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Polymer 42 (2001) 2621–2626

polymer

www.elsevier.nl/locate/polymer

Solution ^{13}C NMR spectroscopy of polyamide homopolymers (nylons 6, 11, 12, 66, 69, 610 and 612) and several commercial copolymers

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Received 2 May 2000; received in revised form 1 June 2000; accepted 12 June 2000

Abstract

Well-resolved ^{13}C NMR spectra of nylons 6, 11, 12, 66, 69, 610, and 612 dissolved in 4:1 TFE/$CDCl_3$ allowed complete assignment of all major backbone peaks. In addition, several low intensity peaks were identified representing *cis* amide groups, acid end-groups and amine end-groups. Several peaks associated with the *trans* amide units in the spectra of each polyamide homopolymer were identified as uniquely characteristic of that polymer. Using these unique peaks, all the polyamides studied could be distinguished from each other as homopolymers and as repeat units in copolymers. For example, three unknown polyamides (supplied by a colleague) were identified as nylon 6, nylon 66 and nylon 610 using only solution ^{13}C NMR spectroscopy. Based on these results, several commercial polymers were examined. Using solution ^{13}C NMR spectroscopy, the copolymer compositions, molecular weights, end-group and *cis* amide contents, plus the amount of residual ε-caprolactam were all determined. For example, Spiderwire Super Mono® fishing line was found to have a number average molecular weight of 25,333 g/mol and to contain 82 mol% nylon 6 repeat units and 18 mol% nylon 66 repeat units. The residual ε-caprolactam, acid end-group and amine end-group contents were calculated as 1.25, 0.61 and 0.0 mol%, respectively. The *cis* amide contents were calculated to be 1.2 mol% for nylon 6 units and 0.61 mol% for nylon 66 segments. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polyamide homopolymers; Low intensity peaks; Unknown polyamides

1. Introduction

We recently reported that solution ^{13}C NMR analysis of nylon 66 dissolved in a 2,2,2-trifluoroethanol/deuterochloroform solvent mixture (4:1 TFE/$CDCl_3$) gave well-resolved peaks and allowed observation of several low intensity peaks that previously had not been reported or identified [1–3]. Based on model compounds and previous results [4,5], we assigned these peaks to *cis* amide conformers, acid end-groups, amine end-groups and residual ε-caprolactam, all observable at concentrations as low as 0.2 mol%.

Our earlier publications extensively discuss previous work related to traditional polyamide solvents and solution NMR characterization [1–3]. Two publications have come to our attention (thanks to a referee). Goodman and coworkers made peak assignments for solution ^{13}C NMR spectra of nylon 612 and related copolymers [6], Krejsa and coworkers assigned peaks for solution ^{1}H NMR spectra of UV and heat degraded nylon 66 and model compounds [7]. Krejsa and coworkers also used solution ^{15}N HMQC and ^{13}C HMQC NMR characterization in conjunction with various model compounds to assign solution ^{1}H NMR peaks for end-groups possessing methyl, aldehyde, formamide, olefinic, amide NH_2, and OCH moieties.

Here we report an extension of our prior research to include the identification of solution ^{13}C NMR peaks representing *trans* amide conformers, *cis* amide conformers, acid and amine end-groups and residual monomer in nylons 6, 11, 12, 66, 69, 610, and 612 homopolymers and several commercial copolymers dissolved in TFE/$CDCl_3$. In addition, we identified several peaks that had chemical shift values uniquely characteristic to each polyamide. Using these unique peaks, three polyamide homopolymers whose identities were not known to us at the time of characterization were correctly identified as nylon 6, nylon 66 and nylon 610. This method was then extended to analysis of several commercial fishing lines and a trimmer line, which were found to contain varying amounts of nylon 6, nylon 66 and nylon 610 (trimmer line only). Copolymer compositions, end-group contents, *cis* amide contents, molecular

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PII: S0032-3861(00)00501-2

Table 1
Solution ^{13}C NMR chemical shift values of nylons 6, 66, 69, 610 and 612

