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A new non-acidic mixed solvent system for nylon nuclear magnetic resonance: *cis* amide quantitation in nylons and model amides

Scott J. Steadman and Lon J. Mathias*
Department of Polymer Science, Southern Station 10076, University of Southern Mississippi, Hattiesburg, MS 39406-0076, USA
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Use of binary fluorinated alcohol-chloroalkane solvents is demonstrated for solution nuclear magnetic resonance (n.m.r.) analysis of nylons. These solvents, through a combination of low viscosity and low acidity, promote decreased linewidths and allow observation of features masked by traditional acidic solvents. Peaks for *cis* amide linkages have been identified for selected nylons and model compounds by ^{1}H, ^{13}C and ^{15}N observation. Surprisingly, the *cis* content increases with increase in the number of methylene linkages between amide groups for both A-B and AA-BB nylons. The temperature dependencies of the *cis* amide contents of nylon 6,6 and a model amide were followed by ^{1}H and ^{13}C n.m.r. over the useful temperature range of the binary solvent (−10 to 75°C); both showed an increase in *cis* content up to the onset of desolvation and/or line-broadening caused by amide hydrogen exchange. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Analysis of polyamides by solution nuclear magnetic resonance (n.m.r.) methods has been hampered in the past due to use of perturbing solvents which are either acidic (*m*-cresol, formic acid) or rely on strong interactions between the amide carbonyl and/or N–H groups and salts such as LiCl in CH_3OH[1]. These interactions caused large solvent-dependent chemical shift changes of peaks for the amide group and adjacent carbons, and can also modify or mask conformational and configurational information. Such solvents also form highly viscous polyamide solutions which increase peak widths, decrease resolution and give relaxation times that reflect solvent–polymer interactions rather than intrinsic polymer mobility. A particular example of this spectroscopic masking is the lack of observation of separate resonances for *cis* and *trans* amide isomers of aliphatic polyamides.

Cis–trans isomerization of the amide carbonyl–nitrogen bond is normally slow on the time scale of n.m.r. measurements. Amides consequently exhibit separate resonances for nitrogen substituents attached *cis* and *trans* to the carbonyl oxygen. Previous work has shown that both *cis* and *trans* isomers are easily observed for secondary amides where both are of comparable energy. In primary amides, steric interactions cause the *trans* isomer to be greatly favoured. Even for primary amides such as formamide and acetamide, the amide content is heavily biased towards *trans* (88% for *N*-methylformamide, 97% for *N*-methyl-acetamide)[2]. With larger substituents, the *trans* isomer is even more favoured; in fact, linear primary amides larger than acetamide have been erroneously reported to contain negligible *cis* content[3].

The *cis* content of polyamides should have an enormous effect on their solution and melt properties despite its low concentration; even 1–2% *cis* segments would place 'kinks' in the polymer chain that would substantially increase segmental mobility and reduce hydrodynamic volume. In fact, an observed decrease in nylon characteristic ratios is consistent with an increase in *cis* content with increasing temperature[4].

Reliable methods for determining the *cis* content of polyamides in solution and in the solid state have not been available until now. Solid state infra-red (i.r.) and n.m.r. spectra do not normally show sufficient sensitivity or resolution to detect such small concentrations, and the hydrogen bonding or acidic solvents normally used for solution n.m.r. analysis broaden the *cis* peaks until they are unrecognizable, or moved under the peaks of the main *trans* segments (*vida infra*). Such problems were addressed early for polypeptides, once it became clear how important n.m.r. is for observing molecular properties of these polymers[5,6].

The solvent system used here is one of a family combining fluorinated alcohols and chlorinated alkanes. Polymer solutions in such systems often show a change in intrinsic viscosity with solvent composition, resulting in a maximum at some characteristic solvent ratio. Phase

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* To whom correspondence should be addressed

diagrams for selected pairs of solvents have been generated for several nylons which demonstrate that mixtures of trifluoroethanol (TFE) or hexafluoroisopropanol with methylene chloride or chloroform are excellent solvents for nylon 6 and nylon 6,6[7]. This behaviour has been argued to *not* involve amide group protonation[8], and we confirm this here. More importantly, the viscosities of solutions containing as much as 15% polymer are still low enough to give excellent n.m.r. spectra. Samples of 10% (wt-vol) concentration give peaks that are narrow and intense enough that end-groups and contaminants present in concentrations below 0.2% can readily be observed using ^{13}C and ^{15}N n.m.r. methods (*vida infra*).

We describe here the use of these solvent mixtures for high resolution n.m.r. analysis of nylons, and specifically, for the quantitative determination of *cis* amide content in a variety of nylon samples and lactam model compounds.

