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Complete Assignment of ^{1}H and ^{13}C NMR Spectra of Poly(*N*-vinylcarbazole)

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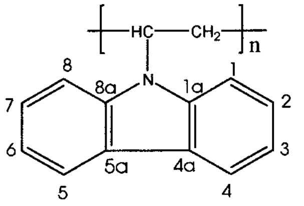
Introduction

Although poly(*N*-vinylcarbazole) (PNVC) (**1**) has been the subject of intensive investigation in the past 20 years mainly because of its photoconductive and photophysical properties,[1,2] its proton and carbon NMR spectra have not been assigned unambiguously. Natansohn[3] has offered the most satisfactory analysis of the complex ^{1}H and ^{13}C NMR spectra of PNVC by using two-dimensional COSY and HETCOR experiments. However, no justification has been given for the assignment of the quaternary carbon signals, and some proton and carbon signals appear to be erroneously assigned.



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This note reports the complete and unambiguous assignment of the proton and carbon-13 spectra of poly(*N*-vinylcarbazole) by employing a number of modern gradient two-dimensional NMR experiments conducted at magnetic field of 11.74 T. The correct assignment of these spectra is important for our current investigation concerning the conformational and dynamic properties of this polymer.

Magnetic field gradients have been exploited, recently[4,5] in two- and three-dimensional NMR spectroscopy, emerging as an important alternative to traditional phase-cycling techniques. The use of the gradients for the selection of the desired coherence pathways considerably improves 2D NMR experiments in terms of (a) suppression of unwanted magnetization (artifacts), avoiding thus add/subtract errors as in phase-cycling techniques, (b) shortening the measuring time leading to a better signal-to-noise-ratio,[5] and (c) yielding pure absorption spectra resulting in a better resolution of signals in crowded spectral regions.[6]

Results and Discussion

Before analyzing the 2D NMR spectra of PNVC, it is important to mention the magnetic nonequivalence of the two benzene rings resulting in an asymmetric spectrum despite the fact that the carbazole moiety belongs to the C_{2v} symmetry group.[3,7] This nonequivalence, which is not observed in model compounds, is reflected in the ^{13}C NMR spectrum of the polymer but is more pronounced in its ^{1}H NMR spectrum. This observation has been attributed to restricted rotation of the bulky carbazole combined with ring current effects of neighboring rings.[3,7]

The gradient COSY (gCOSY) spectrum of PNVC obtained at 500 MHz in chloroform solution is shown in Figure 1. Starting with the unequivocal of more shielded H-1 proton at δ 4.94, the spectrum shows connectivity of this proton with the H-2 proton at δ 6.18. In turn, the H-2 proton shows a cross-peak with resonance at δ 6.44, which should be attributed to the H-3 proton and not to the H-7 proton previously assigned.[3] The signal for the H-4 proton is assigned by following the cross-peak with the H-3 proton. The assignment of the protons of the less shielded ring is achieved by starting with the reasonable assignment of proton H-5 δ 7.72 and following the cross-peaks all the way back to H-8 proton. The signal of the H-7 proton now appears at δ 6.95.

Support for this assignment of the proton spectrum is offered by a gTOCSY experiment, which reveals remote signal connectivities by employing a spin-locking pulse. In this experiment, cross-peaks are observed between spins k and m, which are not directly coupled but share a mutual coupling partner l, or between spins that are *J*-coupled with a magnitude less than the line widths of the individual resonances. Using spin-lock length 45 ms, the gTOCSY contour plot in Figure 2 shows several remote connectivities. The connectivity pattern of protons H-1 and H-3 of the less shielded ring and that of protons H-5 and H-7 of the more shielded ring verify the correct assignment of protons H-3 and H-7. It should be noted that additional gTOCSY experiments with longer mixing times have been performed in the course of this study. The longer mixing times were based on the coupling constants observed in the ^{1}H NMR spectrum of the model compound *N*-ethylcarbazole. None of these spectra gave a better connectivity around each ring than that observed in the gTOCSY spectrum of Figure 2.

