in the present study are deemed promising in the so-called "molecular designing" of polymer modifications.

Registry No. (**1a**)(oxirane) (block copolymer), 118018-34-1; **5**, 40743-18-8; *N*-methyl-*N*-(2-acryloloxy)ethylpyridium tosylate, 118018-33-0; pyridine, 110-86-1; *N*-methyl-*N*-(2-acryloloxy)ethylacetamide, 45029-68-3; acrylic acid, 79-10-7.

References and Notes

(1) Kobayashi, S.; Kaku, M.; Sawada, S.; Saegusa, T. *Polym. Bull.* **1985**, *13*, 447.
(2) Kobayashi, S.; Shoda, S.; Masuda, E.; Shimano, Y. *Polym. Prepr., Jpn.* **1987**, *36*, 1541.
(3) Saegusa, T.; Kobayashi, S. *J. Macromol. Sci. Chem.* **1979**, *A13*, 295.
(4) Odian, G.; Gunatillake, P. A.; Tomalia, D. *Macromolecules* **1985**, *18*, 605.
(5) Miyamoto, M.; Sano, Y.; Kimura, Y.; Saegusa, T. *Macromolecules* **1985**, *18*, 1641.
(6) Kobayashi, S.; Igarashi, T.; Moriuchi, Y.; Saegusa, T. *Macromolecules* **1986**, *19*, 535.
(7) Brown, H. C.; Gintis, D.; Podall, G. *J. Am. Chem. Soc.* **1956**, *78*, 5375.
(8) Miyamoto, M.; Sano, Y.; Saegusa, T. *Polym. Bull.*, in press.
(9) Miyamoto, M.; Sano, Y.; Saegusa, T.; Kobayashi, S. *Eur. Polym. J.* **1983**, *19*, 955.
(10) Miyamoto, M.; Hayashizaki, K.; Tokumizu, M.; Saegusa, T., submitted to *Polym. Bull.*
(11) (a) Kobayashi, S.; Kaku, M.; Saegusa, T. *Macromolecules* **1988**, *21*, 334. (b) Kobayashi, S.; Iijima, S.; Igarashi, T.; Saegusa, T. *Macromolecules* **1987**, *20*, 1729.

End-Group and Main-Chain Resonance Assignments for the Aliphatic Polyamide-4,6, -6,6, and -6 via Two-Dimensional NMR Methods

Koen de Vries, Harry Linssen, and Geert v. d. Velden*

DSM Research BV, 6160 MD Geleen, The Netherlands.

Received May 23, 1988; Revised Manuscript Received August 24, 1988

ABSTRACT: The end-group and main-chain resonances in the ^1H and ^{13}C NMR spectra of a low molecular weight oligomer of polyamide-4,6 (PA-4,6) have been assigned by using various 2D NMR techniques (H-H and X-H COSY, RCT, and COLOC). Model compounds, mimicking the amine, carboxylic, and pyrrolidone end groups present in PA-4,6, were synthesized to assist in the assignments. Results have been interpolated to the observed ^{13}C chemical shifts of the end groups of high molecular weight PA-6 and -6,6, which has led to a partial assignment in these aliphatic polyamides. Main-chain resonances of PA-6 and -6,6 have been assigned unambiguously via H-H and X-H COSY measurements.

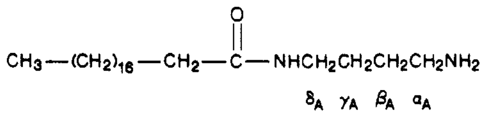
Introduction

Since the pioneering work of Carothers[1] on the synthesis of homo- and copolyamides, several reports have appeared in the literature dealing with the characterization of aliphatic, mixed aliphatic–aromatic, and aromatic polyamides using ^1H, ^{13}C, or ^{15}N NMR. Both due to the intrinsic simplicity of the ^1H and ^{13}C NMR spectra of homopolyamides and the availability of other methods for the characterization of the homopolyamides (IR spectroscopy, the combination of hydrolytic cleavage techniques and thin-layer chromatography),[2,3] the majority of these publications have dealt with sequence analysis of aliphatic copolyamides and aromatic copolyamides using either ^{13}C NMR[4,5] or ^1H NMR, respectively.[6,7]

