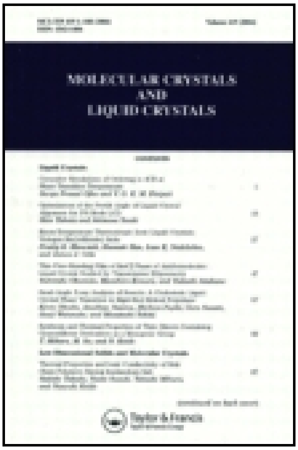

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Thermally Annealed Solid State Polymerization of 2,3-Dicyano-5,7-Dimethyl-6H-1,4-Diazepine: An NMR Study

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Thermally Annealed Solid State Polymerization of 2,3-Dicyano-5,7-Dimethyl-6*H*-1,4-Diazepine: An NMR Study

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*The thermally annealed solid state polymerization of 2,3-dicyano-5,7-dimethyl-6*H*-1,4-diazepine(**A**) was studied by ^1H, ^{13}C, and ^{15}N CP/MAS solid state NMR spectroscopy, and by a ^1H solution state NMR deuterium exchange experiment of **A**. Collectively, the NMR data suggests that a tautomeric form of the monomer is responsible for the solid state reactivity of the crystalline monomer. The solid state polymerization of crystalline **A** proceeds as a heterogeneous decomposition of the crystalline lattice resulting in an insoluble, amorphous material. A plausible reaction scheme involving a tautomeric form of **A** is proposed. The scheme is consistent with the NMR spectra.*

Keywords: ^{13}C NMR spectroscopy; deuterium exchange; diazepine; ^{1}H NMR spectroscopy; ^{15}N NMR spectroscopy; solid state polymerization

INTRODUCTION

Solid state chemistry of organic crystals, though relatively rare, presents a unique approach to the synthesis of polymers due to the inherent synergy between restricted, yet specific molecular motion, and the three dimensional order provided by the crystalline lattice [1]. Regarding the synthesis of conjugated polymers, polydiacetylenes have long represented a unique paragon [2]. Here we present an unusual, novel example of a solid state polymerization. Crystalline

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monomer 2,3-dicyano-5,7-dimethyl-6*H*-1,4-diazepine (**A**) undergoes a solid state polymerization via thermal annealing yielding a conjugated polymer [3,4]. In this report, we discuss the idea of tautomerization of **A** as an integral aspect of the solid state polymerization process. Consequently, ^{1}H solution state NMR deuterium exchange experiments were used to study tautomerization of the diazepine monomer. These experiments attempt to elucidate the existence of a tautomeric form that is relevant to the mechanism of the solid state polymerization. The solid state polymerization product of crystalline **A** yielded a black, insoluble amorphous product, and thus solid state CP/MAS NMR spectroscopy was necessary for characterization of the structure of the polymer product.

EXPERIMENTAL SECTION

Characterizations

All solid state NMR spectra were recorded on a 300 MHz Bruker DMX wide-bore spectrometer operating at 75.47 and 30.41 MHz for ^{13}C and ^{15}N, respectively. Measurements were carried out at ambient temperature using cross-polarization (CP), magic angle spinning (MAS), and dipolar decoupling (DD) techniques. Samples were packed into 4 mm Zirconium oxide (ZrO_2) rotors with Kel-F caps. The ^{1}H MAS NMR experimental parameters used are: pulse width of 4 µs, a recycle delay of 3 sec, and a sweep width of 31 kHz. The ^{13}C CP/MAS NMR experimental parameters used are as follows: pulse width of 4 µs, a recycle delay time of 3 sec, contact time of 3 ms (unless noted otherwise), and a sweep width of 31 kHz. Likewise, the ^{15}N CP/MAS NMR experiments utilized a pulse width of 4.8 µs, a recycle delay time of 4 sec, a contact time of 3 ms, and a sweep width of 31 kHz. The total number of scans per spectrum varied between 20–40 k. The ^{1}H MAS spectra were externally referenced to the proton signal of adamantane, calibrated at 0 ppm. ^{13}C CP/MAS spectra were externally referenced to glycine by calibrating the carbonyl resonance to 176.03 ppm with respect to TMS. The ^{15}N CP/MAS spectra were externally referenced to ammonium sulfate ($\mathit{N}H_4SO_3$) at 0 ppm. ^{1}H and ^{13}C samples were spun at 12 kHz (unless noted otherwise), and the ^{15}N samples were spun at 5 kHz. The solution state NMR spectra were recorded on a 500 MHz Bruker AMX spectrometer. Measurements were carried out in CD_3CN at room temperature (unless noted otherwise), and internally referenced to TMS. The IR spectra were recorded on a Perkin-Elmer 1720 FT-IR spectrometer from samples dispersed in KBr pellets.