Although protons H-4 and H-5 are expected[3] to appear at the lowest field, we attempted to support their assignment by performing a series of NOESY experiments using different mixing times. Unfortunately, none of the recorded NOESY spectra (not shown) reflected the expected dipole−dipole interaction between protons H-5 and H-4.

The protonated aromatic carbons of the carbazole side groups are easily assigned through the phase-sensitive gradient-selected heteronuclear multiple quantum coherence (gHMQC) experiment, which detects one-bond $^{13}C-^{1}H$ connectivities. The gHMQC spectrum of PNVC is shown in Figure 3. This spectrum obtained with a delay time $\tau = 3.52$ ms ($^{1}J_{C,H} = 142$ Hz) and processed with forward f_1 linear prediction[8] demonstrates superior sensitivity and resolution than the spectrum recorded by using the simple HETCOR experiment.[3] These advantages permit the correct assignment of carbons of the carbazole segment. Although the peaks of carbons C-2 and C-7 as well as those of carbons C-3, C-4, and

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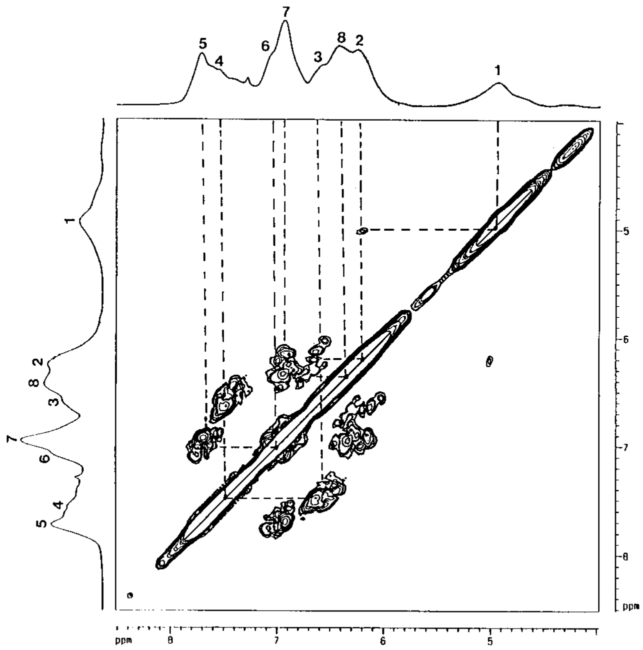

Figure 1. gCOSY spectrum of the aromatic region of PNVC in $CDCl_3$.

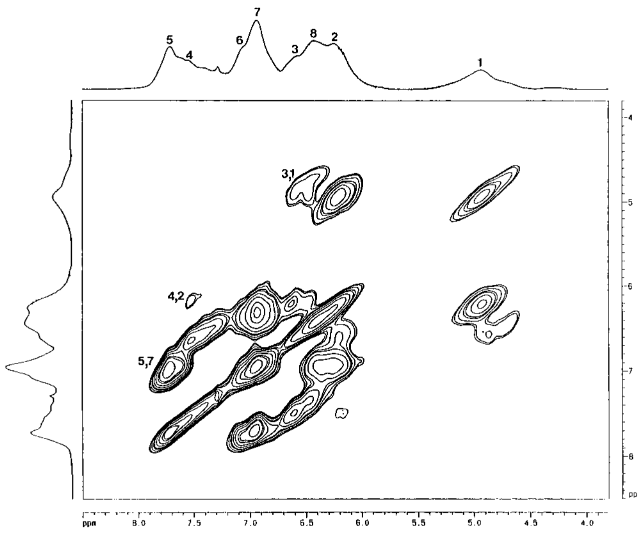

Figure 2. gTOCSY spectrum of the aromatic region of PNVC in $CDCl_3$.

