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^{15}N NMR CHARACTERIZATION OF MULTIPLE CRYSTAL FORMS AND PHASE TRANSITIONS IN POLYUNDECANAMIDE (NYLON 11)

by

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ABSTRACT

Polyundecanamide (nylon 11) was synthesized with 99+% ^{15}N labeling of the amide nitrogen. Polymer samples were thermally treated to give the stable triclinic α-crystal form and the metastable δ'-smectic form. The γ-from was obtained by precipitation from neat trifluoroacetic acid upon evaporation. ^{15}N CP/MAS NMR clearly differentiated the samples by chemical shift. Confirming previously reported x-ray and thermal analysis, the α-crystal form transforms above 95°C to the pseudohexagonal δ-crystal form. ^{15}N spin lattice (T_1) relaxation experiments confirmed decreasing relative mobility in the order $\delta' < \delta < \alpha$ consistent with increasing molecular rigidity and density. Previous studies suggested that the α-δ transition involves the onset of rapid hydrogen bond disruption and reformation within the crystal lattice above the 95°C transition temperature. ^{15}N chemical shift anisotropy (CSA) spectra showed that the hydrogen bonded amide units remain conformationally rigid in the crystal lattice despite increasing librational motion. Combining ^{15}N T_1 information with wide-angle x-ray data, a model is presented which accounts for the crystal-crystal transition as well as the relative stability of the three crystal forms.

INTRODUCTION

Polyundecanamide (nylon 11) is an important commercial polyamide with curious morphological properties. Evidence of polymorphism has been demonstrated by several workers and found to be dependent on the thermal history of the sample as well as the test temperature.[1-5] Thermal analysis and x-ray point to two morphologies in samples isothermally annealed below the melting point: the triclinic α-form which is stable at temperatures below 95°C[2,6] and the δ-form which exists at temperatures above 95°C.[6] The δ-form is unstable at room temperature and reverts to the α-form very rapidly on cooling. Samples quenched from the melt, on the other hand, have been shown to crystallize into the kinetically favored but metastable δ'-form.[7,8] Various molecular models have been offered to explain the differences in nylon 11 crystal packing for these three forms. Nevertheless, contradictions remain in the literature concerning the details of packing in the α and δ crystal forms.[2,4-6]

We undertook a study of the morphology of nylon 11 using x-ray and thermal analysis to examine, first, the effect of the α-δ crystal-crystal transition on the melting behavior and second, to attempt quantitation of the relative amounts of each crystal form produced by different thermal treatments.[9] The transition has been rationalized as a disruption of the layer-like hydrogen bonding between adjacent chains into hydrogen bonds which form and disrupt randomly between chains in a pseudohexagonal array.[6] The fluctuations of dipoles and hydrogen bonds in nylon 11 is crucial to the validity of this model. Unfortunately, this question cannot be conclusively answered using the above microscopic and macroscopic techniques, and studies on the electrical properties of nylon 11 gave puzzling results with respect to this question.[10,11,12-14]

Recently, we have shown that ^{15}N CP/MAS NMR is a sensitive technique for examining the crystal structure of solid polyamides[15,16] with chemical shift changes related to specific conformations about the amide group.[17] Isotopic ^{15}N enrichment of nylon 6 allowed observation of crystalline and non-crystalline resonances accurately, and determination of specific T_1 relaxation times.[18] The unique ability of ^{15}N NMR to directly observe amide behavior at the molecular level in solid polyamides prompted us to prepare isotopically-labeled nylon 11 to specifically examine the roles of conformational order and hydrogen-bonding mobility in the α-δ transition. We report here the synthesis of the labeled material (Figure 1), formation of various ordered forms through thermal treatment or precipitation, and sample characterization with various ^{15}N solid state NMR techniques. The NMR results are compared with x-ray and thermal analysis obtained on these same samples.