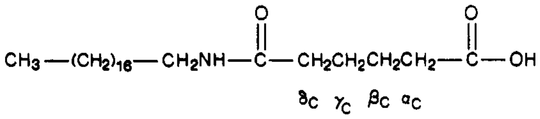
So far no unambiguous ^{13}C chemical shift assignments exist for the main-chain aliphatic carbons in the polyamides PA-6, PA-6,6, and the recently introduced polyamide-4,6 (Stanyl, trademark of DSM). Moreover, to our knowledge, hardly any or no ^1H and/or ^{13}C chemical shift data exist for the end groups, being present in the above-mentioned polyamides. The absence of these data might be due to a number of reasons: (i) the partial failure of ^{13}C chemical shift increment data in polar solvents as formic acid, fluorosulfonic acid, and sulfuric acid; (ii) the absence of model compounds mimicking the expected end groups, (iii) the unavailability of 2D NMR techniques (see, for a detailed discussion, ref 8).

In this work we have exploited at least one advantage of the recently introduced new synthesis of PA-4,6.[9] This polyamide is prepared in a two-step polymerization process, leading initially to a low molecular mass oligomer, which is subsequently postcondensed in the solid or molten state to the corresponding high molar mass PA-4,6. The number of end groups present in the oligomer and the polymer, amine (a), carboxyl (c), and pyrrolidone (p), can be determined via titration methods.[10,11]

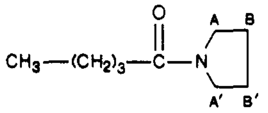
Chart I


$$CH_3-(CH_2)_{16}-CH_2-\overset{\overset{O}{\|}}{C}-NHCH_2CH_2CH_2CH_2NH_2$$

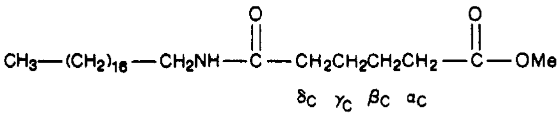
1


$$CH_3-(CH_2)_{16}-CH_2NH-\overset{\overset{O}{\|}}{C}-CH_2CH_2CH_2CH_2-\overset{\overset{O}{\|}}{C}-OH$$

2



3


$$CH_3-(CH_2)_{16}-CH_2NH-\overset{\overset{O}{\|}}{C}-CH_2CH_2CH_2CH_2-\overset{\overset{O}{\|}}{C}-OMe$$

4

We have extensively investigated this particular oligomer of polyamide-4,6, being the target molecule for the end-group analysis, with a variety of 2D NMR techniques (H-H COSY,[12] X-H COSY,[13] RCT,[14] and COLOC[15]).

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Table I
Assignments for the ^{13}C NMR Signals of the Model Compounds 1, 2, and 4 and of the Polyamide-6, -6,6, and -4,6

compd	1	2	3	4	5	α_A	β_A	γ_A	δ_A	α_C	β_C	γ_C	δ_C
1						40.55	24.67	25.97	42.42				
2										33.29	23.83	25.28	33.40
4										33.57	23.99	25.33	33.44
PA-4,6	35.46	25.19	39.65	25.95		40.33	24.33	25.59	39.19	33.33	23.88	25.1	35.5
PA-6,6	36.05	25.80	40.78	29.13	26.72	41.30			40.38	34.01	24.60		
PA-6	35.99	25.88	40.86	28.64	26.40				40.30	34.23	24.66		

The assignments of the ^{13}C NMR resonances of the end groups have been verified experimentally by using ^{13}C NMR data obtained on the model compounds **1**–**3**, mimicking the expected end groups a, c, and p, respectively.