	Nylon 6		Nylon 66		Nylon 69		Nylon 610		Nylon 612	
	trans	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*
Main chain										
1	39.85	43.12	40.03	43.36	40.03	43.36	40.03	43.36	40.03	43.36
2	28.81	29.76	29.08	29.99	29.08	29.99	29.08	29.99	29.08	29.99
3	26.39	*	26.49	*	26.49	*	26.49	*	26.49	*
4,5	*	*	*	*	*	*	*	*	*	*
1′	36.47	32.03	36.10	31.68	36.77	31.99	36.77	31.99	36.77	32.27
2′	25.61	24.77	25.39	24.43	26.10	25.43	26.10	25.43	26.10	25.43
3′	*		*		29.21	*	29.21	30.27	29.33	*
4′	*		*		29.21	*	29.21	30.27	29.62	*
5′	*		*		*		*		29.62	*
6′	*		*		*		*		*	
7′	176.53	178.80	176.15	178.35	176.95	179.41	176.95	179.41	176.95	179.41
End groups										
αNH_2	40.47	*	40.67	*	40.63	*	40.77	*	40.92	*
βNH_2	27.49	*	27.67	*	27.51	*	28.01	*	27.42	*
ωNH_2	*		39.06	*	39.47	*	39.55	*	39.42	*
αCO_2H	35.95	*	34.98	*	35.60	*	34.20	*	35.50	*
βCO_2H	24.87	*	24.89	*	25.42	*	25.29	*	25.66	*
$7'CO_2H$	181.05	*	180.44	*	179.02	*	178.98	*	180.67	*
M_n (g/mol)	13,502		15,480		14,071		14,499		16,210	

weights and residual ε-caprolactam contents were identified and quantified based on relative peak intensities. The focus of this study was to identify and quantify copolyamide compositions using these characteristic solution ^{13}C NMR peaks and to develop this information into a routine technique to quantitatively characterize unknown polyamides.

Table 2
Solution ^{13}C NMR chemical shift values of nylons 11 and 12 and ε-caprolactam

	Nylon 11		Nylon 12		ε-Caprolactam
	trans	*cis*	*trans*	*cis*	
Main chain					
1	40.03	43.12	40.03	43.12	43.40
2	28.79	29.76	28.81	29.76	30.52
3	26.94	*	26.94	*	*
4,5	28.56	*	28.56	*	*
1′	36.76	31.96	36.76	31.96	35.70
2′	25.74	24.98	25.74	24.98	23.12
3′	28.80	*	28.80	*	*
4′	28.63	*	28.63	*	*
5′	28.63	*	28.63	*	*
6′	*		28.80	*	*
7′	176.34	178.48	176.34	178.48	183.44
End groups					
αNH_2	40.95	*	40.95	*	*
βNH_2	27.71	*	27.71	*	*
ωNH_2	*		*		*
αCO_2H	34.15	*	34.15	*	*
βCO_2H	25.06	*	25.06	*	*
$7'CO_2H$	178.95	*	178.95	*	*
M_n (g/mol)	15,498		16,213		*

2. Experimental

Polyamide homopolymers were used as received from Aldrich Chemical Company. Commercial fishing and trimmer lines were purchased from a retail store and characterized as obtained. The unknown polyamide homopolymers were selected at random by a colleague from seven polyamides purchased from Aldrich Chemical Company. This test was used as a preliminary demonstration of the utility of the method for identifying unknown polyamides using only solution ^{13}C NMR spectroscopy.

