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Quantum-Chemical Calculations of ^{13}C Chemical Shifts of the Alkoxide Form in Zeolites

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Abstract: Quantum-chemical calculations of ^{13}C NMR chemical shifts and a mass spectrometry investigation of products of the reaction of propene on zeolite HY are presented. Saturated hydrocarbons, surface alkoxides, alkanes, cycloalkanes, aromatic compounds, and carbocations in the form of protonated aromatics have been identified. No isopropyl cation in zeolite HY has been detected.

1. Introduction

The state of adsorbed molecules has been the subject of numerous ^{13}C NMR spectroscopy investigations.[1-4] ^{13}C NMR spectra of organic compounds adsorbed on porous solids contain important information about the structure and properties of the active sites of the catalyst in the zeolites and the products of chemical reactions on zeolite surfaces. At the same time, the interpretation of these spectra is not easy. Moreover, one may make an erroneous assignment of the peaks in the NMR spectra, as in the work of Zardkoohi et al.[1] if the composition of the chemical reaction products on the surface of the zeolite is unknown. As a rule, this is due to false selection of the analogue (in the gas phase or in the solution) for the surface structure, which leads to an incorrect conclusion about its range of chemical shifts (CS). Quantum-chemical methods can be very useful to interpret these complex spectra.

In this paper, the semiempirical INDO-CS method[5,6] is applied to the interpretation of the ^{13}C NMR spectrum (obtained by Zardkoohi et al.[1]) of products resulting from the reaction of propene in zeolite HY.

Our paper consists of two main parts. In the first part (section 2), the interpretation of the ^{13}C spectrum represented in the work of Zardkoohi et al.[1] and the results of our calculations of ^{13}C CS of the clusters simulating the surface structures (suggested by the work in ref 1) are discussed. In the second part (section 3), the mass spectrometry data on the composition of products of the reaction of propene in zeolite HY are presented.

2. Discussion of the ^{13}C Spectrum

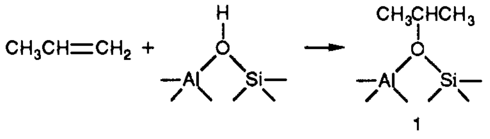
In the recent work by Zardkoohi et al.,[1] the ^{13}C NMR spectrum of products resulting from the reaction of propene on zeolite HY at 25 °C under a pressure of 30–40 Torr of propene-*2*-^{13}C (99.2% enriched) was reported. There are four peaks in the ^{13}C spectrum: two low-intensity peaks at ca. 250 ppm and at ca. 160 ppm, a peak of greater intensity at ca. 70 ppm, and a complex peak of the highest intensity at ca. 30–40 ppm.

It should be noted that ^{13}C low-field shifts of neutral molecules (in the gas state or in the solution) are less than 220 ppm. Therefore, it is readily seen that the peak at 250 ppm is in the characteristic range for carbocations. For this reason, Zardkoohi et al.[1] have assigned the peak at ca. 250 ppm to the isopropyl cation which is formed on Brönsted acidic sites immediately after adsorption of propene in zeolite HY in the form

Table I. ^{13}C CS Calculated by the INDO-CS Method[5,6] for the $CH_3C^+HCH_3$ Carbocation and the $(CH_3)_2CHOH$ Molecule in Comparison with the Results of the IGLO Method[8] and Experimental Data. ^{13}C CS (in ppm) Are Referenced to TMS

	$CH_3C^+HCH_3$		$(CH_3)_2CHOH$	
	$\delta(C^+H)$	$\delta(CH_3)$	$\delta(CH)$	$\delta(CH_3)$
INDO-CS	375	44	59	33
IGLO	365	51		
exp[c]	321[a]	52[a]	64[b]	25[b]

[a] Reference 8. [b] Reference 12. [c] In solution.



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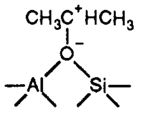
In the work of Zardkoohi et al.,[1] **1** was represented in the form



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which illustrates **2** the carbocationic character of the structure. However, in ref 7, Zhidomirov et al., using quantum-chemical methods, demonstrated that surface structures of this type are closer to surface alkoxides in their electronic structure and properties.