A fourth compound **4**, the methyl ester of **2**, was also measured for assignment purposes (Chart I).

An interpolation of the observed chemical shifts for the end-group carbons in PA-4,6 to the corresponding end-group resonances in high molar mass PA-6 and -6,6 has led to a partial assignment of the resonances in these polyamides. Finally, an unambiguous assignment of the ^{13}C NMR resonances of the main-chain carbons of PA-6, -6,6 and -4,6 has been carried out by using a combination of two 2D NMR homo- and heteronuclear correlation techniques (H–H COSY,[12] X–H COSY[13]).

Experimental Section

Materials. Polyamide-6 (Ultramid B3) and polyamide-6,6 (Ultramid A3) were obtained from commercial sources (BASF, FRG). Various polyamide-4,6 oligomers and the high molar mass polymer have been synthesized according to literature data.[10] The model compounds **1**–**4** were generously donated by H. Nelissen (**1**, **2**, and **4**) and J. Warnier (**3**).

NMR Methods. For the H–H COSY experiments a $90°–t_1–45°$–Acquisition sequence has been employed for optimum suppression of diagonal peaks. Two-dimensional proton–carbon correlation spectroscopy[13] (X–H COSY) was carried out by using the standard pulse sequence $90°(^1H)–t_{1/2}–180°(^{13}C)–t_{1/2}–D_1–90°(^1H,^{13}C)–D_2–$Acq. In this sequence $D_1 = {}^1/_2J_{CH}$, whereas D_2 was set to an average value of ${}^1/_4\, J_{CH}$ in order to observe all carbons. Two-dimensional heteronuclear HHC relayed coherence transfer[14] (RCT) experiments were executed by using the sequence $90°(^1H)–t_{1/2}–180°(^{13}C)–t_{1/2}–90°(^1H)–D_1–180°(^1H)–D_1–D_2–90°(^1H,^{13}C)–D_3–$Acq(^{13}C,BB^{1}H). In this sequence, the twin set of proton pulses, separated by a time increment t_1, transfers magnetization between protons. Once the magnetization transfer has been carried out from the non-nearest-neighbor proton to the neighbor proton, it can be relayed to the carbon atom, which occurs with the proton and carbon pulses at the end of time $D_1 + D_2$.

This latter time should be chosen in such a manner that $2D_1 + D_2 = {}^1/_4J_{HH}$. The delay periods D_2 and D_3 are again equal to ${}^1/_2J_{CH}$ and ${}^1/_4J_{CH}$, respectively. Finally, the pulse sequence employed for the COLOC experiment is schematically given by $90°(^1H)–t_{1/2}–180°(^{13}C,^1H)–D_1–t_{1/2}–90°(^{13}C,^1H)–D_2–$Acq(^{13}C,BB^{1}H). This sequence is specially designed to observe long-range couplings via proton–carbon connectivities by introducing 180° pulses, which are stepped incrementally through a fixed proton evolution time, to effect broad-band decoupling in the F_1 domain. The values for D_1 (typically ${}^1/_2J$) and D_2 have been optimized by using a refocusing INEPT experiment for decoupled spectra (Bruker pulse program INEPTRD.AUR).

NMR Measurements. Unless indicated otherwise, spectra have been recorded on a Bruker AM-400 spectrometer, equipped with an Aspect 3000 computer and array processor. All measurements have been carried out at 323 K, using deuteriated formic acid (DCOOD) as solvent and internal locking agent. Chemical shifts were referenced to DCOOD (^{13}C C=O resonance at 166 ppm) and HCOOD (^{1}H chemical shift at 8.2 ppm).

The concentration used in the 1D ^{13}C and 2D measurements were typically 400 mg of polymer in 3 mL of DCOOD.