EXPERIMENTAL

Samples of Zytel nylon 66 and its 100% ^{15}N-labelled analogue were provided by Du Pont Central Research and Development. 2-Azacyclononanone (the lactam of 8-aminooctanoic acid), nylon 6, and nylon 11 were obtained from Aldrich Chemical Company and used as received. Nylon 4 was donated by the Barson Corporation, and nylon 13,13 was a gift from Prof. Roger S. Porter, University of Massachusetts. Nylon 7 and nylon 12 were synthesized by anionic ring-opening polymerization of their respective lactams[9]. *N*-propylstearamide (NPS), *N*-stearylpropanamide (NSP) and *N*-hexylmyristamide (NHM) model amides were synthesized from their respective amines and acid chlorides. Solvents were commercial reagent grade and used without drying or purification. Nylon solutions were prepared by dissolution with heat and vigorous mixing (care must be taken not to volatilize these low boiling solvents and explode the n.m.r. tubes). Typically, a finely divided nylon sample was added to an n.m.r. tube along with *ca* 1 ml of the solvent mixture, and the tube was capped. The tube was quickly heated with a hot air gun and shaken by hand or with a vibro-mixer to prevent aggregation and promote dissolution. Intermittent heating and agitation for approximately 1 h gave non-viscous solutions at 10% polymer concentration; higher concentrations required greater time and care to prevent agglomeration and gelation.

N.m.r. spectra were obtained on a Bruker AC-300 at 300.15 MHz for proton and 75.05 MHz for carbon, and on a Bruker MSL-400 at 46.11 MHz for nitrogen. DMSO-d_6 in a capillary insert was initially used as an external lock and reference; later work used $CDCl_3$ added directly to the solvent mixture. While this slightly changed the solvent properties, we have confirmed all the results discussed below using trifluoroethanol–chloroform mixtures which allow higher dissolution and analysis temperatures.

RESULTS AND DISCUSSION

The advantages of the low viscosity with relatively high concentrations of polymer is illustrated with nylon 6,6 solutions in TFE–CH_2Cl_2 (*Figure 1*) where a spectrum obtained in this solvent is compared to those acquired in trifluoroacetic acid (TFA) and phenol; spectra were scaled to give approximately the same peak heights for the more intense *trans* peaks. Chemical shift changes of as much as 3–4 ppm were observed in TFA, indicating protonation or very strong association of the solvent with the amide groups. The latter two solvents gave solutions which were very viscous, even at much lower concentrations, and which required more scans for comparable signal-to-noise values. More importantly, peaks are noticeably narrower in the mixed solvent which gave peak widths at half-height of *ca* 4.1 Hz compared to 10.7 Hz for phenol and 8.0 Hz for TFA. In addition to *cis–trans* isomers, which are the focus of this study, sharp peaks are seen for low-concentration end-groups and cyclic oligomers; these will be discussed in detail in a forthcoming paper.

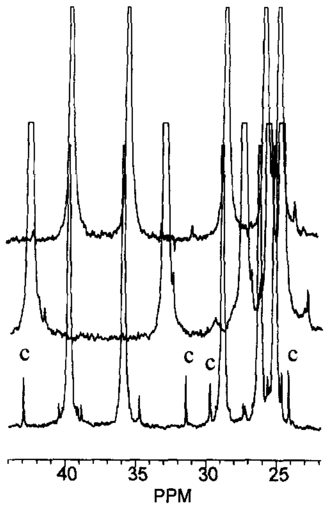

Figure 1 Stack plot of ^{13}C n.m.r. spectra of nylon 6,6 (aliphatic region) employing phenol (top trace), trifluoroacetic acid (middle) and a binary solvent 3/1 trifluoroethanol/chloroform (bottom); 'c' indicates *cis* peaks and the main *trans* peaks are off-scale

The four peaks in the bottom spectrum of *Figure 1* (marked with 'c') have now been assigned to *cis* amide carbons corresponding to (from highest to lowest ppm values) methylenes attached to the nitrogen ($C_{N\alpha}$ at 42.9 ppm) and carbonyl carbon (C_α at 31.4), and the methylenes attached to each of these, one carbon removed from each of the amide atoms ($C_{N\beta}$ at 29.6 and C_β at 24.2 ppm). The *cis* amide carbonyl carbon peak (spectrum not shown) has also been identified and appears at 176.4 compared to 175.6 ppm for the *trans* isomer. The doublets observed for the ^{15}N labelled sample (spectrum not shown) helped confirm these assignments; the ^{15}N–^{13}C coupling constants for methylenes $C_{N\alpha}$ and C_α were 9 and 5 Hz, respectively, for *both* the *cis* and *trans* isomers, while the one-bond coupling constant to the carbonyl carbon was 14 Hz for the *cis* isomer and 16 Hz for the *trans*. This sample also allowed ready observation of the *cis* amide nitrogen peak at 1.2 ppm upfield of the *trans* amide peak (spectrum not shown). In the proton spectrum of the unlabelled sample, the somewhat broadened hydrogen peak of the *cis* amide was seen 0.6 ppm upfield of the *trans* analogue, consistent with previous assignments[10]. All *cis* amide peaks (except for those of the amide hydrogen) were sharp and easily distinguished from the more intense but still sharp *trans* amide peaks. These findings clearly confirm the utility of this solvent system for n.m.r. analysis of polyamides.