Synthesis of Monomer

2,3-dicyano-5,7-dimethyl-6*H*-1,4-diazepine (**A**) was prepared by utilizing a previous method [5] involving the condensation of diaminomaleonitrile with acetylacetone. The monomer (**A**), a colorless crystal, was characterized by its infrared, ^{1}H, and ^{13}C spectra, and mp 199–200° (dec) [5].

Solid State Polymerization of A (Polymer E, F)

Transparent, colorless single crystals of **A** were grown from an acetonitrile solution. **Polymer E**: 8 g of crystalline **A** were heated under Argon at 145°C for one week. The material was washed extensively with hot acetone to remove the unreacted monomer and dried in a vacuum oven. A black, reflective powder was obtained in 7.5% yield. **Polymer F**: 12 g of crystalline **A** were heated under Argon for 24 hours at 175°C. The material was rinsed with hot acetone and dried. A black powder was obtained in 72% yield. Both **E** and **F**: UV-vis (DMF/nm) λ_{max} below 300, peak at 490 and tailing out past 1000. IR (KBr, cm^{-1}): 3400 (NH), 2923 (CH), 2210 (CN), 1612 (C=N), 1525 (C=C).

Deuterium Exchange

In a dry box, 20 mg of **A** was dissolved in 1 ml of CD_3CN with 2 drops of CD_3OD, and the sample tube was sealed. Significant exchange was observed in the ^{1}H and ^{13}C NMR spectra after several days along with a yellow coloring of the initially clear solution.

SOLUTION STATE ANALYSIS

Previous studies have revealed two interesting observations, regarding the methyl and methylene protons, in the ^{1}H solution state NMR spectra of **A**. One particular report indicates that tautomerization is responsible for the chemistry at the methyl group, which undergoes a condensation with aryl aldehydes [6]. The methylene protons in **A** display two broad ^{1}H NMR chemical shifts, indicating a ring inversion process at room temperature [5,7]. Delving further into the issues of tautomerization, Figure 1 summarizes AM1 calculations of **A**, with three tautomeric forms (**B**–**D**). The calculations suggest that tautomerization likely occurs through the methylene group (**C**), or one methyl group (**B**), which are 5.1 and 6.5 kcal/mol greater in energy with respect to the monomer (**A**). Deuterium exchange experiments,

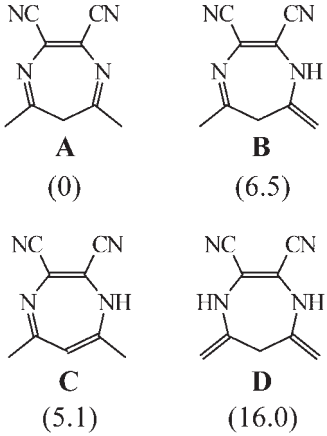


FIGURE 1 Relative energies (kcal/mol) of the monomer (**A**), and three tautomeric forms (**B**–**D**) of **A** by AM1 calculations.

however, suggests involvement of form **B** despite the relatively higher energy in comparison with form **C**.