For the COSY-45 experiment, typically 16 transients were accumulated per t_1 value with a recycle time of 3 s. The initial data matrix size was 1000 Hz (1 K) and 500 Hz (256 t_1 values) in ω_2 and ω_1, respectively. Before Fourier transformation, zero filling was used once in the F_1 dimension.

The X–H COSY spectrum was obtained by using a 1K × 1K data matrix (after Fourier transformation, covering 3400 Hz in F_2 and 1000 Hz in the F_1 dimension). The repetition time was 5 s with 32 scans collected for each of the 256 spectra. In the F_2 dimension a line broadening of 1 Hz was used. Delay times were set to 3.3 (D_1) and 2.0 ms (D_2). For the RCT experiment a 256 × 1K data matrix was used, covering the same region as in the X–H COSY experiment. A repetition rate of 2 s was used with 16 scans collected for each of the 64 spectra. Delay times D_2 and D_3 were 3.3 and 2.2 ms, respectively, while D_1 was 16 ms.

Finally, for the COLOC experiment, 32 scans were accumulated per t_1 value with a recycle delay of 5 s. Initial data matrix 3400 Hz (1K) and 1000 Hz (256 t_1 values), zero filling once in the F_1 domain, and no window functions were applied. Delay times D_1 and D_2 were set to 100 and 40 ms, respectively. For the observation of the carbonyl region, a separate COLOC experiment was run with delay times D_1 and D_2 of 32 and 30 ms, respectively. The data matrix was 1800 Hz (1K) and 1000 Hz (128 t_1 values, 256 scans each).

Zero filling was used once in the F_1 domain and no window functions were applied.

Results and Discussion

Methodology. All resonances being present in the ^{1}H and ^{13}C NMR spectra of PA-4,6 can be classified in three groups in an order decreasing in signal intensity (see ref 10, 11): (i) the main-chain ^{1}H and ^{13}C resonances; (ii) the resonances of amine (a) and carboxylic (c) end groups; (iii) the pyrrolidone end-group resonances.

(i) The resonances of the main-chain carbons and protons can be assigned unambiguously by a combination of two 2D NMR techniques (H–H and X–H COSY[12,13]).

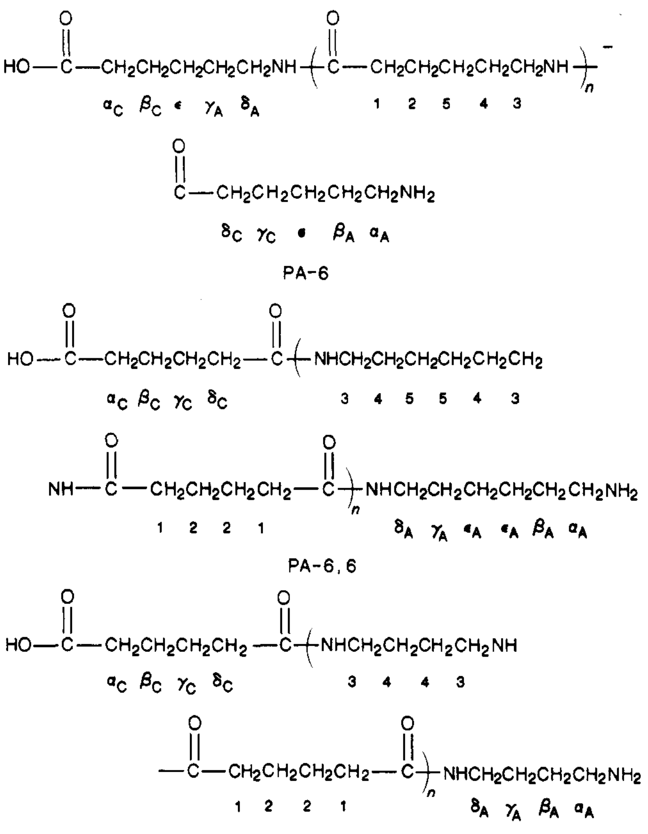
(ii) Concentrating on the aliphatic regions in both ^{1}H and ^{13}C NMR spectra, theoretically four aliphatic ^{13}C and four aliphatic ^{1}H resonances can be expected for each of the amine and carboxylic end groups. At 400 MHz (proton frequency), only four signals can be resolved. Six ^{13}C resonances can be resolved at 25–100 MHz, independent of the frequency. The resolved resonances can be partly assigned by COSY techniques.[12,13] The hidden end-group signals are subsequently assigned by two techniques (RCT and COLOC[14,15]) which detect C–H connectivities with non-nearest protons. In favorable cases, even resonances completely obscured by main-chain resonances, both in the proton and carbon spectrum, can be detected.

