen at 128, 132, and 142 ppm in the former spectrum. Subtracting the spectrum for nonlabeled PPA from that for labeled PPA, we obtain spectrum [A] shown in Figure 2c, which represents the signals of the labeled olefin carbons. Apparently, spectrum [A] has two lines at 132 and 142 ppm and no peak at 128 ppm. Accordingly, the lines at 132 and 142 ppm are assigned to the olefin carbons, and therefore the line at 128 ppm is assigned to the aromatic carbons. Parts a−c of Figure 3 show ^{13}C dipolar-dephasing spectra for labeled PPA and nonlabeled PPA and their differential spectrum [B], respectively. Dipolar-dephasing experiments present only signals due to weakly ^{13}C—^{1}H dipolar-coupled carbons, as is well-known,[17] giving only nonprotonated carbon signals in the present case. Therefore, remaining in Figure 3, the line at 142 ppm in Figure 2 can be ascribed to the nonprotonated olefin carbons. On the other hand, the line at 132 ppm in Figure 2 can barely be seen in Figure 3, so that it can be assigned to the protonated olefin carbons. The intensity of the aromatic carbon signal at 128 ppm is much weaker in Figure 3 than in Figure 2, indicating that the protonated aromatic carbon signal vanishes and only the nonprotonated natural-abundant aromatic carbon signal remains. Spectrum [B] shown in Figure 3c displays only the labeled nonprotonated olefin carbon signal. Furthermore, subtracting properly scaled spectrum [B] from spectrum [A], we obtain spectrum [C], represented by the thick line in Figure 4, which can be ascribed to the protonated olefin carbons. Consequently, spectra [B] and [C] show that the isotropic chemical shift values of

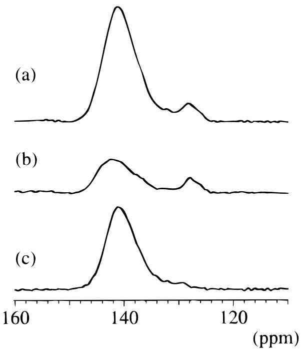

Figure 3. Dipolar-dephasing CPMAS spectra of poly(phenylacetylene) polymerized from (a) 5% [1,2-^{13}C]phenylacetylene and from (b) natural abundant poly(phenylacetylene) using the Rh(C≡CC$_6$H$_5$)(2,5-norbornadiene)[P(C$_6$H$_5$)$_3$]$_2$ initiator and (c) the dipolar-dephasing CPMAS spectrum [B] due only to the ^{13}C-labeled nonprotonated olefin sites. The bottom spectrum [B] was obtained by subtracting the spectrum in (b) from the spectrum in (a). The contact time for cross polarization is 2 ms (a, b). In (b), the ^{1}H−^{13}C dipolar dephasing time is 1 ms.

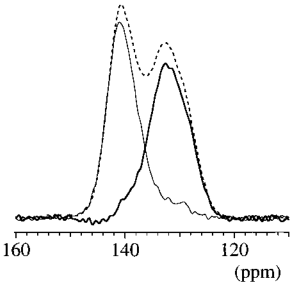

Figure 4. Decomposition of the ^{13}C-labeled olefin spectrum [A] (dotted line) into the spectra due only to the nonprotonated olefin carbons [B] (thin line) and the protonated olefin carbons [C] (thick line). Spectra [A] and [B] are from the bottom spectra in Figures 2 and 3, respectively. Spectrum [C] was obtained by subtracting spectrum [B] from spectrum [A].