In this paper, the ^{13}C CS quantum-chemical calculations for the $(CH_3)_2CHOH$ molecule, the $CH_3C^+HCH_3$ carbocation, and the surface structure **1** using the INDO-CS method[5,6] are presented.

The ^{13}C CS calculations for isopropyl cation ($CH_3C^+HCH_3$) and isopropyl alcohol ($(CH_3)_2CHOH$) have shown that the results of this method are in good agreement with the experimental data and IGLO method data[8] (see Table I). The carbocation and the molecule have been selected since their structure and properties are close to that of the examined structure.

To simulate structure **1**, cluster **3** has been chosen. Clusters of this type have been used successfully in quantum-chemical calculations of the processes of adsorption of hydrocarbons in zeolites.[7,9] However, we calculated ^{13}C CS for a cluster bigger

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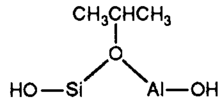
Table II. ^{13}C CS Calculated by the INDO-CS[5,6] Method of Cluster **1** for a Set of Lengths of the C–C, C–O, Si–O, and Al–O Bonds for This Cluster. ^{13}C CS (in ppm) Are Referenced to TMS

lengths of the bonds, Å	δ(CH)	δ(CH_3)
$R_{C-C} = 1.54$, $R_{C-O} = 1.45$, $R_{Si-O} = 1.67$, $R_{Al-O} = 1.90$	62	33
$R_{C-C} = 1.64$, $R_{C-O} = 1.45$, $R_{Si-O} = 1.67$, $R_{Al-O} = 1.90$	75	35
$R_{C-C} = 1.44$, $R_{C-O} = 1.45$, $R_{Si-O} = 1.67$, $R_{Al-O} = 1.90$	51	33
$R_{C-C} = 1.54$, $R_{C-O} = 1.55$, $R_{Si-O} = 1.67$, $R_{Al-O} = 1.90$	77	31
$R_{C-C} = 1.54$, $R_{C-O} = 1.35$, $R_{Si-O} = 1.67$, $R_{Al-O} = 1.90$	48	35
$R_{C-C} = 1.54$, $R_{C-O} = 1.45$, $R_{Si-O} = 1.77$, $R_{Al-O} = 1.90$	64	33
$R_{C-C} = 1.54$, $R_{C-O} = 1.45$, $R_{Si-O} = 1.57$, $R_{Al-O} = 1.90$	61	33
$R_{C-C} = 1.54$, $R_{C-O} = 1.45$, $R_{Si-O} = 1.67$, $R_{Al-O} = 2.00$	62	33
$R_{C-C} = 1.54$, $R_{C-O} = 1.45$, $R_{Si-O} = 1.67$, $R_{Al-O} = 1.80$	63	32

than cluster 3 too. Unlike cluster **3**, in the new cluster (cluster 4), one of the OH groups connected to the silicon atom was replaced by the $OSi(OH)_3$ group. The increase of the cluster size led to the insignificant ^{13}C shift (≈0.6 ppm upfield) for the central carbon atom connected to the oxygen atom. Obviously, it is an unessential shift, and the choice of cluster **3** is quite reasonable. Therefore, all the other calculations were done with cluster **3**. The geometric parameters of cluster **3** have been chosen by analogy with the geometry of isopropyl alcohol and the results of the semiempirical and nonempirical calculations of similar clusters.[7,9] These values are $R_{C-C} = 1.54$ Å, $R_{C-O} = 1.45$ Å, $R_{Si-O} = 1.67$ Å, $R_{Al-O} = 1.9$ Å, $R_{Si-OH} = 1.62$ Å, $R_{O-H} = 0.96$ Å, and $R_{C-H} = 1.105$ Å. The calculations are made for the cluster with this geometry and for the clusters with R_{C-C}, R_{C-O}, R_{Si-O}, and R_{Al-O} changed by ±0.1 Å. The results of these calculations are listed in Table II.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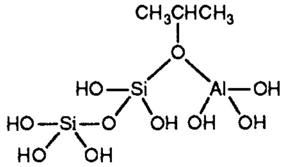
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The data in Table II demonstrate that the ^{13}C CS of the central carbon atom is changed from 45 to 72 ppm when geometric parameters are changed by ±0.1 Å. As follows from the results of nonempirical calculations,[15] the bond length R_{C-O} of CH_3–OH is by 0.088 Å less than the one of the corresponding surface alkoxide. These results and the data in Table II allow us to expect a shift about 10–15 ppm downfield for some surface alkoxide with respect to the corresponding alcohol. Therefore, one may assume that the ^{13}C CS of the central carbon atom connected with the oxygen of the isopropyl surface alkoxide is at ca. 75 ppm.