(iii) The ^{13}C resonances of the pyrrolidone (p) end groups have been assigned via an inspection of the observed resonances in a low molecular weight PA-4,6 oligomer, where deliberately an unrealistic high level of p end groups was introduced, and of the resonances observed in model compound **3**.

Results. In Table I the ^{13}C NMR data of the model compounds **1**–**2** and **4** and of PA-6, -4,6, and -6,6 are given, using the nomenclature indicated in Charts I and II.

Assignments for the end-group resonances of high molar mass PA-6 and -6,6 are only tabulated for those cases where the ^{13}C resonances are clearly resolved. The assignments of these end-group resonances are based on an interpolation of the rigourously established chemical shifts of the end groups present in low molar mass PA-4,6 (vide infra).

Chart II



Inspection of Table I shows that there exists a satisfactory agreement between chemical shifts of carbon atoms with similar chemical surrounding; however, for all resonances a slight but consistent downfield shift of approximately 0.7 ppm for PA-6 and PA-6,6 has been observed. The strategy used in this work, i.e., end-group assignment via 2D NMR techniques for a low molecular weight oligomer to establish end-group signals in related high molar mass polyamides (for which low molar mass oligomers are difficult to obtain), is to our knowledge new and deserves to be followed in related systems (polyesters or polycarbonates).

Assignments of Resonances. In a discussion of the peak assignment for the end groups of PA-4,6, main-chain signals are easily discernible from end-group signals because of their intensity. Subsequently, the main-chain signals 1–4 are easily assignable as is shown in the H–H COSY spectrum in Figure 1 and the X–H COSY spectrum in Figure 2.

The end-group signals of the amine end group α_A–δ_A can also be assigned on the basis of these COSY spectra, whereas for the signals of the carboxylic endgroup, α_c–δ_c, only a partial assignment can be given because of chemical shift degeneracy in the ^{1}H spectrum (see Figure 1). Consequently, also only a partial assignment can be given for the ^{13}C end-group resonances via X–H COSY techniques (see Figure 2).

Assignments for α_C–δ_C were accomplished by two 2D techniques (COLOC and relayed coherence transfer (RCT) which establish proton–carbon connectivities over more than one bond and thereby lift the chemical shift degeneracy). The RCT experiment (spectrum not shown) only gives the assignment of the carbon resonance of β_C via its two-bond correlation with the α_c proton, because of the apparent shift equivalency of the atoms γ_C and δ_C and the main-chain atoms 2 and 1, respectively (this holds for ^{1}H and ^{13}C NMR spectra). Therefore, the final assignments for γ_c and δ_c had to be done via a COLOC experiment