NMR samples were prepared by dissolving the pellets, powder or monofilament in TFE with heating, then adding $CDCl_3$ to the cooled solution to give a sample with 10–20 wt% polymer in a solvent mixture consisting of a 4:1 ratio of TFE to $CDCl_3$. Solution ^{13}C NMR spectra were collected on a Bruker AC-300 MHz NMR operating at 75.469 MHz spectral frequency. A 5-mm NMR probe was used with an average of 15,000 scans (∼12 h) to give sufficient signal-to-noise for quantitation of end-groups, *cis* amide content and the mol ratios of copolymer units. Determination of molecular weights, plus quantitation of *cis* amide units and end-groups, were based on previous work [1–3]. Copolyamide content was determined by relative intensity of solution ^{13}C NMR peaks that had chemical

Table 3
Solution ^{13}C NMR peaks used identify and differentiate between polyamides; italicized peaks show the greatest chemical shift difference

	Nylon 6	Nylon 66	Nylon 69	Nylon 610	Nylon 612	Nylon 11	Nylon 12
Nylon 6	*	$1, 2, 3, \mathit{1'}, 1'_{cis}, \mathit{2'}, 7'$	$2, 3, \mathit{1'}, 1'_{cis}, 3', 4', 7'$	$1, 2, 3, \mathit{1'}, 1'_{cis}, \mathit{2'}, 3', 4', 7'$	$1, 2, 3, \mathit{1'}, 1'_{cis}, \mathit{2'}, 3', 4', 5', 7'$	$3, \mathit{4}, \mathit{5}, 2', 4', 5', 6', 7'$	$3, \mathit{4}, \mathit{5}, 2', 4', 5', 6', 7'$
Nylon 6-6	$1, 2, 3, \mathit{1'}, 1'_{cis}, \mathit{2'}, 7$	*	$1'_{cis}, \mathit{2'}, 3', 4'$	$\mathit{1'}, \mathit{2'}, 3', 4'$	$\mathit{1'}, \mathit{2'}, 3', 4', 5'$	All: $\mathit{4}, \mathit{5}, \mathit{4'}, \mathit{5'}$	All: $\mathit{4}, \mathit{5}, \mathit{4'}, \mathit{5'}$
Nylon 6-9	$2, 3, \mathit{1'}, 1'_{cis}, 3', 4', 7'$	$1'_{cis}, \mathit{2'}, 3', 4'$	*	Height of $3'/4'$ peak	$1'_{cis}, 3', 4', \mathit{5'}$	All: $\mathit{4}, \mathit{5}, \mathit{4'}, \mathit{5'}$ Except: 1	All: $\mathit{4}, \mathit{5}, \mathit{4'}, \mathit{5'}$ Except: 1
Nylon 6-10	$1, 2, 3, \mathit{1'}, 1'_{cis}, \mathit{2'}, 7$	$\mathit{1'}, \mathit{2'}, 3', 4'$	Height of $3'/4'$ peak	*	$3', 4', \mathit{5'}$	All: $\mathit{4}, \mathit{5}, \mathit{4'}, \mathit{5'}$	All: $\mathit{4}, \mathit{5}, \mathit{4'}, \mathit{5'}$
Nylon 6-12	$1, 2, 3, \mathit{1'}, 1'_{cis}, \mathit{2'}, 3', 4', 5', 7'$	$\mathit{1'}, \mathit{2'}, 3', 4', 5'$	$1'_{cis}, 3', 4', \mathit{5'}$	$3', 4', \mathit{5'}$	*	All: $\mathit{4}, \mathit{5}, \mathit{4'}, \mathit{5'}$	All: $\mathit{4}, \mathit{5}, \mathit{4'}, \mathit{5'}$
Nylon 11	$3, \mathit{4}, \mathit{5}, 2', 4', 5', 6', 7'$	All: $\mathit{4}, \mathit{5}, \mathit{4'}, \mathit{5'}$	All: $\mathit{4}, \mathit{5}, \mathit{4'}, \mathit{5'}$ Except: 1	All: $\mathit{4}, \mathit{5}, \mathit{4'}, \mathit{5'}$	All: $\mathit{4}, \mathit{5}, \mathit{4'}, \mathit{5'}$	*	Height of $2/3'$ peak
Nylon 12	$3, \mathit{4}, \mathit{5}, 2', 4', 5', 6', 7'$	All: $\mathit{4}, \mathit{5}, \mathit{4'}, \mathit{5'}$	All: $\mathit{4}, \mathit{5}, \mathit{4'}, \mathit{5'}$ Except: 1	All: $\mathit{4}, \mathit{5}, \mathit{4'}, \mathit{5'}$	All: $\mathit{4}, \mathit{5}, \mathit{4'}, \mathit{5'}$	Height of $2/3'$ peak	*

shift values unique and specific to each nylon; these peaks will be discussed later in this publication.