On this basis, we have concluded that the assignment of the peak at ca. 250 ppm to structure **1** made by Zardkoohi et al.[1] is incorrect. The range of ^{13}C CS of structure **1** almost coincides with the range of ^{13}C CS of the alcohol ((CH_2OH) at 58 ppm and (>CHOH) at 72 ppm[10]). This supports our conclusion that structure **1** corresponds to alkoxide—rather than to carbocation. Therefore, in the ^{13}C spectrum of adsorbed propene,[1] we have assigned the peak at ca. 70 ppm to structure **1**.

The peak at ca. 160 ppm is assigned by Zardkoohi et al.[1] to a "dynamic carbocation" (rapid exchange between alkyl cations) and the peak at ca. 70 ppm to the carbon which is β to the carbenium center. However, as follows from the results of quantum-chemical calculations[7] and the above discussion, structures **1** and **2** are closer to surface alkoxides in their electronic structure and properties. There is no isopropyl cation or similar cation in zeolite HY at room temperature. Therefore, the assignment of the peaks at ca. 160 and ca. 70 ppm to some carbon atoms of free saturated uncyclic hydrocarbons made by Zardkoohi et al.[1] is incorrect. We assign the complex peak at ca. 30–40 ppm to methylene and methyl groups of the chain of neutral molecules adsorbed in zeolite HY, which is in agreement with the conclusion made by Zardkoohi et al.[1]

On the basis of our calculations, we assign the peak at ca. 70 ppm to the central carbon atom of structure **1** and the complex peak at ca. 30–40 ppm to the carbon atoms of methylene and methyl groups of saturated hydrocarbons. No unambiguous conclusions about the assignment of peaks at ca. 250 and ca. 160 ppm can be made from our calculations. Some new additional information about the possible surface structures is needed.

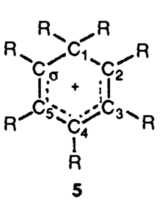
3. Mass Spectrometry Investigation

In order to further examine the composition of products on the surface of zeolite HY after adsorption of propene, we have carried out a mass spectrometry investigation of the products of thermodesorption from the zeolite surface. For this investigation, a zeolite of HNaY type containing 3 wt % Na ions was used. The examination of the adsorption of the propene on zeolite HNaY was carried out in the reactor equipped with a quartz balance. Prior to adsorption of propene, the zeolite was activated by heating the sample under argon and then under oxygen diluted with argon in the molar ratio O_2:Ar = 20:80 at 500 °C. After activation, the sample was cooled to room temperature and exposed to 70–80 Torr of propene over half an hour. After adsorption of propene, the weight of the zeolite sample increased by 20 wt %. Then the sample was unloaded from the reactor equipped with a quartz balance under air, and the thermodesorption products were analyzed mass spectrometrically. A LKB-2091 chromomass spectrometer was used to obtain the mass spectrum.

It would be better if the sample wasn't exposed to atmospheric moisture before mass spectroscopy. However, the increase of the sample weight by 20 wt % after adsorption of propene indicates that the cavities of zeolite HY are blocked by hydrocarbons. In this case, one may expect insignificant chemical changes of products in zeolite HY after short contact with air. A single wide thermodesorption peak was observed by heating the sample from 50 to 300 °C (with a constant heating rate equal to 10 g/min). The mass spectra received at temperatures from 50 to 300 °C were slightly distinguished. Therefore, one may conclude that the composition of products in the sample changes insignificantly. Consequently, the velocity of the secondary reactions of the surface products is smaller than the desorption velocity. In other cases, one must expect significant changes of mass spectra during heating. The masses of these products determined in the beginning of the thermodesorption are listed in Table III.