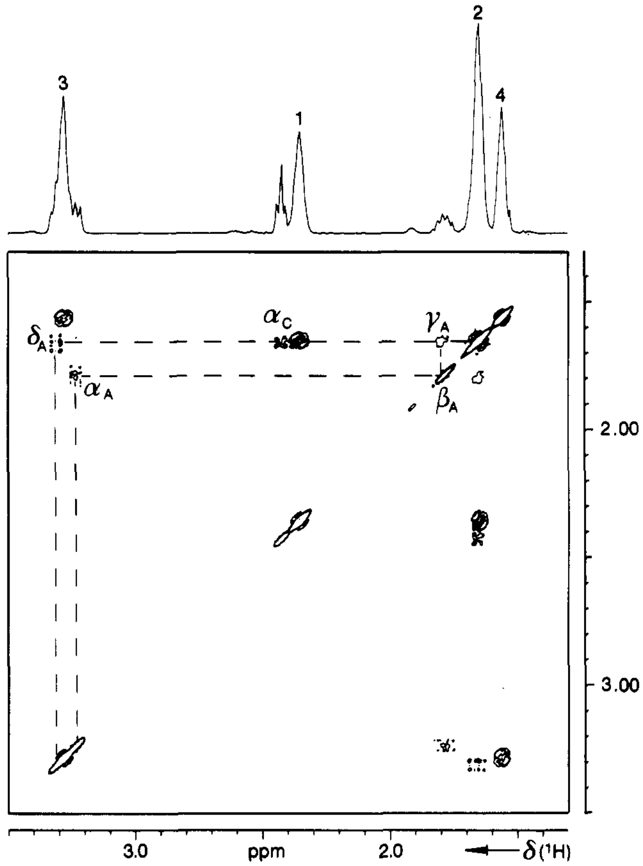


Figure 1. 400-MHz H-H COSY spectrum of a low molecular weight polyamide-4,6 at 50 °C in DCOOD.

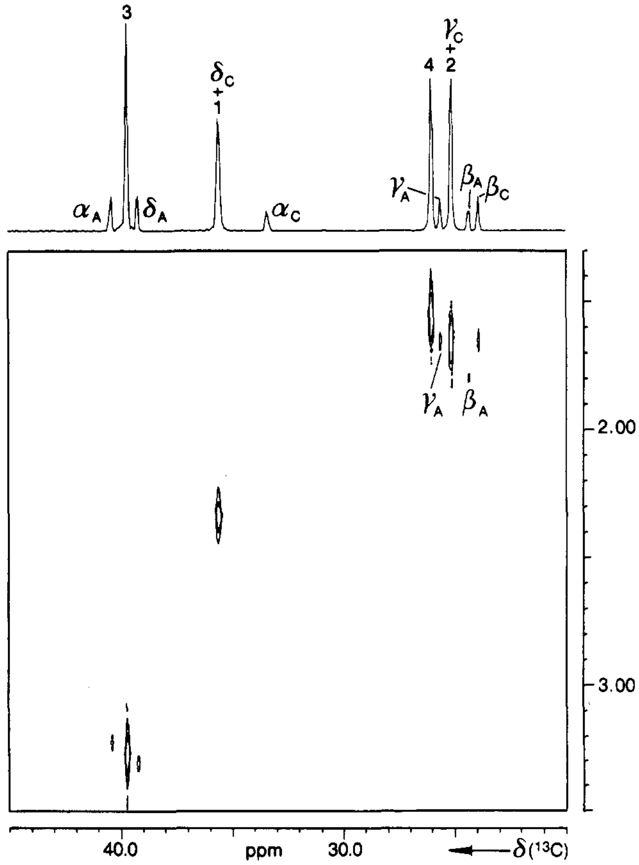


Figure 2. 400-MHz ^{13}C–^{1}H correlated (X–H COSY) spectrum of a low molecular weight polyamide-4,6 at 50 °C in DCOOD.