3. Results and discussion

3.1. Polyamide homopolymers

In previous publications, solution ^{13}C NMR spectroscopy was used to identify and quantify polyamide compositions, end-group content, *cis* amide conformer content and residual ε-caprolactam in nylon 66 [1–3]. As an extension of this research, we have acquired solution ^{13}C NMR spectra of nylons 6, 11, 12, 66, 69, 610, and 612 dissolved in TFE/CDCl$_3$. Careful analysis has allowed us to identify and quantify methylene carbons representing *trans* amide conformers, *cis* amide conformers, acid end-groups, amine end-groups and unreacted ε-caprolactam (Tables 1 and 2). In addition, we identified several ^{13}C NMR peaks that have chemical shift values uniquely characteristic to each polyamide (Table 3).

Table 1 lists the solution ^{13}C NMR chemical shift values for all polyamides characterized and Fig. 1 illustrates the peak position labeling employed. An asterisk, *, indicates that specific methylene carbon was not observed in that particular polyamide. All NMR samples were prepared using the same procedure and in the same concentration, but the end-group content varied with molecular weight and end-capping. Since variances in end-group content altered solution pH values and, therefore, the end-group chemical shift values [1], the chemical shifts of specific carbons associated with end-groups, varied from sample to sample. Thus, these peaks were not used to identify or differentiate polyamides, although further work involving effects of pH on end-group behavior in all of these polymers should allow even more discriminating qualitative and quantitative characterization. Table 3 lists the solution ^{13}C NMR peaks that had chemical shift values that were uniquely characteristic to each polyamide under as-prepared conditions. The italicized peaks showed the greatest peak differences and/or resolution, and were the most sensitive for identification of that particular polyamide. These peaks are therefore the most useful for identifying and differentiating unknown polyamides.

Based on these unique peaks, many polyamides can be identified or differentiated based solely on ^{13}C NMR chemical shift values of the $1'$ and $2'$ peaks, which are the methylene carbons α and β to the carbonyl of the amide linkages. These peaks typically showed the greatest change in chemical shift value from polyamide to polyamide, and were the best indicators of the general type of polyamide under investigation. In some cases, however, polyamides cannot be differentiated by the $1'$ and/or $2'$ peaks; i.e. nylons 69 and 610 from 612, nylon 69 from 610, nylon 6 from nylons 11 and 12, and nylon 11 from nylon 12. In these cases, other

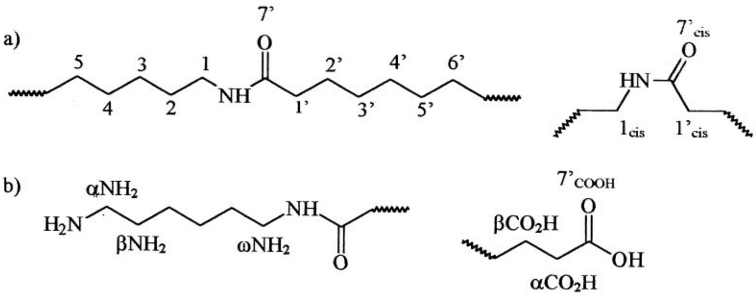

Fig. 1. Structure and solution ^{13}C NMR position labeling of a generic nylon (a) in the *trans* and *cis*-amide conformation and (b) with acid and amide end-groups.

peaks and relative peak heights were used to identify polyamide composition.