C-6 are not resolved in the spectrum, the resolution of the cross-peaks of the gHMQC spectrum allows the determination of the correct order of their chemical shifts. Carbon C-7 resonates at lower field than carbon C-2, and carbon C-4 resonates at lower field than carbon C-3 (Figure 3). The assignment of the latter two signals differs from that reported earlier.[3]

The assignment of the signals of the nonprotonated aromatic carbons for carbazole has been achieved by using the phase-sensitive gradient-selected heteronuclear multiple bond correlation (gHMBC) experiment, which correlates proton and carbon nuclei via long-range couplings. The gHMBC spectrum of the aromatic region presented in Figure 4 is obtained with delay times $\tau_1 = 3.52$ ms and $\tau_2 = 65$ ms calculated for couplings $^1J_{C,H} = 142$ Hz and $^{2/3}J_{C,H} \approx 8$ Hz, respectively. The correlations, which allow the assignment of the nonprotonated carbons, are given in the figure. It is easily seen that each nonprotonated carbon correlates with protons via $^3J_{C,H}$ couplings. Thus, the signals at

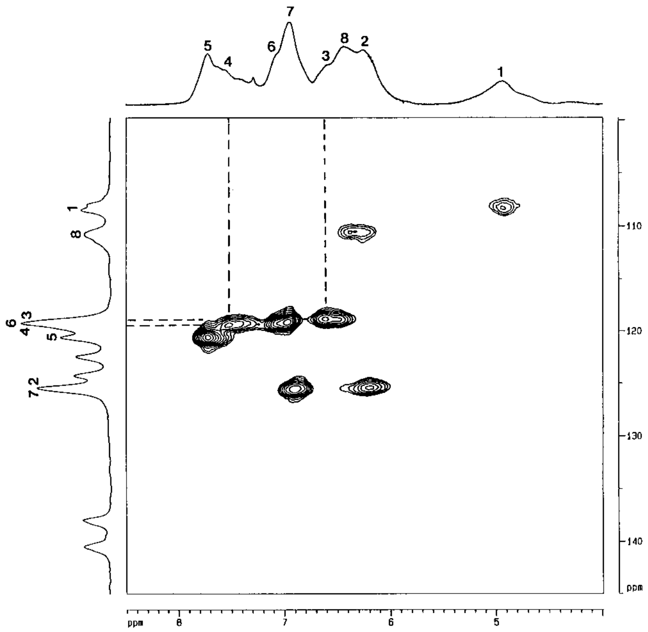

Figure 3. gHMQC spectrum of the aromatic region of PNVC in $CDCl_3$.

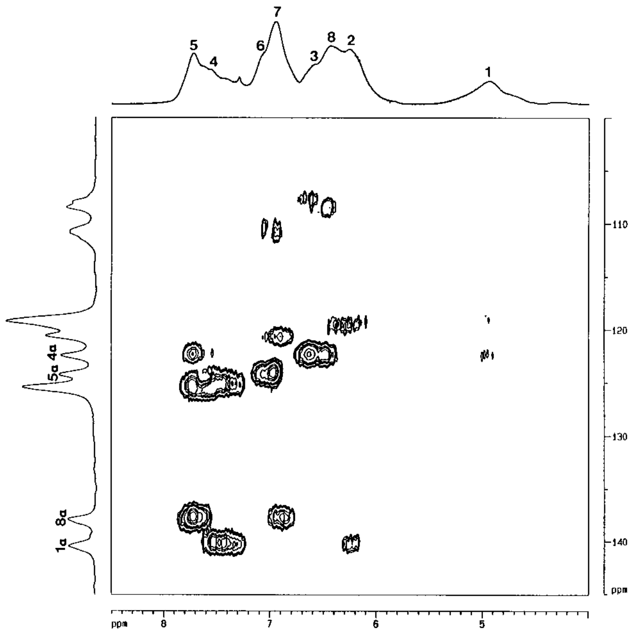

Figure 4. gHMBC spectrum of the aromatic region of PNVC in $CDCl_3$.

low fields are assigned to the C-1a (connected with H-2 and H-4) and C-8a (connected with H-5 and H-7), whereas the signal at higher fields are attributed to carbons C-4a (connected with H-1, H-3, and H-5) and C-5a (connected with H-4 and H-6). Among the other long-range C−H connectivities in the spectrum, those between C-1−H-3 and C-7−H-5 reinforce the assignment of the H-3 and H-7 in the gCOSY spectrum.

