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Solution ^{13}C NMR Characterization of Nylon 66: Quantitation of Cis Amide Conformers, Acid and Amine End Groups, and Cyclic Unimers

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ABSTRACT: Using a 2,2,2-trifluoroethanol/deuteriochloroform solvent mixture (TFE/$CDCl_3$), well-resolved solution ^{13}C NMR spectra of nylon 66 samples were obtained that showed several low-intensity peaks not seen in other, more acidic solvents. These low-intensity peaks were correlated to the methylene carbons near cis amide conformers, acid and amine end groups, and within cyclic oligomers. On the basis of relative peak intensities, the quantitative contents of these components for a typical sample of nylon 66 were determined to be 1.1 mol % cis amide conformers, 1.0 mol % acid end groups, and 0.5 mol % amine end groups. A number-average molecular weight of 30 177 g/mol was calculated from end group concentrations, which is a typical value for commercial nylon 66 samples. The chemical shift values of methylene carbons contained in end groups and in cyclic oligomers were found to be pH sensitive and therefore dependent on the relative concentrations of acid and amine end groups present in each sample. Understanding this behavior, in conjunction with the peak assignments described here, allows identification and quantitation of structural units and contaminants important in controlling chemical and physical properties.

Introduction

Historically, analytical and spectral characterization of polyamides required dissolution in aggressive solvents. Most of these were acidic and/or contained water (formic acid, *m*-cresol),[1] while others consisted of metal salt−solvent mixtures such as LiCl in CH_3OH[1] and LiCl or $CaCl_2$ in polar nonprotic solvents such as *N*,*N*-dimethylacetamide, *N*,*N*,*N*′,*N*′-tetramethylurea, and *N*-methylpyrrolidinone.[2−4] The acidic solvents often degraded the polyamides during analysis, especially when elevated temperatures were used to facilitate the dissolution process. Acidic solvents also protonated amine end groups and interacted so strongly with the amide carbonyls of the polyamides that very viscous solutions were formed due to the polyelectrolyte effect even at low polymer concentrations (<5 wt %).[1] The metal salt−solvent systems also strongly interacted with the amide carbonyls and caused similar increases in viscosity, making it difficult to obtain high-resolution spectra due to peak broadening. Both the decrease in resolution and the strong polymer−solvent interactions masked important compositional and configurational information.

Aharoni and co-workers[5] described use of nonacidic and mild solvent systems combining fluorinated alcohols (2,2,2-trifluoroethanol or hexafluoro-2-propanol) and chloroalkanes (chloroform, methylene chloride, or 1,2-dichloroethane) to dissolve linear aliphatic polyamides. For example, they constructed phase diagrams for various nylons along with plots of percent volume expansion and intrinsic viscosity versus concentration of 2,2,2-trifluoroethanol (TFE) in solvent mixtures with chloroalkanes. Most important, these polyamide solutions had markedly reduced viscosities compared to those obtained with *m*-cresol, formic acid, or LiCl/methanol solvents, for example.

Solvation of polyamides apparently occurs in two steps. First, the TFE disrupts amide hydrogen bonding through strong interactions with the nitrogen and oxygen of the amide linkages. The CH_2Cl_2 or $CHCl_3$ then solvates and dissolves this polymer−TFE complex. Other chloroalkanes were either not miscible with TFE or showed a decrease in polyamide dissolution ability. We have determined that the best polyamide solutions for spectral analysis contain 10−20 wt % polymer in an 80:20 mixture of TFE to $CHCl_3$ or CH_2Cl_2. Hexafluoro-2-propanol was not studied in detail because it is more toxic and much more expensive than TFE.