Table 1 *Cis* amide content quantitation by ^{13}C and ^{1}H peak height or integration values at 25°C

Compound	% *Cis* ^{13}C Peak Ht α to Nitrogen	% *Cis* ^{13}C Peak Ht α to Carbonyl	% *Cis* H Integration
Nylon 13,13	2.70	2.79	2.55
Nylon 12	2.31	2.29	2.09
Nylon 11	2.65	2.61	2.65
Nylon 7	1.90	1.93	1.96
Nylon 6,6	1.64	1.64	1.10
Nylon 6	1.57	1.45	0.98
Nylon 4	0.76	0.76	0.71
Cyclooctane lactam	15.60	15.73	–
Cyclic unimer of nylon 6,6	2.02	2.18	–
NPS	2.00	–	–
NSP	1.70	–	–
NHM	2.40	–	–

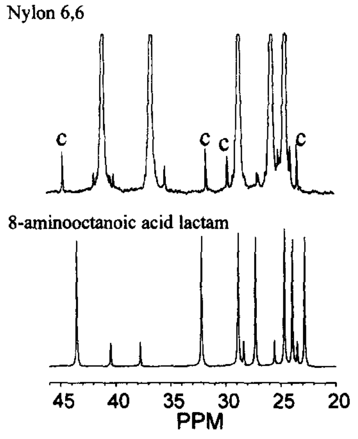

Figure 2 Stack plot of ^{13}C n.m.r. spectra of nylon 6,6 (top) and 8-aminooctanoic acid lactam (bottom) illustrating similar chemical shifts for *cis* amide peaks (marked with 'c' in the top spectrum)

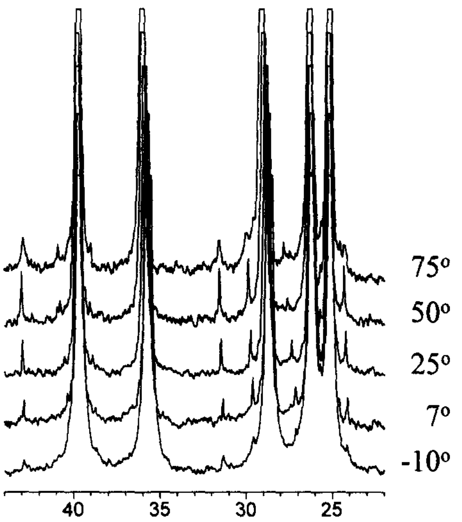

Figure 3 Stack plot of ^{13}C n.m.r. spectra of nylon 6,6 (aliphatic region) at various temperatures illustrating increased *cis* content as a function of temperature

Figure 2 compares the ^{13}C spectra of nylon 6,6 and the 9-membered ring cyclic lactam model compound which was used to assist in peak assignments. The *cis–trans* conformers of this model lactam are of roughly comparable energy with the *cis* being slightly favoured due to relief of ring strain. The chemical shift values observed for the cyclic amide in this solvent mixture were consistent with the peaks assigned to the *cis* and *trans* amide units of the linear nylon, and with those previously reported for several homologous lactams in chloroform[11]. It should be noted that this lactam is the only one we are aware of that gives significant amounts of both amide isomers at room temperature. Changes in chemical shifts caused by *cis* incorporation are similar for both cyclic and linear structures: all carbons within two bonds on both sides of the amide groups appear in the same relative order for both materials. However, it should be noted that the ^{15}N shift for the *cis* amide was found upfield of the *trans* peak for nylon 6,6 while it was reported downfield (by 2–3 ppm, depending on solvent) for the lactam[11].

Unexpected was the variable amount of *cis* content among different nylons, as detailed in *Table 1*. The room temperature *cis* content ranged from a low of 0.7% for nylon 4 to a high of 2.7% for nylon 13,13. The higher aliphatic-content nylons (nylons 11, 12 and 13,13) were more soluble in a 1/1 mixture of TFE/chloroform, while all other nylons dissolved more readily in a 3/1 mixture. However, solvent composition had no influence on the *cis–trans* ratio; i.e. nylon 6,6 dissolved in 100% TFE, 1/1 TFE/$CDCl_3$ and 3/1 TFE/$CDCl_3$ yielded comparable *cis–trans* ratios at room temperature. We have no rationale for the increase in *cis* content with increasing ratio of methylenes to amide group, although it is in direct contradiction with behaviour described in the literature for a series of linear, low molecular weight amides: increasing the *N*-alkyl chain length reportedly caused a *decrease* and disappearance of the *cis* isomer[2,3].