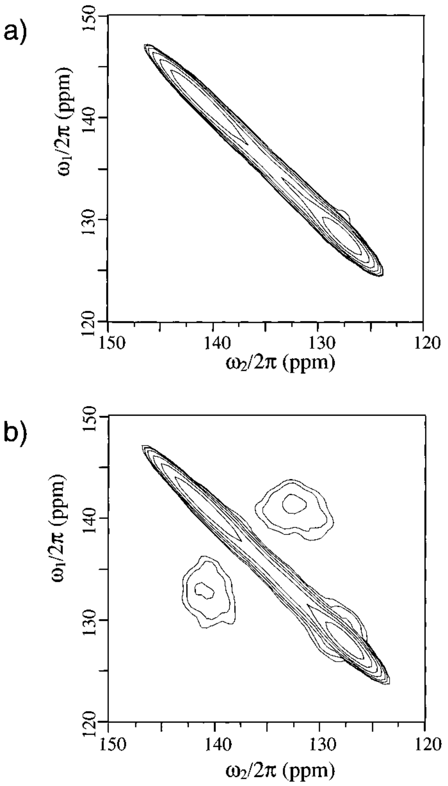

Figure 5. ^{13}C CPMAS 2D exchange spectra of poly(phenylacetylene) polymerized from 5% [1,2-^{13}C]phenylacetylene using the Rh(C≡CC$_6$H$_5$)(2,5-norbornadiene)[P(C$_6$H$_5$)$_3$]$_2$ initiator for mixing times of 1 ms (a) and 35 ms (b).

nonprotonated and protonated olefin carbons in the cis configuration are 141.6 and 131.7 ppm, respectively.

In the solution state of PPA, the olefin chemical shifts have been reported to be 139.9 and 132.2 ppm for the nonprotonated and protonated carbons, respectively.[6,18] These shifts are close to the above values obtained in the solid state. Unsubstituted polyacetylene has a ^{13}C chemical-shift difference of almost 10 ppm between the cis and trans configurations.[19] These facts suggest that the structure of the PPA in the solution state is similar to that in the solid state, and hence it is of rigid cis configuration.

Figure 5 shows two-dimensional (2D) ^{13}C CPMAS exchange spectra with mixing times of (a) 1 ms and (b) 35 ms. There is no cross-peak in (a), indicating that no fast molecular reorientation exists. The line width of the projection of the diagonal peak onto the secondary diagonal is much narrower (~2 ppm) than those (~8 ppm) of the separated 1D spectra shown in Figure 4. It demonstrates that the broadening of the 1D signals is inhomogeneous, and therefore that the isotropic chemical shifts of all the carbons are substantially distributed. From this fact, we can conclude that the conformation of the main chain is not homogeneous but is inhomogeneously distributed. In (b), a couple of cross-peaks are clearly shown between 132 and 142 ppm. They can be assigned to the exchange signals due to spin diffusion between the doubly ^{13}C labeled olefin sites, confirming the above signal assignments of the olefin carbons. Another couple of cross-peaks can be recognized in a narrow range around 128 ppm. It suggests the presence of slow π-flip motion of the phenyl ring; slow π-flip motion of side-chain phenyl rings is known to exist in poly(styrene) through solid-state ^{2}H NMR studies.[20,21] All the carbons in the phenyl ring usually have slightly different shift values around 130 ppm in rigid solids,[22] because even the two ortho or meta positions may be unequivalent in a fixed environment. Hence, the appearance of the cross-peak around 128 ppm shows that π-flip motion of the phenyl ring occurs on the time scale of several tens milliseconds.

Rh(C≡CC$_6$H$_5$)(nbd)[P(C$_6$H$_5$)$_3$]$_2$ (**1**) was synthesized according to the procedure described previously.[6,23] An addition of an ether solution (3.6 mL) of phenylacetylene (1.20 mmol), [1, 2-^{13}C]phenylacetylene (0.11 mmol), and tetraline (0.22 mL, as an internal standard for GC analysis) to an ether solution (6 mL) of **1** (0.03 mmol) and 4-(dimethylamino)pyridine (0.3 mmol) at room temperature leads to polymerization of phenylacetylene in a living manner. The polymerization proceeds rapidly to completion within 80 min, giving a red brown precipitate. Treatment of the resulting ether suspension with 100 equiv of acetic acid affords PPA with M_n of 15 100 and M_w/M_n of 1.16 in an almost quantitative yield.

The MLEV4−4′ experiment was carried out using a Chemagnetics CMX-300 spectrometer operating at 75.55 MHz for ^{13}C with rf-field intensities of 60 kHz for both ^{1}H and ^{13}C during cross polarization, 34.7 kHz for the pulses applied to ^{13}C, 70 kHz for proton decoupling during the pulse intervals, and 110 kHz for proton decoupling during the pulses to avoid the C−H recoupling.[24] The CPMAS experiments, including 2D exchange NMR, were performed using a Chemagnetics CMX-400 Infinity spectrometer operating at 100.66

MHz for ^{13}C. The spinning speed of the rotor is 8 kHz. The rf-field intensities are 60 kHz for ^{1}H and 52 kHz for ^{13}C during cross polarization and 70 kHz for proton decoupling.

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