Using a TFE/$CDCl_3$ solvent system, we obtained well-resolved and high signal-to-noise solution ^{13}C NMR spectra of nylons 6, 11, 12, 66, 69, 610, and 612 and various copolymers of A−B and AA−BB monomer systems. We communicated our initial results, focused on cis amide observation, in earlier papers.[6,7] We have now greatly extended our NMR observations of these and other nylon systems and have observed a number of useful and unique peaks that provide important qualitative and quantitative data about each. In this paper, only nylon 66 will be discussed in detail, although the detailed model studies and peak assignments described here serve as the basis for assigning and quantifying peaks for the other nylons which will be reported subsequently. At least 15 previously unobserved peaks were revealed in the solution ^{13}C NMR spectra of nylon 66 using this solvent mixture. These peaks were identified as described below and were then used to quantify a variety of contaminants and polymer components present at concentrations as low as 0.2 mol %. We will discuss each type of newly identified sets of peaks with the individual components that contributes these peaks in the context of literature and model compound analyses.

Experimental Section

Solution ^{13}C NMR samples were prepared by dissolving in 2,2,2-trifluoroethanol (TFE) with heating and then adding $CDCl_3$ to the cooled solution to give a sample with 10−20 wt % polymer in a solvent consisting of 80:20 TFE to $CDCl_3$. Solution spectra were collected on a Bruker AC-300 MHz NMR operating at 75.47 MHz spectral frequency. A 5 mm NMR probe was used with the average number of transients being

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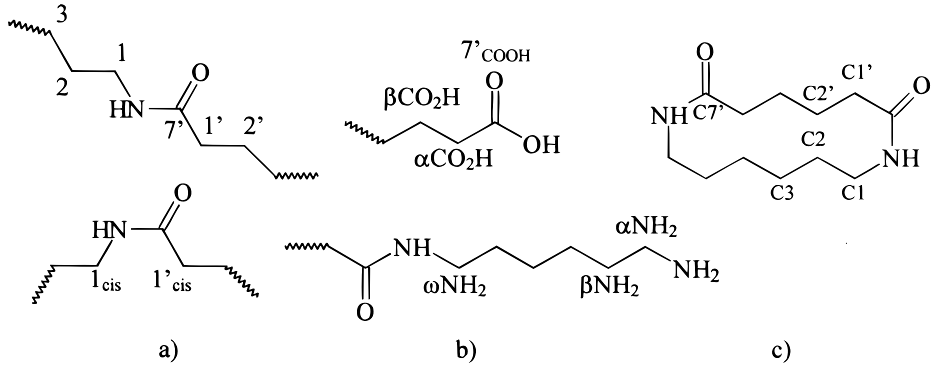

Figure 1. (a) Trans and cis amide conformers, (b) acid and amine end groups, and (c) cyclic unimer. Position labeling for nylon 66 NMR spectra is shown.

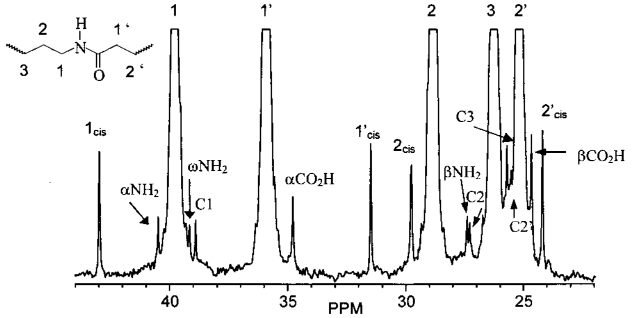

Figure 2. Solution ^{13}C NMR spectra of nylon 66 dissolved in TFE/CDCl$_3$ (aliphatic region).

15 000 (~12 h) to give sufficient signal-to-noise to allow quantitation of end groups and cis amide content. No change in the ^{13}C NMR spectrum was observed for a polyamide sample dissolved in TFE/CDCl$_3$ and held at 50 °C for over 1 month, indicating that hydrolysis and degradation are not occurring in this solvent system. NMR samples acquired in phenol and 2,2,2-trifluoroacetic acid (TFA) were prepared using the same procedure. (A CDCl$_3$ capillary insert was used as NMR lock for the phenol and TFA samples.) Approximately 24 000 scans (~18 h) were needed to obtain spectra with adequate signal-to-noise.