To illustrate the utility of this solvent system in addressing fundamental polymer questions, we carried out a variable temperature study of the *cis–trans* amide ratio (*Figure 3*). The *cis* and *trans* intensities for each of four distinctly separated pairs of peaks (see *Figure 1* for peaks labelled 'c' for *cis* and the *trans* peaks adjacent to each *cis* peak as discussed above) were averaged at each of four temperatures (30–60 min equilibration at −10, 7, 25 and 50°C). The highest temperature spectrum given here (75°C) shows broadening due to the onset of solvent reflux and associated changes in polymer–solvent interaction presumably involving amide hydrogen exchange. *Figure 4* shows the plot obtained of integrated values for carbon (averages of all four peak ratios at each

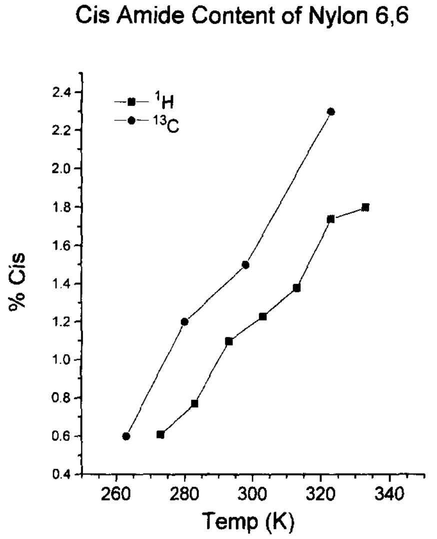

Figure 4 Percent *cis* amide isomers in nylon 6,6 as a function of temperature measured as an average of the *cis*-specific carbons in the ^{13}C spectra (top trace) and the amide hydrogen (bottom)

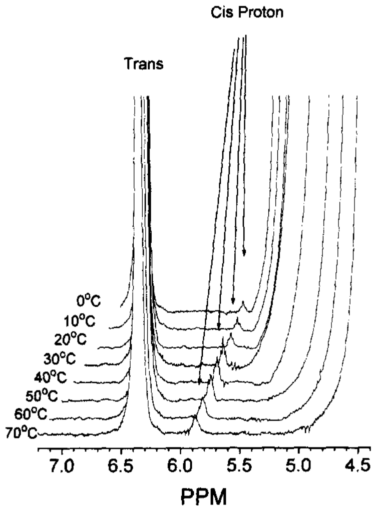

Figure 5 Stack plot of ^1H n.m.r. peaks showing the increase in intensity of the peak assigned to the *cis* amide proton of nylon 6,6 with increasing temperature

temperature) and the amide hydrogen; assuming a simple Boltzman relationship yields an apparent difference in stability of 10.5 kcal mol^{-1}. This value is consistent with calculated values[12] and with previous estimates based on i.r. absorption differences of the amide carbonyl peaks of primary amides and n.m.r. estimates for secondary amides[13]. Corresponding changes in *cis*-proton peak intensities with temperature were consistent with the variable temperature ^{13}C data (*Figure 5*). Interestingly, the OH proton of trifluoroethanol (in the proton n.m.r. spectra) shifts to higher field faster with increasing temperature than the amide protons, allowing better resolution and observation of the *cis* amide proton at elevated temperature. Analogous behaviour is observed for the amide peaks of the NPS, NSP and NHM model compounds (spectra not shown), although the latter material shows hydrogen line-broadening and peak merging at a lower temperature than the polymer and other models.

CONCLUSIONS

To the best of our knowledge, this is the first reported observation of *cis* amide groups in nylons specifically, and in long-chain linear amides in general. It is also the first use of the TFE–CH_2Cl_2 (and related solvent systems) for n.m.r. analysis of polyamides. We believe the results given here demonstrate that these mixed solvents offer enormous capability for n.m.r. analysis of nylons, especially for observing and quantifying previously unknown and/or unseeable components (such as the *cis* isomer content). Extension of the use of these solvent mixtures to include the variety of spectral editing techniques available with all of the n.m.r.-active nuclei present promises to make this an even more useful approach to understanding the molecular composition, conformation and mobility of nylons and related polymers. This is especially exciting in extending our understanding of molecular structure effects on physical properties: a *cis* content of 1–3% in solid or molten polymers would greatly inhibit chain orientation on extrusion and solid state elongation, a possibility that would explain the continued failure of past efforts to obtain ultra-oriented nylon fibres with properties consistent with essentially complete molecular alignment.

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