Figure 2 displays the chemical shift region of the methyl groups in **A** following a deuterium exchange experiment, which shows a singlet for the protons in $-CH_3$, a triplet for $-CH_2D$, and a quintet for $-CHD_2$. Deuterium exchange occurs predominately at the methyl group via tautomeric form **B**. The reason why deuterium exchange favors the methyl group over the methylene group is due to the

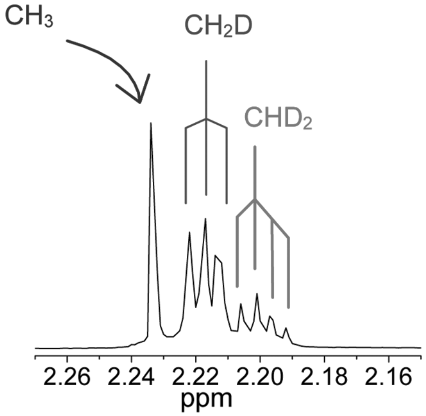


FIGURE 2 Deuterium exchange experiment of **A** displaying the ^1H chemical shift region of the methyl group resonance.

relative orientation of the C–H bonds in **A** with the diazepine moiety [6], but could also be attributed to the 8π non-aromatic system of tautomeric form **C** [8]. Unfortunately, no chemical shifts in either the ^1H or ^{13}C NMR spectra characteristic of form **B** were found, which suggests that the tautomeric intermediate state is short lived with respect to the Larmor period of the NMR signal.

SOLID STATE ANALYSIS

Crystalline **A** undergoes a solid state reaction at temperatures significantly lower than the monomer melting point. Extensive visual observations regarding the solid state reactivity of numerous crystals indicates that the temperature of initiation, and the site of initiation, are clearly dependent upon lattice defects. Heavily defected crystals will react at temperatures as low as 115°C, while crystals with visually minor imperfections react at temperatures in excess of 150°C. The reaction proceeds slowly at an annealing temperature of 140°C, and yields are low (**E**, experimental section). However, the reaction proceeds remarkably faster at 175°C, with a much greater yield (**F**, experimental section). In either case, the monomer sublimes during the thermal annealing, and at 175°C, sublimation is rapid. Because the thermal polymerization of **A** is heterogeneous, and almost certainly depends upon lattice defect sites, propagation is very likely controlled by diffusion of the monomer within the crystal. It is conceivable then, that the high yield obtained at 175°C is a consequence of significant diffusion (internal sublimation) of the monomer inside the crystal.

Figure 3 displays the ^{13}C solid state NMR spectra of **A** and the corresponding solid state polymerization products **E** and **F**. The chemical shift assignments for the monomer in ppm are the following: 26, 28 (CH_3), 52 (CH_2), 113 (t), 116 (d) (CN), 123 (d) (C=C), 159 (C=N). Aside, the monomer spectrum exhibits multiple resonances for the methyl, cyano, and alkene shifts. These splittings are a consequence of inequivalent methyl, alkene, and cyano carbons in the unit cell [9,10] as well as quadrupolar induced dipolar splittings of the cyano $^{13}C-^{14}N$ bonds. Focusing on the polymer spectra, the chemical shift assignments in ppm for polymer **E** are as follows: 14, 23 (CH_3), 48 (CH_2), 121 (=CH, and CN), 138 (sh) (=CR_2), 150 and 158 (C=NH, C=NR). The chemical shifts of **F** are essentially the same as **E**; the only undisputable difference between the two spectra is that polymer **F** clearly does not contain a methylene peak at 48 ppm. The spectrum of polymer **E** is relatively well resolved compared to the spectrum of **F**, and the chemical shifts in the imine and methyl regions of **E** correlate better with the monomer