Structures of trans and cis amide conformers, amine and acid end groups, and cyclic unimers are illustrated in Figure 1 with the labeling used for ^{13}C NMR peak assignments. Quantitation of cis amide conformers, amine end groups, acid end groups, and cyclic nylon 66 unimer were based on relative peak intensities (measured peak heights) in solution ^{13}C NMR spectra. The peaks used for quantitation were 1_{cis}, αNH_2, βCO_2H, and C1, respectively, relative to peak 1 (Figure 2). For example, the ratio of the intensities of the 1_{cis} peak to the 1 peak was used to determine cis amide conformer content. These peaks were the most resolved and were found to accurately reflect the content of the conformers and end groups based on comparisons to well-characterized nylon 66 samples with known monomer contents and molecular weights (data not included here).

The number-average molecular weight was calculated from NMR peak intensities using the following equation:

$$M_n \text{ (g/mol)} = M_0(I_1/2)/[(I_{\alpha NH_2} + I_{\beta CO_2H})/2]$$

M_0 is the molecular weight of the repeat unit for nylon 66 (226.33 g/mol) and $I_{\alpha NH_2}$ and $I_{\beta CO_2H}$ refer to the peak intensities of the methylene carbons α to amine end groups and β to acid end groups, respectively. I_1 represents the intensity of the methylene carbon α to the nitrogen of a trans amide conformer.

Acid Terminated Nylon 66 Oligomer (1). An acid terminated oligomer was synthesized using an adipic acid-rich melt condensation polymerization. The hexamethylenediamine–adipic acid salt was prepared as follows. A 100 mL Erlenmeyer flask was charged with adipic acid (2.92 g, 0.02 mol) and ethyl alcohol (30 mL). The acid was dissolved with heating, and then hexamethylenediamine (2.32 g, 0.02 mol) in 10 mL of ethyl alcohol was added to the cooled solution. The nylon 66 salt slowly crystallized overnight. The salt was filtered under low vacuum, washed with cold ethyl alcohol, and air-dried. This salt (2.5 g) and adipic acid (0.1 g, 0.68 mmol) were placed in a test tube and sealed with a septum. The test tube was evacuated and purged with nitrogen three times, then vacuum was applied, and the temperature increased to 280 °C. After cooling, the test tube was broken, and the plug of oligomer **1** was separated, broken into small pieces, and used for analysis.

Amine Terminated Nylon 66 Oligomer (2). A 200 mL round-bottom flask equipped with a magnetic stir bar was charged with hexamethylenediamine (1.16 g, 10 mmol), triethylamine (3.0 g, 30 mmol), and 50 mL of methylene chloride. A solution of adipoyl chloride (1.5 g, 8.2 mmol) and 40 mL of methylene chloride was added to the diamine mixture under vigorous agitation. Oligomer **2** was precipitated into methanol, filtered, washed with water, and dried under high vacuum and then purified by dissolving in 2,2,2-trifluoroethanol and reprecipitating into methanol. Residual solvent was removed under high vacuum at room temperature.

Cyclic Nylon 66 Unimer (3) and Dimer (4). The nylon 66 cyclics were obtained (1) from purified nylon 66 debris accumulated from an industrial spinning facility, (2) by sublimation from nylon 66 pellets at high vacuum, and (3) by extraction from nylon 66 with boiling water or warm methanol. Cyclic unimer **(3)** was separated from higher cyclics by extraction into ethyl acetate. Cyclic dimer **(4)** was separated from the remaining higher order cyclics by sublimation at 0.05 Torr and 200 °C. The identities of **3** and **4** were confirmed after purification by melting point depression in acetic acid, mass spectrometry, and NMR spectrometry. Only the cyclic unimer was distinguishable from the nylon 66 polymer by solution ^{13}C NMR spectral analysis.