EXPERIMENTAL SECTION

^{15}N NMR. High resolution solid state 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 ^1H was 200.13 MHz. Samples were placed in fused zirconia rotors fitted with Kel-F caps and spun at 3.0 to 3.2 KHz with dry air. Crystalline glycine was placed in the rotor with most samples and used as an internal chemical shift reference (0 ppm), or was used as an external reference prior to obtaining sample data. CP/MAS spectra were obtained with a standard crosspolarization pulse sequence using a 3.5 μs ^1H 90° pulse and a mixing pulse of 2 ms. High power decoupling was used during a 50 ms acquisition time with a nutating field of 62-68 KHz. ^{15}N spin-lattice relaxation times (T_{1N}) were obtained using the CP-90-τ-90 pulse sequence developed by Torchia.[19] Static chemical shift anisotropy (CSA) ^{15}N spectra were obtained using the CP acquisition parameters described above. MAS spectra without cross-polarization were obtained with a 90° ^{15}N

pulse with high power proton decoupling during the acquisition period and a recycle delay of 7s.

Monomer Synthesis. Potassium phthalimide (99.6% ^{15}N), 11-bromoundecanoic acid, and anhydrous hydrazine were obtained from Aldrich Chemical Company, Milwaukee, Wisconsin, and used as received. Other solvents were reagent grade materials and used without further purification.

Ethyl 11-bromoundecanoate (1). A 50 ml round bottom flask was charged with 10g (0.037 moles) 11-bromoundecanoic acid and 40 ml thionyl chloride. The flask was fitted with a condenser and drying tube, then heated in an oil bath until HCl evolution was observed from the condenser. After the initial vigorous reaction, the flask was heated at reflux for 3 h. The condenser was removed and the excess thionyl chloride was allowed to distill from the solution. The product was carefully poured with stirring into a 250 ml Erlenmeyer flask containing 100 ml absolute ethanol. The ethanol solution warmed to approximately 60°C. The top of the flask was fitted with a stopper and drying tube, and the solution allowed to stir overnight. The excess ethanol was evaporated in a stream of dry air to give a yellow oil. The crude product was taken up in 150 ml diethyl ether and washed with two 50ml portions of 3% aqueous sodium carbonate followed by two 50ml portions of distilled water. After evaporation of solvent, the oil was distilled under vacuum at 120-122°C (0.02 torr) to give 9.88g (89%) of the ester 1 as a colorless oil. ^{13}C NMR (in $CDCl_3$, δ from TMS): 172.2 (carbonyl), 59.4 ($-OCH_2-$), 44-27 (other CH_2's), 13.8 ($-CH_3$).

Ethyl 11-phthalimido undecanoate.(2) A 50 ml round bottom flask was fitted with a stir bar and heated in an oven at 120°C for 4 h. The flask was removed and flushed with a stream of dry nitrogen while cooling. The flask was charged with 30 ml dry N,N-dimethylformamide (DMF), 2g (0.01 moles) potassium phthalimide (99.6% ^{15}N), and 3.16g (0.01 moles) of ethyl 11-bromoundecanoate (1). The flask was capped with a rubber septum and placed in an oil bath at 65°C for 2 h. The phthalimide salt was only partially soluble in DMF and formed a finely divided suspension with stirring.

The flask was removed from the oil bath and the contents poured into 150 ml distilled water to dissolve the precipitated potassium bromide. 300 ml ether was poured into the aqueous solution, and the mixture vigorously shaken in a 500 ml separatory funnel. The aqueous portion was removed from the funnel and the ether layer decanted. The aqueous portion was extracted with two additional 50 ml portions of ether. The ether fractions were combined and washed with two 50 ml portions of distilled water. The ether was evaporated in a stream of dry air to give a white solid. The product was recrystallized from hot methanol, filtered, and then dried under vacuum at room temperature to give 3.54g (0.0092 mol, 92%) of ethyl 11-phthalimido undecanoate (2, 99.6% ^{15}N), mp 43-45°C. ^{13}C NMR (in $CDCl_3$, δ from TMS): 173.6 (C=O, ester); 168.2 (C=O, imide); 133.6, 132.1 and 122.9 (aromatic); 59.2 ($-OCH_2-$); 37.9 ($>NCH_2-$); 34-24 (other CH_2's); 14.1 (CH_3).