The analysis of the mass spectra allows us to conclude that alkanes, alkenes, cycloalkanes, and aromatic compounds are the greatest part of thermodesorption products. The presence of cycloalkenes and (or) dienes is possible too.

The results of the mass spectrometric investigation corroborate our previous conclusions about the presence of saturated hydrocarbons on the surface of zeolite HY in the form of alkoxides (after thermodesorption they must be observed in the form of alkenes). The presence of aromatics in mass spectra products (IR spectroscopy data point to the presence of aromatic compounds under identical conditions[11] too) allows us to assume the existence of carbocations in zeolite HY in the form of protonated cyclic polyenes. The arene ion (**5**) is one of these possible structures.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The ^{13}C CS for the C-1, C-2, C-3, and C-4 atoms of the carbocation are 70.1, 203.8, 148.6, and 198.2 ppm, respectively[13] (in the solution). According to the nonempirical calculations of the

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Table III. Mass Spectrum of the Products of Thermodesorption from Zeolite HY (after the Adsorption of Propene)[a]

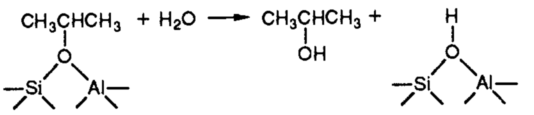
m/e	*J*	*m/e*	*J*	*m/e*	*J*
35	749	91	69	146	
36	298	92	83	147	131
37	423	93		148	
38	5301	94	1013	149	
39	1908	95	360	150	187
40	10000	96	631	151	124
41	2303	97	825	152	166
42	4351	98	138	153	305
43	1034	99		154	131
44	562	100		155	256
45	145	101	152	156	104
46		102		157	
47	194	103	201	158	
48	124	104	76	159	
49	194	105		160	69
50	943	106	166	161	
51	569	107		162	513
52	916	108	222	163	
53	340	109	367	164	166
54	6960	110	242	165	97
55	3962	111	395	166	326
56	4198	112	659	167	499
57		113	499	168	187
58	333	114		169	138
59	187	115	90	170	235
60	138	116	131	171	333
61	194	117	117	172	111
62	145	118	145	173	
63	104	119		174	117
64	256	120	242	175	
65	263	121	111	176	
66	1207	122	638	177	117
67	1186	123	416	178	
68	4142	124	229	179	
69	2130	125	499	180	
70	1526	126	235	181	76
71	41	127	180	182	326
72	298	128	90	183	562
73	319	129		184	242
74	256	130		185	
75		131	90	186	159
76	249	132	69	187	
77	298	133		188	
78	541	134		189	
79	215	135	104	190	83
80	458	136	430	191	
81	451	137	138	192	104
82	1970	138	131	193	
83	631	139	76	194	
84	575	140	159	195	138
85		141		196	222
86	152	142		197	
87	263	143	138	198	
88		144	111	199	
89	270	145	166	200	
90	111				

[a] The most intensive mass of 40 is taken as 10000.

^{13}C CS of the carbocations,[8] one would expect more downfield shifts for this arene ion in the gas phase (extremely large gas-to-liquid shifts for the most deshielding atoms may be expected—in this case for C-2, C-4, and C-6).

The spatial configuration of the large carbocation (see structure **5**) can obstruct the interaction between this ion and an active site of the zeolite. In this case (unlike the case of adsorbed $CH_3C^+HCH_3$ carbocation), one may expect small ^{13}C CS for the large adsorbed arene ion with respect to the gas phase. Therefore, we assume that one may assign the peak at ca. 250 ppm to C-2, C-4, and C-6 atoms and the peak at ca. 160 ppm to C-3 and C-5 atoms of structure **5**. The mass spectrum contains the mass signals that may be assigned to structure **5**. For example, the peak with m/e = 162 and intensity 513 may be corresponding to structure **5**, if one of the substitutes is H and all the others are CH_3 (the most intensive mass of 40 is taken as 10000). Our supposition allows us to assign all the peaks in the discussed NMR spectrum. Nevertheless, it should be noted that, possibly, there are some other, more complex protonated cyclic polyenes in zeolite HY.