Acid and Base Shift Reagents. Acid and base shift reagents were synthesized as follows. The acid shift reagent was generated by bubbling approximately 10 mL of gaseous HCl through 5 mL of TFE. The base shift reagent was a dilute solution of sodium 2,2,2-trifluoroethoxide formed by the addition of approximately 0.03 g of NaH to 5 mL of TFE. Various pH plots were generated by sequential addition of shift reagents directly into 5 mm NMR tubes containing nylon 66 or the cyclic oligomer solutions. All chemical shifts are given relative to those seen in pure TFE/CDCl$_3$, which had a pH value of 5 (as measured with standard pH paper). The amount of shift reagent added each time varied between 0.04 and 0.20 mL. Smaller quantities were added in pH regions undergoing greater chemical shift changes per volume of shift reagent added; i.e., the pH plots have qualitative and not quantitative meaning.

Results and Discussion

Previous Work. The advantages of low viscosity at relatively high polyamide concentrations on ^{13}C NMR spectra were illustrated in a previous publication with spectra from nylon 66 dissolved in TFE/$CDCl_3$ compared to those in phenol and 2,2,2-trifluoroacetic acid (TFA) solvents.[6] The phenol and TFA solutions were viscous, even at much lower polyamide concentrations (<5 wt %), and required approximately 8000 more transients to achieve a signal-to-noise ratio similar to that obtained for the TFE/$CDCl_3$ sample. More importantly, peak width at half-height was over twice as large in phenol and TFA solvents: >10 Hz for TFA and phenol versus 4.7 Hz for TFE/$CDCl_3$. While some of the characteristic small peaks (assigned to acid and amine end groups and cis amide conformers) were seen in the TFA and phenol solution spectra, peak broadening and position varied considerably which made assignment difficult. Higher temperatures partially eliminated this broadening, but usually at the expense of degradation and other problems. The use of TFE/$CDCl_3$ resulted in sharp, well-resolved peaks (assigned in the following sections) for all of the methylene carbons near cis and trans amide conformers, acid end groups, and amine end groups produced. In addition, these peaks were easily quantified by either peak integration or peak height comparisons. In this work, we found that both methods are effective as long as peak height comparisons are made between similar types of carbons, and for ease of use, peak heights provide a much more rapid determination of relative concentrations; values reported here are based on peak height ratios.

a. Cis Amide Group Assignments. Solution ^{13}C NMR peak assignments of cis amide conformers were based on the small molecule studies of Huigsen,[8] Williamson,[9] and our previous work.[6,7] It should be remembered that the amide groups of nylons, peptides, and small molecules consist of flat arrays of sp^2-hybridized atoms with inhibited rotation around the nitrogen and carbonyl carbons that allows observation of both cis and trans conformations (actually configurations); even common solvents such as *N*,*N*-dimethylacetamide show individual peaks for each conformer. Huigsen used IR to show how the ring size of cyclic lactams influenced the ratios of cis and trans conformations (configurations) of amide groups. Cis amide conformers were preferred in five- to eight-membered cyclic lactams while the trans amide conformer was preferred in ring sizes greater than 10. They also reported that the nine-membered lactam (1-aza-2-cyclononanone) preferred the trans amide conformer in the crystalline state and the cis amide in dilute chloroform solution. Williamson[9] observed the same trend using solution ^{13}C NMR with D_2O, DMSO-d_6, or $CDCl_3$. By varying the solvent and temperature, the ratios of cis and trans amide conformers were altered for the nine-membered cyclic lactam. The solution ^{13}C NMR spectrum of the all trans conformer was acquired at -35 °C in chloroform while the spectrum of the mixture with predominately cis conformer was acquired at temperatures greater than -5 °C in chloroform. It was also reported that in ethanol, dimethyl sulfoxide, and 1,1,2,2-tetrachloroethylene the populations of cis and trans amide conformers were about equal. These results confirm that, while the amide linkages in cyclic and linear polyamides greatly prefer the trans conformation, solvent and temperature can influence equilibrium populations.