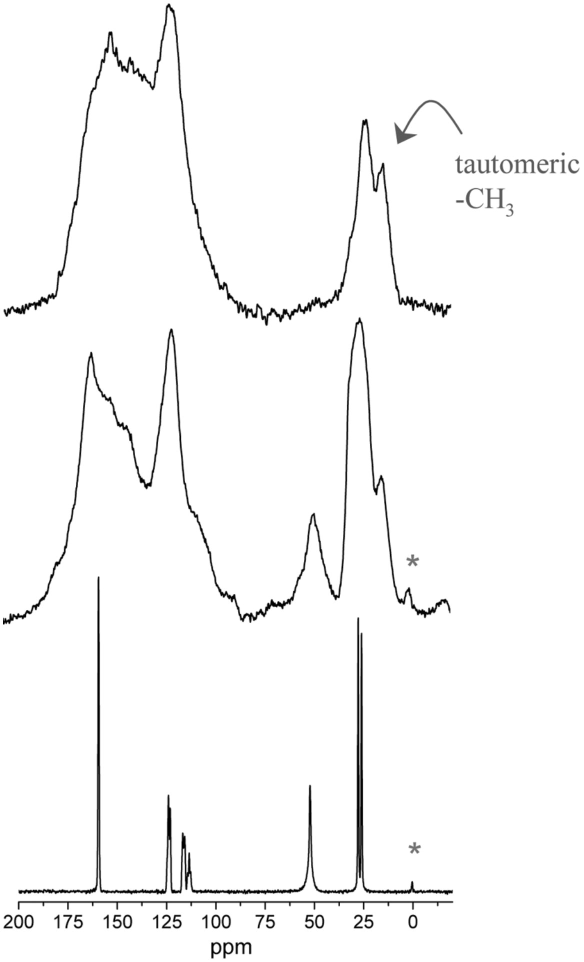


FIGURE 3 Solid state ^{13}C CP/MAS NMR spectra of the monomer **A** (lower), polymer **E** (middle), and polymer **F** (upper). * indicates spinning side bands.

spectrum than the same regions displayed in the spectrum of **F**. It is plausible that **E**, with the methylene peak and relatively enhanced resolution, is either an oligomeric product or a polymer product that does not contain a considerable degree of cross-linking (*vide infra*).

Regardless, the spectra of both **E** and **F** contain several noteworthy features, the most prominent being the two distinct chemical shifts representing the methyl carbons. Overall, the entire trace of the polymer spectra exhibit rather broad peaks, indicative of amorphous broadening. Yet, despite the broad chemical shifts, two distinguishable chemical shifts for the methyl groups are present in the polymer spectra. The two chemical shifts must be a result of two chemically distinct methyl carbons. The more intense, downfield chemical shift in the polymer spectra at 23 ppm represents the methyl groups bonded to the imine (C=N) carbons, similar to the chemical shifts of the methyl carbons in the monomer spectrum at 26 and 28 ppm. The less intense, upfield chemical shift in the polymer spectra at 14 ppm represents methyl groups bonded to alkene groups, like that of the methyl group bonded to the C=C moiety in tautomer **C**. This assignment correlates well with theoretical NMR spectra using ACD software. Another significant feature in the polymer spectra is the broad, intense chemical shift peak at 121 ppm, which tails upfield encapsulating all the chemical shifts up to approximately 90 ppm. The corresponding monomer spectrum displays very weak resonances for the alkene and cyano carbons in the region about 121 ppm. The relatively small intensities of these particular alkene and cyano carbons in **A** is a consequence of poor polarization transfer in the cross-polarization (CP) experiment, and thus cannot account for the broad, intense chemical shift at 121 ppm in the polymer spectra.

Similar to the spectra in Figure 3, Figure 4 displays the ^{13}C solid state NMR spectra of the monomer (**A**) and polymers **E** and **F** utilizing a contact time of 50 μs. The spectra are actually slices of the ubiquitous $T_{1\rho}(^{1}H)$ 2D NMR experiment [11], used extensively to separate the chemical shifts of carbons near and/or directly bonded to protons, from those that are not by consecutively incrementing the polarization transfer time between the thermally connected ^{13}C and ^{1}H spin baths. The monomer spectrum exhibits large signals for the methyl and methylene carbons, a relatively weaker signal for the imine carbons, and virtually no signal for the alkene and cyano carbons. The rationale is simple, the methyl and methylene groups are directly bonded to protons, the imine group is relatively near the methyl and methylene protons, and the alkene and cyano groups are relatively distant from the proton spins. On the other hand, the polymer spectra show large peaks at 121 ppm, with intensity greater than the methylene carbon at 48 ppm in the spectrum of **F**. The logical interpretation of the chemical shift at 121 ppm in the polymer spectra is the existence of alkene (=CH) chemical species in the polymer structure. However, the IR spectra of polymers **E** and **F** display a considerable absorption at 2210 cm^{-1}, which indicates that the cyano group is not entirely consumed in the conversion.