11-Aminoundecanoic acid (3). 1.2g (3.3 mmol) of the phthalimide product 2 was dissolved in 30 ml absolute methanol in a 50 ml round bottom flask fitted with a stir bar. To this solution was added 0.22g (6.9 mmol) anhydrous hydrazine. The flask was fitted with a condenser, placed in an oil bath, and heated to reflux for 1 h. The methanol was evaporated under reduced pressure to give a solid precipitate. To the solid was added 10 ml concentrated HCl and 25 ml water,and the aqueous mixture heated at reflux for 1 h. On cooling to 0°C, phthalyl hydrazide precipitated from the solution and was removed by filtration through a glass frit. The filtrate was concentrated by boiling to near dryness to remove water and HCl. The remaining solvent was evaporated in a stream of air to yield a white paste. This paste was dissolved in 50 ml of distilled water, then neutralized to pH 7 with sodium carbonate to precipitate the crude amino acid product. The product was filtered, then recrystallized twice from boiling water to yield 0.58g (2.9 mmol, 87%) 11-aminoundecanoic acid (3, 99.6% ^{15}N), mp 189-190°C (lit. mp 190°C[20]).

Poly(aminoundecanoic acid) (Nylon 11): Nylon 11 was prepared by thermal polycondensation of the amino acid as described by Sorenson and Campbell.[20] The polymer was recovered in quantitative yield as a tough, white solid. Samples were prepared by positioning a small amount of polymer between two sheets of aluminum foil coated with a fluorinated mold release agent, then placing the foil and sample in a hydraulic press heated to 220°C. The press was adjusted to 10-20 ksi. To anneal nylon 11 samples, the press was cooled to 170°C and held there for 1 h. The quenched nylon 11 sample was similarly prepared, except the foil and molten polymer were removed and quickly immersed in a bath of dry ice/isopropanol. Nylon 11 in the γ-crystal form was prepared by evaporating a TFA solution of the polymer. The crystallinity and morphology were confirmed by wide-angle x-ray and DSC measurements.

RESULTS AND DISCUSSION

The ^{15}N CP/MAS spectrum of nylon 11 annealed at 170°C is shown in Figure 2, trace A. The most intense resonance is seen at 84.2 ppm (downfield of glycine at 0 ppm) with a broad shoulder further downfield. The main resonance was identical to that previously found for the α crystal form of nylon 6[15] and a variety of other nylon samples.[15,16] The downfield resonances have not been previously assigned to any particular crystal form although the "amorphous" region of nylon 6 was observed as a broad resonance centered in this region.[18] Using a 90° ^{15}N pulse with decoupling, the MAS spectrum in trace B was obtained. The α crystal magnetization has been saturated, leaving only the fast relaxing "amorphous" component shown in trace B. Spectral subtraction of B from A gives the narrow α crystal resonance seen in trace C at 84.2 ppm. Trace D in Figure 2 shows the CP/MAS spectrum of the annealed sample obtained at 388K (115°C), well above the reported α to δ transition temperature. Clearly the peak for the α crystal form has disappeared, leaving only downfield resonances at 85.5 and 86.7 ppm. On cooling, the spectrum becomes identical to trace A again, confirming the reversibility of the α-δ transition.

The ^{15}N CP/MAS spectrum of nylon 11 quenched from the melt (δ' crystal form) is shown in Figure 3, upper trace. The α crystal form resonance is absent in this spectrum, confirming x-ray and thermal analysis results on quenched samples. Also, the resonance at 86.6 ppm is identical to that seen for the δ-form in the annealed sample (Figure 2). The kinetic stability of the δ' crystal form is confirmed by the spectrum shown in the lower trace of Figure 3 which was obtained at 107°C. The peak appears to narrow but the chemical shift remains identical. Extended annealing at elevated temperatures is required to convert the δ' form to the more stable α form. Although the relative thermodynamic stability of δ and δ' form are quite different, even at 107°C, the average conformation states of the amide groups in each are apparently similar at the molecular level as evidenced by ^{15}N NMR.

In the spectra of both quenched and annealed nylon 11, a broad peak centered at 86.5-87 ppm is seen for the amorphous fraction of the polyamide. Since this peak overlaps the chemical shift region of the δ and δ' crystal forms, it was initially unclear how the δ and δ' morphologies were different from the bulk amorphous material. Spin lattice relaxation T_{1N} experiments were performed on both annealed and quenched samples to evaluate the relative mobilities of each phase. The results are shown in