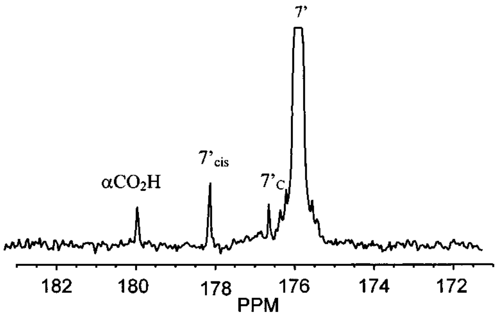

Figure 3. Solution ^{13}C NMR spectra of nylon 66 dissolved in TFE/$CDCl_3$ (carbonyl region).

Table 1. Solution ^{13}C NMR Chemical Shifts for Nylon 66 Cis and Trans Amide Conformers, Acid and Amine End Groups and Cyclic Unimers and Dimers in TFE/$CDCl_3$

	nylon 66		cyclic nylon 66 unimer	cyclic nylon 66 dimer
	trans	cis		
main chain				
1	40.03	43.23	38.79	40.03
2	29.08	29.76	27.21	29.08
3	26.49	*	25.73	26.49
1′	36.10	31.68	36.07	36.10
2′	25.39	24.43	25.56	25.39
7′	176.01	178.15	176.44	176.01
end groups				
αNH_2	40.67	*	*	*
$\beta$$NH_2$	27.67	*	*	*
$\omega$$NH_2$	39.06	*		
αCO_2H	34.98	*	*	*
$\beta$$CO_2H$	24.89	*	*	*
7′CO_2H	180.44	*	*	*

In a previous publication we compared the solution ^{13}C NMR spectra of nylon 66 and the eight-membered lactam and confirmed that the peaks labeled “cis” possessed similar chemical shifts to the cis amide form of 1-aza-2-cyclooctanone dissolved in $CDCl_3$ at room temperature.[6] Chemical shift assignments for the methylene carbons representing cis and trans amide segments are included in Table 1.

Our identification of the cis amide conformer in nylons allowed analysis of variable temperature solution ^{13}C NMR spectra of nylon 66 dissolved in TFE/$CDCl_3$ obtained at -10 to 75 °C. The gradual growth of the five very small cis amide peaks with increasing temperature lead to a maximum cis content of approximately 1.1 mol % at 50 °C. Peak broadening at 75 °C resulted from decreased solvent−polymer interactions and solvent reflux in the NMR tube. Using these data, a plot of cis content versus temperature allowed calculation of apparent activation energy of 10.5 kcal/mol.

Current Work. a. End Group Assignments. Solution ^{13}C NMR peak assignments of methylene carbons contained in acid and amine end groups were based on two polyamide oligomers synthesized with excess acid and amine end groups, respectively. Acid terminated oligomer was obtained by bulk thermal polymerization using excess adipic acid. Amine terminated oligomer was obtained by solution polymerization using adipoyl chloride, excess hexamethylenediamine, and excess triethylamine as acid scavenger. The key assignment made first for the free acid carbonyl carbon was facilitated by the acid terminated oligomer **1**, which showed a large increase in peak height for the peak labeled αCO_2H in Figure 3. Methylene peak assignments were not so straightforward.