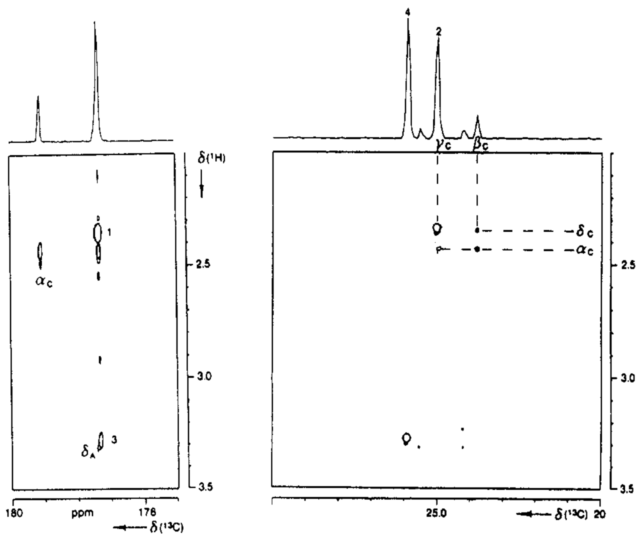


Figure 3. COLOC spectrum of the aliphatic and carbonyl region of low molecular weight polyamide-4,6 at 50 °C in DCOOD, determined in two experiments (see Experimental Section for details).

which establishes heteronuclear couplings through two and three bonds.[16,17] This technique has been used for quarternary carbons,[15-18] as well as for nonquarternary aliphatic carbon atoms.[16] The contour plot of the COLOC measurement is shown in Figure 3. Starting from the already assigned proton α_c a three-bond correlation with the γ_c carbon establishes its position under main-chain resonance 2. (Also, the two-bond correlation of α_c with β_c, assigned via the RCT experiment, is visible.) Similarly a three-bond correlation of β_c with δ_c proves that the resonances of δ_c are obscured by the main-chain resonance 1. Note that although all end-group resonances are now assigned, one cannot actually decide on the basis of these 2D experiments whether α_A/α_c or δ_A/δ_c resonances are at high field. Therefore, a second COLOC experiment was run which gives a three-bond correlation of δ_A with the carbonyl end group, a correlation which α_A cannot show (see Figure 3).

Although there is some spectral overlap between the cross-peaks connecting δ_A and 3 to the neighboring carbonyl, a slice at δ 177.4 clearly showed two cross-peaks at δ 3.32 (δ_A) and δ 3.27 (3).

The assignment α_c/δ_c has been accomplished with the aid of model compounds **2** and **4**. Comparison of the molecular structures of **2** and **4** shows that a chemical shift difference should exist for α_c but not for δ_c, due to the presence of the ester group near α_c.

As can be seen in Table I, this establishes the assignment of α_c for **2** and **4**. COSY experiments then establish the assignment for β_c and γ_c.

As can be seen in Table I, these values perfectly match with the ^{13}C values of β_c and γ_c for PA-4,6. Thus, indirectly, the assignments of β_c and δ_c are established, and via the COSY spectra, α_c/δ_c for PA-4,6 can also be unambiguously assigned.

Finally, the ^{13}C spectra of pyrrolidone-terminated PA-4,6 is compared with the corresponding spectrum of the reaction product of pyrrolidine and pentanoic acid, model compound **3** (see Figure 4). The carbon resonance at δ ~48 is characteristic for the two ring carbons being nearest neighbors to nitrogen.

Conclusions

The combination of modern 2D NMR techniques allows detailed assignments to be made in the ^1H and ^{13}C spectra of polyamides, both for main-chain and end-group resonances. The results thus obtained in this study can serve as a starting point for the assignments for other polyamides.