Table 1. As expected, the α-crystal form possesses the longest T_{1N}, consistent with its highly ordered structure. The relaxation data for both the δ- and δ'-forms (86.6 ppm) were found to fit a bi-exponential relaxation curve indicative of at least two components with different relaxation times. The short component times (2-7s) are similar to that obtained for the bulk amorphous fraction of nylon 6.[18] The long T_1 component of this resonance varies greatly between samples, and may depend on crystallite size. For the δ-form, the relaxation time T_{1N} is 112s while that of the δ'-form is 13s. The longer T_{1N} for the δ-form indicates that, while the amides in the δ and δ'-crystals may be similar chemically, the relative mobility of the δ'-form is much greater than that of the δ-form. The γ crystal form value is given for comparison. The long T_{1N} confirms that this is a crystalline resonance although, like the other semicrystalline samples, it contains a broad shoulder centered about 86.6 ppm characteristic of the amorphous fraction. The chemical shift of the crystalline peak (88.8 ppm), however, is clearly different from any of the other crystal forms discussed so far. The combination of ^{15}N chemical shift coupled with T_{1N} measurements allows clear and concise identification of all four individual crystal forms and the amorphous regions of various nylon 11 samples making this one of the most versatile methods for solid state characterization of polyamides.

The subject of rapidly re-orienting hydrogen-bonds in the δ-form has been discussed in a model requiring rapid molecular motion without destroying the crystal structure.[6] Such a model has been used to explain the Brill transition seen in nylon 66.[21] English and coworkers have recently studied segmental motion in nylon 66 using deuterium NMR.[22] While the methylene groups between amide units were found to have substantial librational motion well below the melting point, no evidence for amide reorientation was observed. In fact, the amide N-D bond in nylon 66 was shown to remain in a rigid lattice up to just below the melting point, although some librational motion was observed. This result cast doubt on such motion occurring above the α-δ transition in nylon 11.

To further examine the possibility of rapid hydrogen-bond reorientation in nylon 11, static chemical shift anisotropy (CSA) spectra were obtained at various temperatures on the α-form nylon 11 sample obtained by annealing at 170°C. Increased molecular motion has been shown to cause narrowing of the ^{13}C CSA spectra of various semicrystalline polymers,[23] and we have seen similar behavior in the ^{15}N CSA spectra of nylon 6.[18] Figure 4 shows the ^{15}N CSA spectra of annealed nylon 11 at several temperatures. The patterns obtained are similar in shape and chemical shift range to those observed for low molecular weight model amides[24-26] and those we obtained for nylon 6.[18] The lower traces at 27°C and 47°C show broad ^{15}N CSA spectra for both crystalline and glassy amorphous components seen below T_g. At temperatures above the T_g, the amorphous component spectrum collapses to a relatively narrow resonance in the center of the still rigid crystalline CSA pattern. Peak intensities here are probably not quantitative because cross-polarization efficiency can vary with temperature, causing the relative intensity of the crystalline and amorphous components to also vary with temperature.[27] Most important for this sample, however, is that the <u>crystalline</u> component shows no evidence of narrowing at the 95°C α-δ transition. Even heating up to 420K (147°C) failed to narrow the crystalline CSA pattern. The ^{15}N CSA data, coupled with the deuterium NMR results for nylon 66, argues against rapid reorientation of hydrogen bonds in the crystal. Intuitively, motion of the amide groups in the crystalline regions should occur only after melting since the loss of this high-energy intermolecular interaction should allow molecular motion.

As mentioned, deuterium NMR studies of nylon 66 have shown that large amplitude librations of the methylene chains can occur well below the polymer melting point.[22] Such motions may be responsible for the transition seen in nylon 11; i.e., rapid wagging motion of methylene groups could result in a change in the crystal structure or dimensions without completely disrupting the long range order maintained by the hydrogen bond lattice. Rapid librations would also be consistent with decreases in spin lattice relaxation times for the observed crystal resonances. Such a model is supported by x-ray data given in Table 2. Interchain distance in the d_{010} direction increases between the α and δ-forms. At the same time, the d_{001} distance along the chain axis decreases from 12.1Å to 11.3Å. Figure 5 shows a proposed model to account for the crystal-crystal transition without disruption of the in-plane hydrogen bonding. Rapid methylene segment librations expand the crystal structure from the triclinic α-form to the pseudohexagonal δ-form. It should be noted that motions of this type are not trans-gauche transitions, but are large amplitude librations of the chain within the crystal lattice.[22] Note also that the layer-like hydrogen bonded structure is maintained in both forms although the interchain distance increases. This is consistent with the rapid reformation of the α-form on cooling back below the 96°C transition temperature. The stability of the hydrogen bonded sheets is further supported by the failure of the CSA to narrow at temperatures close to the polymer melting temperature and is intuitively reasonable since such strong intermolecular interactions should be disrupted only at the melting point.