Changes in chemical shift values of the peaks associated with the two types of end groups depended on the actual concentration of acid and amine end groups, suggesting that the chemical shifts were sensitive to overall solution pH. In other words, the relative amounts

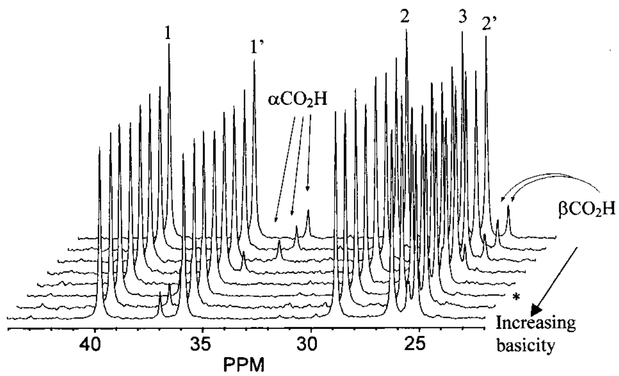

Figure 4. Solution ^{13}C NMR spectra of **1** illustrating chemical shift sensitivity of α and β CH_2s of acid end groups to pH changes (* indicates neutral TFE/$CDCl_3$).

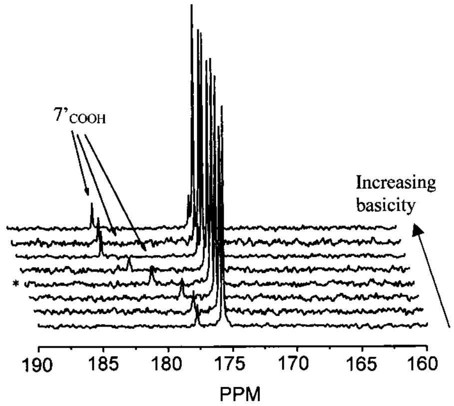

Figure 5. Solution ^{13}C NMR spectra of **1** illustrating chemical shift sensitivity of acid end group carbonyl to pH changes (* indicates neutral TFE/$CDCl_3$).

of acid and amine end groups in the polyamide itself were sufficient to alter the pH value of an otherwise "neutral" TFE/$CDCl_3$ solvent (no added acid or base, exact pH value ~5), thus altering the chemical shift values of peaks associated with end groups. This suggested that assignments could be facilitated by deliberately changing the solution pH value by adding dilute acid and base. To enhance peak heights and decrease NMR analysis time, the acid and amine terminated oligomers **1** and **2** were used. Through a series of solution ^{13}C NMR experiments on these two oligomers, in which the pH value was changed by addition of minuscule amounts (~0.04−0.2 mL) of the acid and base reagents described in the Experimental Section, the effect of pH on chemical shifts of methylene carbons near the end groups was determined qualitatively.

Solution ^{13}C NMR spectra of oligomer **1** dissolved in TFE/$CDCl_3$ and at various pH values are provided in Figures 4 and 5. (Only the spectrum closest to the x-axis gives true chemical shift values; others are offset for clearer observation.) The NMR spectra of **1** in "*neutral*" TFE/$CDCl_3$ (no added acid or base) is indicated by "*". By addition of small amounts of acid or base shift solutions to the NMR sample, the pH value was changed from approximately 2 to 10 (as estimated using pH paper to which a drop of the NMR solution was added). In acidic conditions (pH < 4), the carbonyl of acid end groups was protonated, resulting in upfield shifts of low-intensity peaks for $7'_{COOH}$, αCO_2H, and βCO_2H to 177.5, 33.3, and 24.2 ppm, respectively. In basic conditions (pH > 7), acid end groups were deprotonated, resulting in downfield shifts of these three peaks to 181.2, 37.0, and 25.7 ppm, respectively. This behavior, along with proximity of these peaks close to the larger trans amide peaks, was used to confirm assignments of the low-intensity peaks labeled $7'_{COOH}$, αCO_2H, and βCO_2H in Figures 4 and 5. Not surprisingly, the CH_2 closest to the acid end group is most sensitive to pH changes. The chemical shifts of carbons representing nylon 66 acid end groups in "neutral" TFE/$CDCl_3$ are listed in Table 1.