Scheme I



After the preparation of this manuscript, the paper of Lange et al.[14] dealing with IR and high-resolution solid-state ^{13}C NMR studies of coke formation through the reaction of ethene over hydrogen mordenite appeared. After the samples had been heated at and above 500 K under an atmosphere of ethene, the lines were observed at 310, 245, 185, and 157 ppm and groups of lines between 9 and 50 ppm in the ^{13}C NMR spectra. Lange et al.[14] concluded that there are alkyl and allyl carbocations as well as protonated aromatics on the surface of the zeolite. They have assigned the line observed at 310 ppm to the positively charged carbon of alkyl carbocations such as in $(CH_3)_3C^+$ or $(CH_3)_2C^+C_2H_5$. In our opinion, this line can be referred to as some alkyl carbocation with more complicated ligands obstructing the interaction between the positively charged carbon of this carbocation and an active site of the zeolite. On the whole, their conclusions confirm our statement about the existence of carbocations in the zeolite in the form of protonated aromatics.

4. Conclusion

We have shown that one may successfully use quantum-chemical methods for the assignment of NMR spectra of adsorbed molecules and surface structures. Our calculations of ^{13}C CS of the surface structures allow us to assert that the assignment of peaks at ca. 250, ca. 160, and 70 ppm made by Zardkoohi et al.[1] (without application of quantum-chemical calculation) is incorrect. On the basis of our calculations of ^{13}C CS and the mass spectrometric data, we assign the complex peak at ca. 30–40 ppm to the carbon atoms of methylene and methyl groups of saturated hydrocarbons and surface structures, the peak at ca. 70 ppm to the central carbon atom of surface alkoxides, and the peaks at ca. 160 ppm and at ca. 250 ppm to protonated aromatics. Arene ions (see structure **5**) are some of these possible carbocations.

We hope that further investigations of the processes on the surface of zeolites and surface structure corroborate the correctness of our assignment of the peaks in the discussed spectrum.

Note Added in Proof: After our paper had been submitted for publication in *J. Am. Chem. Soc.*, the paper of Haw et al.[16] was published. In this paper,[16] a very interesting additional investigation of the products of the reaction of propene on zeolite HY by ^{13}C solid-state NMR was done. On the basis of the NMR data, the authors have done significant revision of the results of the work in ref 1, In ref 16, How et al. have reached similar conclusions as ours based on the data of ^{13}C CS quantum-chemical calculations and the results of the mass spectrometry investigation. These are as follows.

(1) No isopropyl cation in zeolite HY is detected.

(2) The peak at ca. 70 ppm[1] (at 87 ppm in ref 16) is assigned to surface alkoxides.

As follows from our results, one may expect a shift about 10–15 ppm downfield of the surface alkoxide with respect to the corresponding alcohol. This is in good agreement with the results of Haw et al.,[16] who assigned the peak at 87 ppm to surface alkoxides and the peak at 67 ppm to alcohols. It is possible to propose the mechanism of alcohol formation after the sample exposure to atmospheric moisture (Scheme I) (for the sake of simplicity, the formation of isopropyl alcohol is considered).

(3) The peaks at 250 ppm and at 143 ppm are assigned to cycloenyl carbocations (the peak at 143 ppm may be assigned to olefinic carbons of oligomeric species[16] or (and) to aromatic

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(16) Haw, J. F.; Richardson, B. R.; Oshiro, I. S.; Lazo, N. D.; Speed, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 2052.

compounds). In our paper, we propose structure **5** as a possible cycloenyl carbocation structure, but Haw et al.[16] propose cyclopentenyl carbocation structures ($C_9H_{15}^+$, structures XIII-XIV from ref 16). In our mass spectrum, there are mass peaks with $m/e = 162$ (this peak may be assigned to structure **5** with R_1 = H and R_{2-7} = CH_3) and with $m/e = 123$ and 122 (these peaks may be assigned to cyclopentenyl structures XIII-XIV from ref 16) with intensities 513, 416, and 638, respectively.

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Registry No. Propene, 115-07-1.