As mentioned before, the nonequivalence of the two rings of carbazole reflected on the different proton and carbon chemical shifts in the spectra has been attributed to ring current effects exerted by neighboring carbazole units. Natansohn has performed[3] a molecular modeling study on a syndiotactic triad and an isotactic pentad using the ALCHEMY software. She concluded that indeed ring current effects are responsible for the

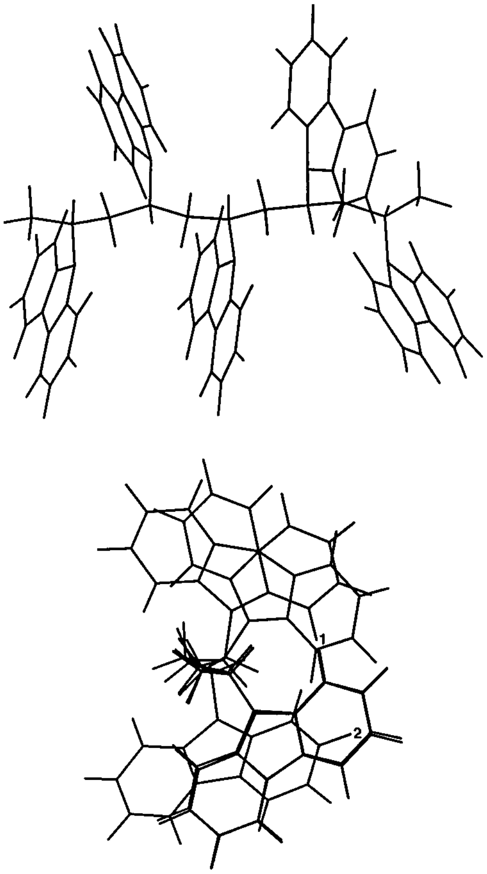

Figure 5. (a, top) Minimum-energy structure of syndiotactic pentad sequence. In (b, bottom), the molecule has been rotated around the helix axis. The numbers indicate the location of protons H-1 and H-2.

observed differences in the chemical shifts for carbons C-1 and C-8 (and the attached protons H-1 and H-8). In an attempt to give an account of the contribution of ring current effects to the observed chemical shifts difference between these protons, it was decided to perform semiempirical PM3 calculations by considering larger segments of isotactic and syndiotactic sequences. Figures 5a and 6a show the minimum-energy structures of a syndiotactic pentad and an isotactic heptad, respectively. The syndiotactic pentad assumes a helical configuration that is similar to the 2/1 helix observed for the syndiotactic sequence in the crystal structure,[9] whereas the isotactic heptad approaches the 3/1 helix.[9,10] To clarify the positions of the protons of the carbazole side group, the structures have rotated properly in Figures 5b and 6b. These models show that not only H-1 but also H-2 proton are located above the phenyl rings of the neighboring carbazole units. In the racemo sequence the H-1 and H-2 protons are at a distance of 4.65 and 4.9 Å, respectively, from the center of the neighboring phenyl ring. In the isotactic sequence, the shortest distances of protons H-1 and H-2 from the center of the neighboring phenyl ring were found to be 3.4 and 5.2 Å, respectively. To approximate the contribution of the ring currents to the chemical shifts of protons H-1 and H-2, we have adopted the ring current model developed by Johnson and Bovey.[11] From the estimated cylindrical coordinates of the protons in the structures of Figures 5 and 6 and Figure 1 of ref 11, we predict that the proton H-1 is shifted upfield by about 0.3 and 1.0 ppm in the syndiotactic and isotactic sequences, respectively, whereas the H-2 proton is shifted upfield by about 0.5 and 0.3 ppm in the syndiotactic and isotactic sequences, respectively. Although these values are only estimates, they show that ring current effects are major contributors to the chemical shifts differences observed between protons H-1 and H-8 ($\Delta\delta = 1.27$ ppm) and between protons H-2 and H-7 ($\Delta\delta = 0.77$ ppm).