Nylon 69 was differentiated from nylon 610 based on the relative peak heights of the $3'/4'$ peak to the $2'$ peak. Nylon 610 has two $4'$ carbons while nylon 69 has only one $4'$ carbon; thus, the $3'/4'$ peak is larger than the $2'$ peak in nylon 610 spectra whereas the $3'/4'$ peak is smaller than the $2'$ peak in nylon 69 spectra. Similarly, nylon 11 can be differentiated from nylon 12 only by relative peak heights. In nylon 12 ^{13}C NMR spectra the $6'$ peak cannot be resolved from the $2/3'$ peak, therefore, the nylon 12 $2/3'/6'$ peak is more intense than the 4/5 peak. In nylon 11, there is no $6'$ carbon, thus the $2/3'$ peak has the same intensity as the 4/5 peak. Nylon 69 can easily be differentiated from nylon 612 because of the different chemical shift values of the $3'$, $4'$ and $5'$ peaks. The $5'$ peak is the best in this case because it does not exist in nylon 69 spectra. The $5'$ peak also does not exist in nylon 610 spectra, and can be used to distinguish nylon 610 from nylon 612. Lastly, nylon 6 can be differentiated from nylon 11 and nylon 12 because the 4 and 5 peaks in nylon 11 and nylon 12 spectra do not exist in nylon 6 spectra.

3.2. Technique to identify unknown polyamides

The sensitivity of the solution ^{13}C NMR chemical shift values to the type of polyamide makes solution ^{13}C NMR spectroscopy the fastest and most reliable technique for identifying unknown polyamides. We have developed a general procedure based on the following easy steps.

- The process is begun by first comparing the chemical shift values for the $1'$ and $2'$ peaks to those listed in Tables 1 and 2.
- If, based on the $1'$ and $2'$ peaks the polyamide is believed to be nylon 69, 610 or 612, then the following steps are taken.
    - If a $5'$peak is observed, it is probably nylon 612.
    - If no $5'$ peak is observed and the $3'/4'$ peak is larger than the 2 peak, the sample is probably nylon 610. If smaller, then nylon 69.
- If based on the $1'$ peaks the polyamide is believed to be nylon 6, nylon 11 or nylon 12 then the following steps are taken.
    - If the $4'/5'$ and 4/5 peaks are observed, then nylon 11 or nylon 12 is indicated. If not observed, then nylon 6.
    - If the $2/3'/6'$ peak is larger than the 4/5 peak, the sample is nylon 12.
    - If the $2/3'$ peak is the same intensity as the 4/5 peak, then the sample is nylon 11.
- Lastly, use the other peaks listed in Tables 1 and 2 to verify that the polyamide is characterized correctly.

3.3. Unknown polyamide homopolymers

This approach was used to identify three unknown polyamides using only solution ^{13}C NMR spectroscopy in approximately 12 h per sample for analysis and 5–10 min for interpretation and quantitation. The solution ^{13}C NMR spectra of the homopolymer unknowns are shown in Fig. 2. Based solely on the chemical shift values of peaks $1'$ and $2'$, the polyamides were identified as nylon 6 (bold font), nylon 66 (normal font) and nylon 610 (italic font) (Fig. 2a–c, respectively). The stack plot also shows that the chemical shift value of the $3'/4'$ is unique in the nylon 610 spectrum and the chemical shift values of the 1 and 2 peaks are unique in the nylon 6 spectrum.

3.4. Unknown commercial polyamide homo- and copolymers

This approach was also used to identify several commercial polyamide fishing lines and a trimmer line in approximately 12 h per sample for NMR analysis and 5–10 min for interpretation and quantitation. The spectra for three of these commercial polyamides and nylons 6, 66 and 610 can be found in Fig. 2 (spectra d–f are the commercial samples). The composition of the commercial copolymers were identified as nylon 6/66 copolymers and a nylon 6/66/610 terpolymer using the chemical shift values of the $1'$, $2'$, $3'/4'$ peaks relative to those reported for nylons 6, 66 and 610. The largest $1'$ and $2'$ peaks were observed at 39.47 and 25.61 ppm, respectively, and no peak was observed at 28.63 ppm (which would have indicated either nylons 11