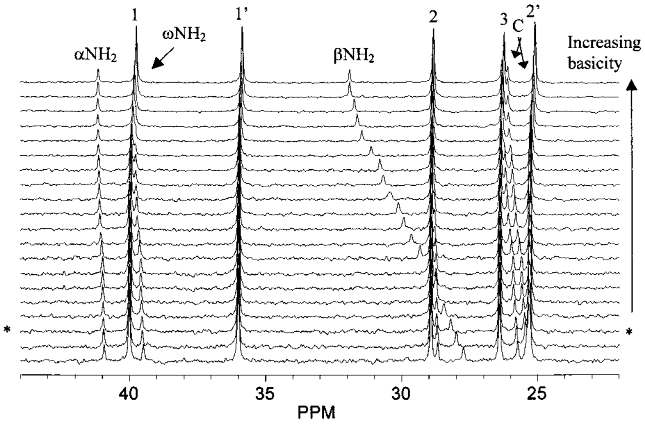

Figure 6. Solution ^{13}C NMR spectra of **2** showing chemical shift sensitivity of α, β, and ω CH_2s of amine end groups to pH changes (* indicates neutral TFE/$CDCl_3$).

Solution ^{13}C NMR peak assignments of methylene carbons located near amine end groups of nylon 66 were based on amine terminated nylon 66 oligomer, **2**. Solution ^{13}C NMR spectra of this model compound dissolved in TFE/$CDCl_3$ and at various pH values are provided in Figure 6. Again, the pH value was adjusted from 2 to 10 by addition of small amounts of acid or base shift solutions to the NMR sample. In acidic conditions (pH < 4), the nitrogens of amine end groups were protonated, resulting in an upfield shift of low-intensity peaks to 40.8, 39.5, and 27.8 ppm for αNH_2, ωNH_2, and βNH_2 carbons, respectively. In basic conditions (pH > 7), the low-intensity peaks shifted downfield to 41.2, 40.0, and 33.0 ppm for αNH_2, ωNH_2, and βNH_2, respectively. These three low-intensity peaks were assigned to CH_2s α to amine end groups, α to the amide nitrogen of amine end groups (ω to the terminal amine), and β to amine end groups, respectively. These assignments are consistent with peak position proximity to larger trans amide peaks and to chemical shift values reported for aliphatic amines and the ammonium ion analogue.[10,11] The large chemical shift sensitivity of the βNH_2 methylene is surprising but consistent with behavior of other aliphatic amines.[10,11] Values reported in Table 1 are for the "neutral" TFE/$CDCl_3$ solution.

b. Cyclic Oligomer Peak Assignments. Major contaminants of all AA−BB nylons include cyclic oligomers ranging from the "unimer," which consists of one each of the diacid and diamine of the polyamide repeat unit, up through the dimer, trimer, and higher oligomers that are observed in decreasing concentration. We obtained relatively pure samples of the cyclic unimer and dimer for nylon 66 from industrial spinning residues and obtained their solution ^{13}C NMR spectra. Peaks of the cyclic nylon 66 unimer (cyclic bis-lactam) were readily identified. The chemical shift values of the methylene carbons contained in this cyclic species were surprisingly sensitive to pH, especially in comparison

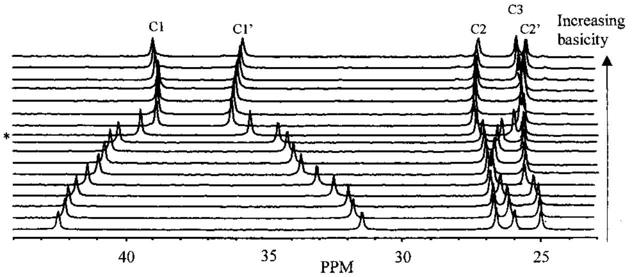

Figure 7. Solution ^{13}C NMR spectra of **3** showing chemical shift sensitivity of CH$_2$s to pH changes (* indicates neutral TFE/CDCl$_3$).