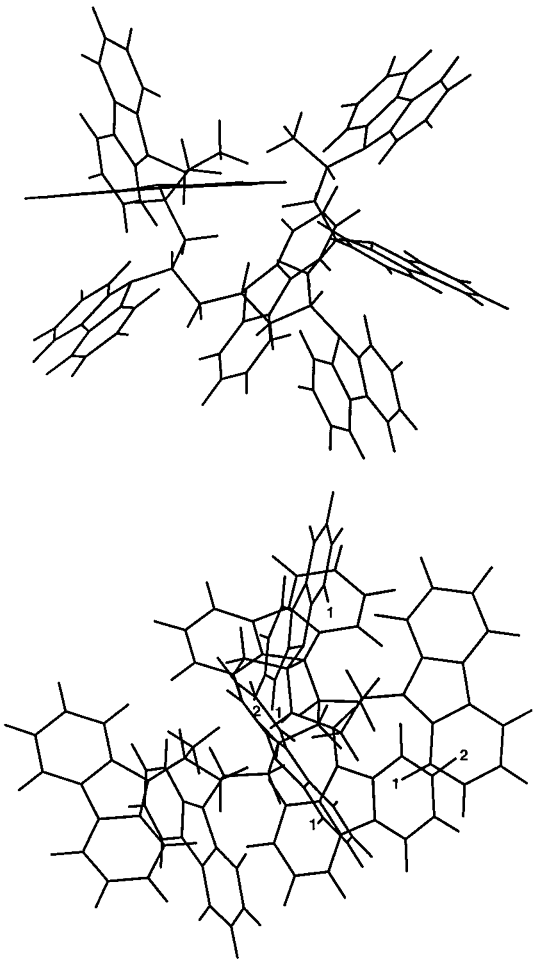

Figure 6. (a, top) Minimum-energy structure of isotactic heptad sequence. In (b, bottom), the molecule has been rotated around the helix axis. The numbers indicate the location of protons H-1 and H-2.

Experimental Section

PNVC was purchased from Aldrich and purified by several reprecipitations from chloroform solutions using acetone as precipitant.

NMR. NMR experiments were conducted on a Bruker AMX500 spectrometer operating at 500.1 and 125.7 MHz for proton and carbon nuclei, respectively. Samples were dissolved in deuterated chloroform. Some details of the two-dimensional NMR experiments for PNVC are given below. (For a review of gradient COSY, TOCSY, HMQC, and HMBC experiments see ref 12.) Application of forward f_1 linear prediction[8] to gHMQC experiment improved the signal-to-noise ratio relative to that of the same experiments processed with zero filling only. However, the application of linear prediction for the rest of the 2D experiments did not improve the sensitivity and resolution obtained with zero filling.

gCOSY. The gradient-selected H, H$-$COSY spectrum[12] was obtained using 128 increments of 2K real data points with 32 transients for each free induction decay and a recycle delay of 1.0 s. Before Fourier transformation the data set was zero-filled to a 2K × 2K matrix. Sinebell weighting were used in both dimensions.

gTOCSY. The gradient-selected TOCSY spectrum[12] was obtained using 128 increments of 2K real data points with 32 transients for each free induction decay and a recycle delay of 1.0 s. Before Fourier transformation the data set was zero-filled to a 2K × 2K matrix. Sinebell weighting functions were used in both dimensions.

gHMQC. The phase-sensitive gradient selected hydrogen−carbon heteronuclear multiple quantum coherence[11] experiment was acquired with 128 increments and 64 transients of 2K. The relaxation delay was 2.0 s. Twofold forward f_1 linear prediction, zero-filling to 2K × 2K, and sine multiplication were performed prior to Fourier transformation.

gHMBC. The phase-sensitive gradient selected hydrogen−carbon heteronuclear multiple bond correlation[12] experiment to obtain long-range C−H couplings was acquired with 128 increments and 64 transients of 2K. The relaxation delay was 2.0 s. Zero-filling to 2K × 2K and sine multiplication were performed prior to Fourier transformation.

Conformational Calculations. Energy minimization was performed with the semiempirical method PM3 using a GAUSSIAN 94 program[13] package in a cluster of Pentium 450 MHz PC's running Linux. All geometries and the structural parameters are fully optimized by the PM3 method.

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