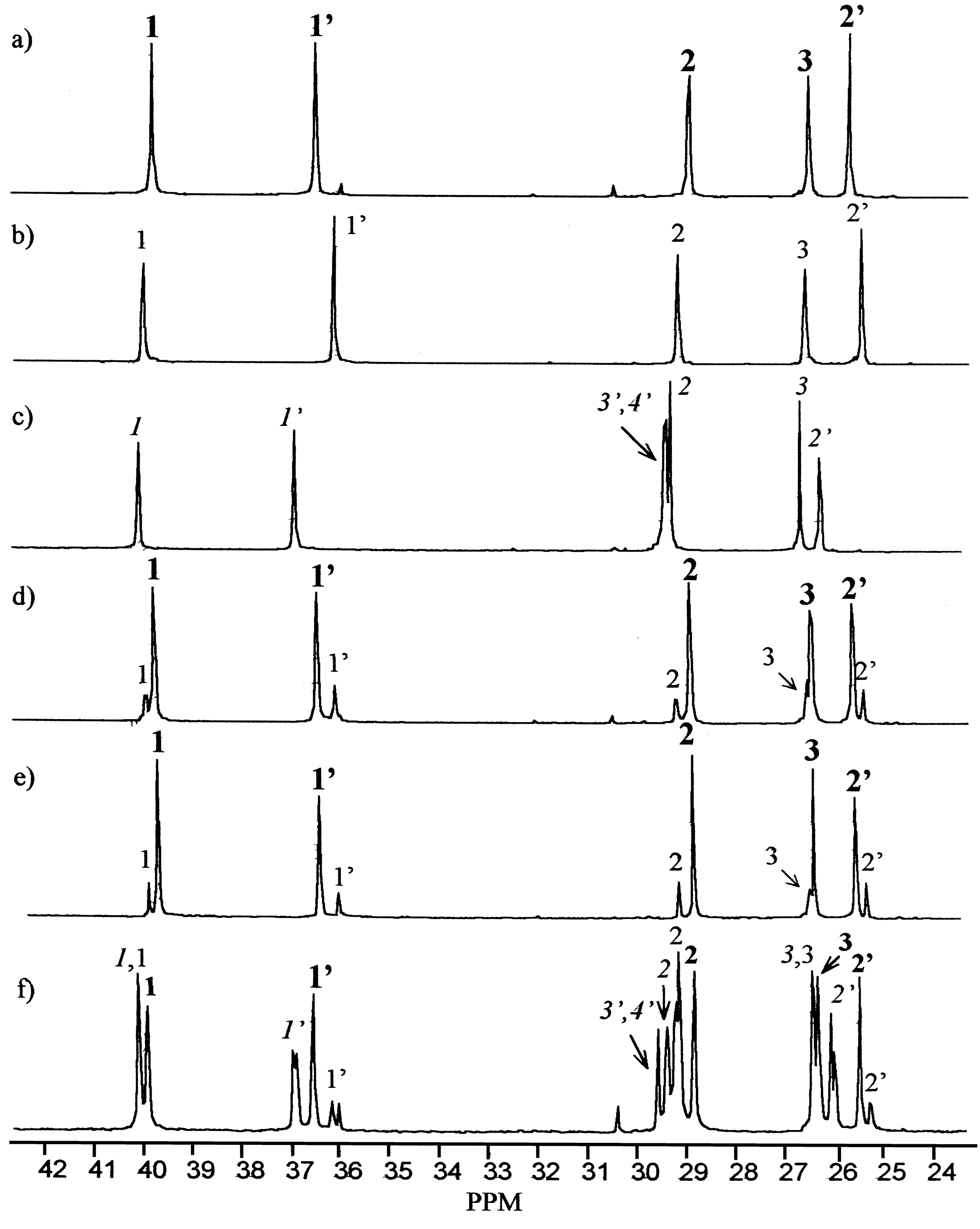

Fig. 2. Solution ^{13}C NMR spectra of: (a) **nylon 6**; (b) nylon 66; (c) *nylon 610*; (d) Spiderwire Super Mono®; (e) Silver Thread Excalibur®; and (f) trimer line dissolved in TFE/CDCl$_3$ (expansion of aliphatic region).