In addition to the ^{13}C spectra, Figure 5 displays the ^{15}N CP/MAS solid state NMR spectra of the monomer **A** and the polymer **E**. The

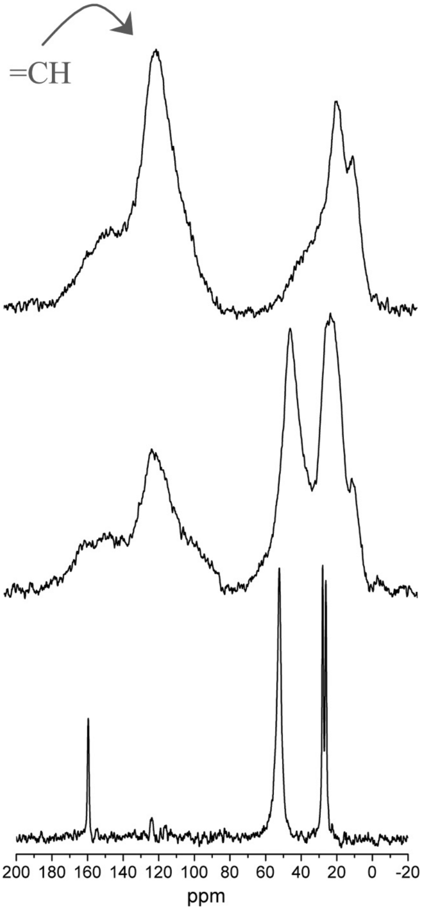


FIGURE 4 ^{13}C CP/MAS NMR spectra of the monomer **A** (lower), polymer **E** (middle), and polymer **F** (upper) utilizing a contact time of 50 ms.

^{15}N spectrum of polymer **F** was unattainable, probably due to significant cross-linking and a relatively higher degree of polymerization compared to that of polymer **E**, which likely contains a significant concentration of radicals. It is well known that the relaxation associated with unpaired spins is very efficient in delocalized, paramagnetic systems [12]. The chemical shift assignments of the monomer in ppm are: 238, 242 (CN), 266, 267 (C=N). Like the splittings in the ^{13}C spectrum of **A**, the multiple resonances in the ^{15}N spectrum are due to inequivalent cyano and imine groups in the unit cell. The ^{15}N chemical shift

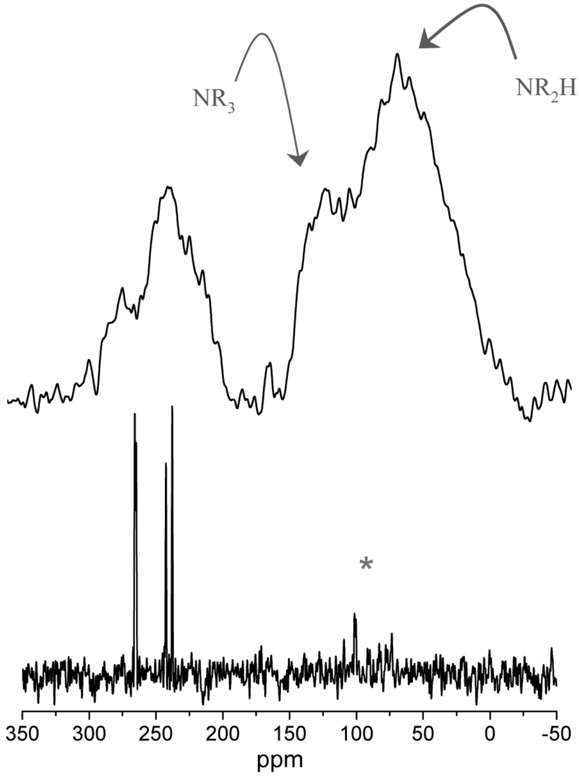


FIGURE 5 Solid state ^{15}N CP/MAS NMR spectra of **A** (lower) and the polymer **E** (upper). * indicates spinning side bands.

assignments [12] in ppm of polymer (**E**) are: 78 (br) (NR$_2$H), 130 (br) (NR$_3$), 236 (br) (CN), 268 (br) (C=N). Though broad, the polymer spectrum displays chemical shifts not present in the monomer spectrum. The polymer spectrum clearly indicates that the polymer product contains secondary (NR$_2$H) and tertiary (NR$_3$) amines within the chemical structure. The chemical shift of the secondary amine is likely similar to the amine in a tautomeric form of the monomer, located in the side chain and/or end groups of the polymeric structure.