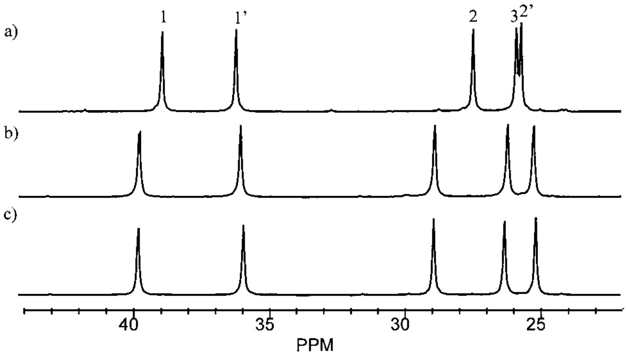

Figure 8. Solution ^{13}C NMR spectra of (a) cyclic unimer, (b) cyclic dimer, and (c) nylon 66 dissolved in TFE/CDCl$_3$ (expansion of aliphatic region).

to the parent nylon 66 (spectra in Figures 2, 3, and 6). Changes with respect to pH were determined and are shown in Figure 7. The surprisingly large changes in peak positions with pH (and the absence of such behavior for the cyclic dimer, nylon 66, and the two oligomers) indicate that there is some kind of complex formed between the unimer and either the proton of the acid (not likely) or the base counterion (sodium ion). The latter would be very similar to the well-known behavior of crown ethers and might involve interaction of either or both of the amide carbonyls with the cation. This behavior is worth further study.

The peaks labeled “C” in Figures 2, 3, 6, and 7 were thus consistently identified as resulting from the carbons of the cyclic nylon 66 unimer. Comparison of the solution ^{13}C NMR spectrum of the cyclic dimer (two diacids and two diamines in a cyclic tetralactam) to the spectra of nylon 66 and the cyclic unimer show that the cyclic dimer can be distinguished easily from the cyclic unimer but not from nylon 66 (Figure 8). Thus, in a solution ^{13}C NMR spectrum of nylon 66, the higher cyclics (dimer or greater) cannot be readily observed or quantified. An important observation is that these cyclic materials (14- and 28-atom multilactams) are almost exclusively in the trans amide conformation, consistent with the behavior of lactams with greater than 10 atoms that also show almost exclusive trans amide conformers. The chemical shifts of carbonyl and methylene carbon peaks of the cyclic unimer and cyclic dimer of nylon 66 dissolved in “neutral” TFE/CDCl$_3$ are listed in Table 1.

Conclusions

A nonacidic binary solvent system containing 2,2,2-trifluoroethanol and CDCl$_3$ allows formation of low-viscosity nylon solutions even at polyamide contents greater than 10 wt %. Sharp, well-resolved peaks are observed for nylon 66 that allow qualitative identification of peaks not possible using traditional solvents such as phenol, 2,2,2-trifluoroacetic acid, and various alkali salts in *N*,*N*-dimethylacetamide, tetramethylurea, and *N*-methylpyrrolidinone. Because this solvent system allows control of pH from acidic to basic, peaks associated with acid and amine end group segments could be easily observed and quantified, allowing rapid determination of number-average molecular weights. Cis amide conformations could be correlated with temperature and were observed in all spectra of nylon 66, possibly having important implications to nylon 66 processing and crystallization behavior. Observation of contamination by residual cyclic unimer was possible, especially with pH change, although higher cyclic oligomers could not be distinguished from polymer. The TFE/CDCl$_3$ spectrum of a typical polyamide gave values of 1.1 mol % cis amide conformer, 1.0 mol % acid end groups, and 0.5 mol % amine end groups. On the basis of these values, the number-average molecular weight was calculated as 30 177 g/mol using the equation in the Experimental Section. Clearly, availability of such a useful and readily available solvent system will extend the utility of solution NMR methods for the analysis of nylons with respect to composition, impurities, additives, deliberate end-capping, and degradation due to oxidation and thermal reactions. We discuss the application of this system to further study a wide variety of nylon homopolymers, copolymers, and terpolymers in another publication.[12]

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