or 12), therefore the commercial materials were constructed of at least nylon 6 repeat units. The spectra of all the commercial polymers contained smaller 1′ and 2′ peaks at 36.10 and 25.39 ppm, respectively, indicating these polymers were also constructed of nylon 66 repeat units. In addition, the trimmer line contained peaks at 25.43 and 29.21 ppm; assigned to the 2′ and 3′/4′ peaks, respectively, of either nylons 69, 610 or 612 repeat units. Since the 3′/4′ was peak was smaller than its associated 2 peak and there was no 5′ peak at 29.62 ppm, the trimmer line was also constructed of nylon 610 repeat units. The compositions were verified by comparing solution ^{13}C NMR spectra of

Table 4
Commercial polymer compositions based on solution ^{13}C NMR characterization

Fishing line	Comp.	% Composition	% End-groups NH_2/CO_2H	M_n (g/mol)	% *cis*	% ε-caprolactam
Nylon 6 Standard	6	100	0.84/0	26,117	1.64	4.99
Nylon 66 Standard	66	100	0.60/0.80	18,040	1.10	0
Nylon 610 Standard	610	100	0.21/0.42	22,140	1.10	0
Stren Original® 17 lbs test	6	100	0.50/1.12	14,000	1.50	7.79
Stren Super Tough® 10 lbs test	6/6	81.0/19.0	0.79/0	10,924	1.25/0	1.05
Trilene® 10 lbs test	6/66	79.8/20.2	0/0	15,924	1.10/0	0
Trilene® 20 lbs test	6/66	76.8/23.2	0.83/0.78	14,078	1.71/0	0.84
Silver Thread Excalibur® 10 lbs test	6/66	76.6/23.4	0.65/0.65	20,802	1.36/1.99	0.68
Spiderwire Super Mono® 12 lbs test	6/66	81.7/18.3	0.61/0	25,333	1.19/0.61	1.25
Trimer line	6/66/610	54.8/12.0/33.1	0.62/0/0	21,210	0.90	2.14

the commercial polymers to the spectra of nylons 6, 66 and 610.

Copolymer compositions were quantified using the relative peak intensities of the nylon 6 1′ peak, the nylon 66 1′ peak and the nylon 610 3′/4′ peak (Table 4). Since these nylon 6, nylon 66 and nylon 610 ^{13}C NMR peaks were well-resolved from other peaks, the copolymer compositions were easily quantified as 55–82 mol% nylon 6, 12–23 mol% nylon 66 and 33 mol% nylon 610 (found only in the trimmer line sample). The amine end-group content was calculated to be as high as 0.84 mol% in Trilene® (10 lbs test) and the acid end-group content as high as 1.12 mol% in Stren Original®. On an average the residual ε-caprolactam content was around 1–2 mol% but in Stren Original® there was almost 7.8 mol% unreacted ε-caprolactam. The M_n was approximately 13,000 g/mol but the Silver Thread Excalibur®, Spiderwire Super Mono® fishing lines and the trimmer line were over 20,000 g/mol.

4. Conclusions

We have developed a simple and effective method for characterization of unknown nylon samples based on solution ^{13}C NMR spectroscopic analysis of samples dissolved in $TFE/CDCl_3$. A straightforward protocol allows qualitative identification of homopolymers and monomer segments in copolymers. Unique peaks for each copolymer segment can then be used to quantitate each component. Additional information about number average molecular weight and the amount of residual monomer is also readily determined, and can be useful for correlating molecular composition with physical behavior. For example, knowing that a large amount of residual monomer is present could help explain property changes of some fishing line since caprolactam extraction by water during use might lead to reduced toughness. Overall, this single method offers an easily implemented procedure for obtaining several important molecular parameters quickly (∼12 h) and reliably (∼ ± 1.5% of value) with a minimum amount of sample (0.1 mg) and a reasonable investment of analysis time (5–10 min).

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