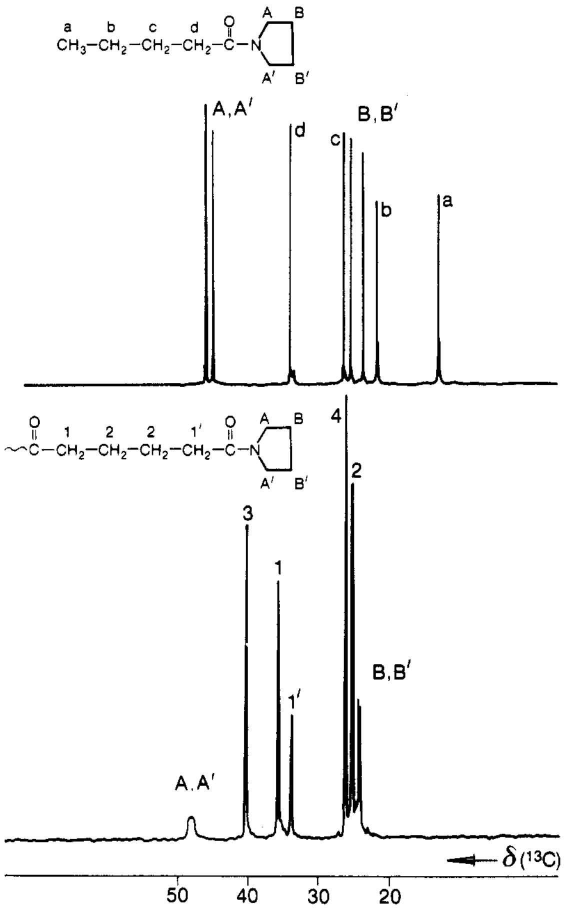


Figure 4. ^{13}C NMR spectra of pyrrolidone-terminated PA-4,6 (lower trace) and model compound **3** (upper trace); 25-MHz ^{13}C NMR spectra.

Registry No. **1**, 118356-64-2; **2**, 118356-65-3; **4**, 118356-66-4; PA-4,6 (SRU), 50327-22-5; PA-4,6 (copolymer), 50327-77-0; PA-6,6, 32131-17-2; PA-6, 25038-54-4.

References and Notes

(1) Carothers, W. H. U.S. Patent 2130948, 1938.
(2) Haslam, J.; Willis, H. A.; Squirrel, D. C. M. *Identification and Analysis of Plastics*, 2nd ed.; Heyden and Son: London, 1982; p 299.
(3) Kelm, J. *Kunststoffe* **1981**, *71*, 514.
(4) Kricheldorf, H. R.; Mühlhaupt, R. *Angew. Makromol. Chem.* **1977**, *65*, 169.
(5) Alekseyeva, S. G.; et al. *Polym. Sci. USSR (Engl. Transl.)* **1982**, *7*, 1659.
(6) Gan, L. H.; Blais, P.; Carlsson, D. J.; Suprunchuk, T.; Wiles, D. M. *J. Appl. Polym. Sci.* **1975**, *19*, 69.
(7) Curnuck, P. A.; Jones, M. E. *Br. Polym. J.* **1973**, *5*, 21.
(8) Mirau, P. A.; Bovey, F. A. *Macromolecules* **1986**, *19*, 210.
(9) Gaymans, R. J.; van Utteren, T. E. C.; van den Berg, J. W. A.; Schuyer, J. J. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 537.
(10) Roerdink, E.; Warnier, J. M. M. *Polymer* **1985**, *26*, 1583.
(11) Roerdink, E.; de Jong, P. J.; Warnier, J. *Polym. Commun.* **1984**, *25*, 194.
(12) Aue, W. P.; Bartholdi, E.; Ernst, R. R. *J. Chem. Phys.* **1976**, *64*, 2229.
(13) Bax, A.; Morris, G., *J. Magn. Reson.* **1981**, *42*, 501.
(14) Bolton, P. H. *J. Magn. Reson.* **1982**, *48*, 336.
(15) Kessler, H.; Griesinger, C.; Zarbock, J.; Loosli, H. R. *J. Magn. Reson.* **1984**, *57*, 331.
(16) Kessler, H.; Bermel, W.; Griesinger, C. *J. Am. Chem. Soc.* **1985**, *107*, 1083.
(17) Kessler, H.; Griesinger, C.; Lautz, J. *Angew. Chem.* **1984**, *96*, 434.
(18) Müller, N. *Magn. Reson. Chem.* **1985**, *23*, 688.