Characterization of Nylon 6 by ^{15}N Solid-State Nuclear Magnetic Resonance

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Abstract: The solid-state ^{15}N NMR characterization of nylon 6 is reported. Nylon 6 (20% ^{15}N-enriched) was prepared by anionic polymerization of isotopically enriched ε-caprolactam. The samples were prepared by three different treatments: quenched from the melt, slowly cooled and annealed, and artificially plasticized with excess caprolactam. CP/MAS spectra of the ^{15}N-enriched samples showed a single sharp peak (α crystal form) at 84.2 ppm (relative to glycine) and a broader resonance at 87.2 ppm. Relaxation experiments were conducted to determine T_{1N}, T_{1H}, and $T_{1\rho}$ for each sample at 300 K. The crystalline resonance was found to have T_{1N}'s of 125–416 s, consistent with crystalline nylon 6. The downfield peak had two measurable T_{1N}'s: a short component with T_{1N} of 1–3 s and a second component with a longer T_{1N} of 19–29 s. The two components for the noncrystalline peak are thought to belong to a liquidlike amorphous region and a more rigid "interphase" region lying between the crystalline and amorphous regions. $T_{1\rho N}$ measurements were consistent with two-phase (crystalline plus amorphous) morphology although the two-component decay for the amorphous region was not observed. The presence of plasticizer (caprolactam) tended to decrease $T_{1\rho N}$ relaxation times, which is consistent with lowered T_g's. ^1H T_1 measurements were apparently dominated by spin diffusion that masked any differences between the regions. The chemical shift anisotropy (CSA) spectra of static samples are also shown. Motion in the amorphous region can be monitored by observing an isotropic peak at elevated temperatures. The effect of plasticizer (caprolactam) contributes to this motion. At temperatures above 100 °C, the most deshielded (σ_{33}) component is lost from the CSA spectrum, suggesting a previously unreported anisotropic motion occurring in the rigid crystalline region. This motion is thought to be associated with the intermolecular hydrogen bond between adjacent chains.

High-resolution solid-state NMR is becoming an important tool for characterizing polymer systems. Cross-polarization and magic angle spinning (CP/MAS) along with high-power decoupling allow acquisition of high-resolution spectra of natural-abundance ^{13}C nuclei with good sensitivity. The ^{13}C solid-state CP/MAS NMR of some important commercial polymers has improved our understanding of their microstructure and phase behavior.[1-5] Relaxation studies have identified noncrystalline regions poorly characterized by X-ray.[3]

Recently, we have demonstrated that solid-state CP/MAS NMR of natural-abundance ^{15}N is readily obtainable on solid polyamides.[6,7] In addition, ^{15}N CP/MAS peaks were shown to correlate with the two predominant crystal forms found in most solid polyamides, i.e., namely α and γ crystal forms. Resonances were observed for other regions that could not be assigned to either crystal form. Further study by NMR and molecular modeling calculations showed nitrogen chemical shifts to be extremely sensitive to conformation about the amide group potentially providing a tool for observing ordered region conformations in solid polyamides.[8]

Although natural-abundance spectra are attractive from a general utility point of view, the low sensitivity of nitrogen makes observation of small amounts of impurities and reaction byproducts difficult or impossible. Relaxation experiments (T_1, $T_{1\rho}$) are also time consuming and may be impossible on most instruments with most samples. Our interest in examining the previously unobserved noncrystalline and amorphous regions in polyamides by ^{15}N CP/MAS prompted us to prepare an isotopically enriched polyamide sample.

We chose to prepare an ^{15}N-enriched sample of nylon 6 because it is an important commercial polyamide that has been thoroughly characterized in the solid state by many techniques (DSC, IR, X-ray) including solid-state ^{13}C NMR.[4,5] Laboratory preparation of nylon 6 is relatively straightforward. Isotopic enrichment was accomplished using commercially available hydroxylamine hydrochloride (99% ^{15}N) as shown in Figure 1. Here we report details of the polymer synthesis as well as ^{15}N NMR characterization of nylon 6 under a variety of conditions using several NMR methods.

Experimental Section

^{15}N NMR. Spectra were obtained on a Bruker MSL-200 NMR spectrometer operating at a field strength of 4.7 T and equipped with a Bruker MAS probe. The ^{15}N resonance frequency was 20.287 MHz, and that of the ^1H was 200.13 MHz. Samples were placed in fused zirconia rotors fitted with Kel-F caps and spun at 3.0–3.2 kHz with dry air. Crystalline glycine was placed in the rotor with the samples and used as

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