Lastly, Figure 6 displays the ^{1}H MAS solid state NMR spectra of the monomer (**A**) and the polymer **E**. The ^{1}H spectrum of polymer **F** is fundamentally the same as polymer **E**, and was excluded. The spectra contain information that correlates with, and possibly verifies, the interpretation of the ^{13}C and ^{15}N solid state NMR spectra. The broad shapes of the spectra are indicative of ^{1}H–^{1}H dipolar broadening, which can exhibit a static interaction strength as high as 40 kHz.

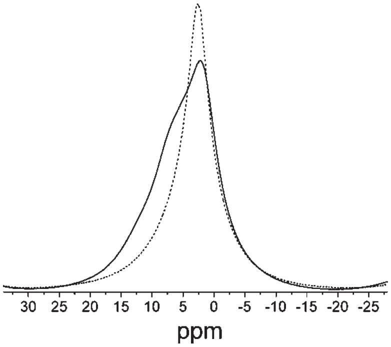
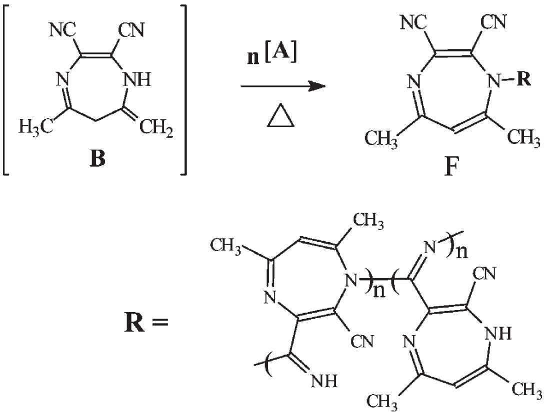


FIGURE 6 Solid state ^{1}H MAS NMR spectra of monomer **A** (dotted line) and the polymer **E** (solid line).

Fortunately, our top spinning rate of 12 kHz was sufficient in averaging out the dipolar broadening to an effective strength of approximately 2 kHz ($\Delta\nu$ at half height). The monomer spectrum exhibits one symmetrical spectral distribution, which represents the chemical shifts of the methyl and methylene protons. Unlike the monomer spectrum, the polymer spectrum is asymmetrical due to the convolution of the methyl and methylene peaks with an additional downfield chemical shift distribution. The additional downfield absorption, manifested as a pronounced shoulder in the polymer spectrum, represents the chemical shifts of the alkene (=CRH) and amine (NR_2H) protons.

Based on the NMR spectra, Scheme 1 suggests a plausible structure of polymer **F**. The IR and NMR data indicate that the polymerization



SCHEME 1 Solid state polymerization of **A** yielding polymer **F**.

involves only one of the two cyano groups, which is justified based on resonance structures of the monomer [4]. Unlike the monomer structure, the structure of the polymer consists of two chemically distinct methyl groups, secondary and tertiary amine groups (NR_2H, NR_3), and alkene (=CH) chemical moieties. The presence of these particular chemical species suggests that a tautomeric form of the monomer is responsible for, and essential to, the solid state reactivity of crystalline **A**. Like the solution state, the initial chemistry in the solid state likely involves the formation of tautomeric form **B**. Either the formation of **B** occurs at a defect site within the crystal, or the formation of the tautomeric form itself creates a defect site within the lattice. The tautomeric form likely reacts with the cyano group of an adjacent monomer molecule by nucleophilic addition by the secondary amine. The propagation, dependant upon diffusion, likely occurs through the imine (=NH) group, or through the secondary amine (NR_2H) of a tautomeric form of the side/end group. Therefore, the tertiary amine (NR_3) is likely the result of the reaction of the secondary amine, of a tautomeric form, from both propagation and cross-linking. Regardless, the polymer structure in Scheme 1 correlates well with the entirety of the solid state NMR spectra, the IR spectra, and with the information obtained from the solution state NMR experiments.

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