The smectic δ'-form shown in Figure 5 is created by quenching from the melt. This crystal structure is virtually identical to that of the δ-form except that hydrogen bonds do not possess lateral orientation (within layers), but are randomly oriented along the backbone and between adjacent chains. The δ'-form is thus a kinetic product generated when rapid sample quenching allows insufficient time for hydrogen bonds to align in thermodynamically stable long-range ordered structures. These random orientations also explain the tendency of the δ' form to crystallize into the thermodynamically more stable α-form upon annealing. The randomly oriented hydrogen bonds break and reform in the layer-like structures of the α-crystal. This is high activation energy process, however, which allows the smectic δ'-form to remain kinetically stable except upon annealing. The crystalline δ-form, on the other hand, reverts easily to the α-form on cooling since the layer-like order is already present and cooling only involves a decrease in libration motion and energy. T_1 data also correlate with the relative amount of ordering in each region, increasing in the sequence $\delta' < \delta < \alpha$.

CONCLUSIONS

Polyundecanamide (nylon 11) was readily synthesized with 99+% ^{15}N labeling of the amide nitrogen. Polymer samples were thermally treated to give the stable triclinic α-crystal form and the metastable δ'-smectic form, and precipitated from trifluoroacetic acid to give the γ-form. ^{15}N CP/MAS NMR coupled with spin lattice relaxation (T_{1N}) measurements clearly differentiated the polymer morphologies. The α- and γ-forms displayed values similar to those observed previously for nylon 6 and many other nylons. Confirming previously reported x-ray and thermal analysis results for nylon 11, the α-crystal form transforms above 95°C to the pseudohexagonal δ-crystal form. ^{15}N spin lattice relaxation experiments were used to observe the relative mobility of the phases, with the relative order and T_{1N} values increasing in the order $\delta' < \delta < \alpha$. Unlike previous studies in which hydrogen bonds were postulated to break and reform rapidly above the 95°C transition, ^{15}N chemical shift anisotropy (CSA) spectra show that the hydrogen bonded amide units are rigidly oriented in the crystal lattice. Combining ^{15}N T_1 information with wide-angle x-ray data, a model is presented involving methylene chain and amide libration which accounts for the crystal-crystal transition as well as the relative stability of the various crystal forms.

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LIST OF FIGURES

Figure 1. Reaction scheme for preparation of ^{15}N enriched nylon 11.

Figure 2. ^{15}N NMR spectra of isothermally annealed nylon 11. Trace A is the CP/MAS spectrum obtained at 300K. Trace B was obtained by applying a 90° ^{15}N pulse with proton decoupling to saturate the crystal resonance. Trace C is the difference spectrum of A and B showing only the α crystal resonance at 84.2 ppm. The α crystal resonance disappears on heating above the 95°C (368K) α-δ transition temperature to give the δ form seen in trace D.

Figure 3. ^{15}N CP/MAS NMR spectra of melt quenched nylon 11 (δ' "smectic" form) at 300K (upper trace) and 380K (lower trace). Chemical shifts for the δ' and δ forms are identical. Unlike the δ crystal form, the metastable δ' form shows no evidence of fast conversion to the α form on cooling.

Figure 4. ^{15}N chemical shift anisotropy (CSA) spectra of nylon 11 at various temperatures. The amorphous signal is seen as a relatively narrow resonance centered at 85 ppm at temperatures above the polymer Tg. The remaining non-axial shielding tensor components for the crystal region remain unchanged up to near the polymer melting point.

Figure 5. Proposed model for α-δ crystal-crystal transition in nylon 11 and of the metastable δ' smectic form.

TABLE 1

^{15}N Spin Lattice Relaxation Times (T_{1N}) and Chemical Shifts[a] for Nylon 11

Sample	Form	88.8 ppm	86.6 ppm[b]	84.2 ppm
Annealed	α	-----	4.9s; 68.1s	178.3s
Annealed (373K[c])	δ	-----	7.2s; 112.2s	
Quenched in Dry Ice/i-PrOH	δ'	-----	2.3s;13.4s	-----
Trifluoroacetic acid	γ	84.1s	4.2s; 19.5s	-----

[a] Downfield of solid glycine

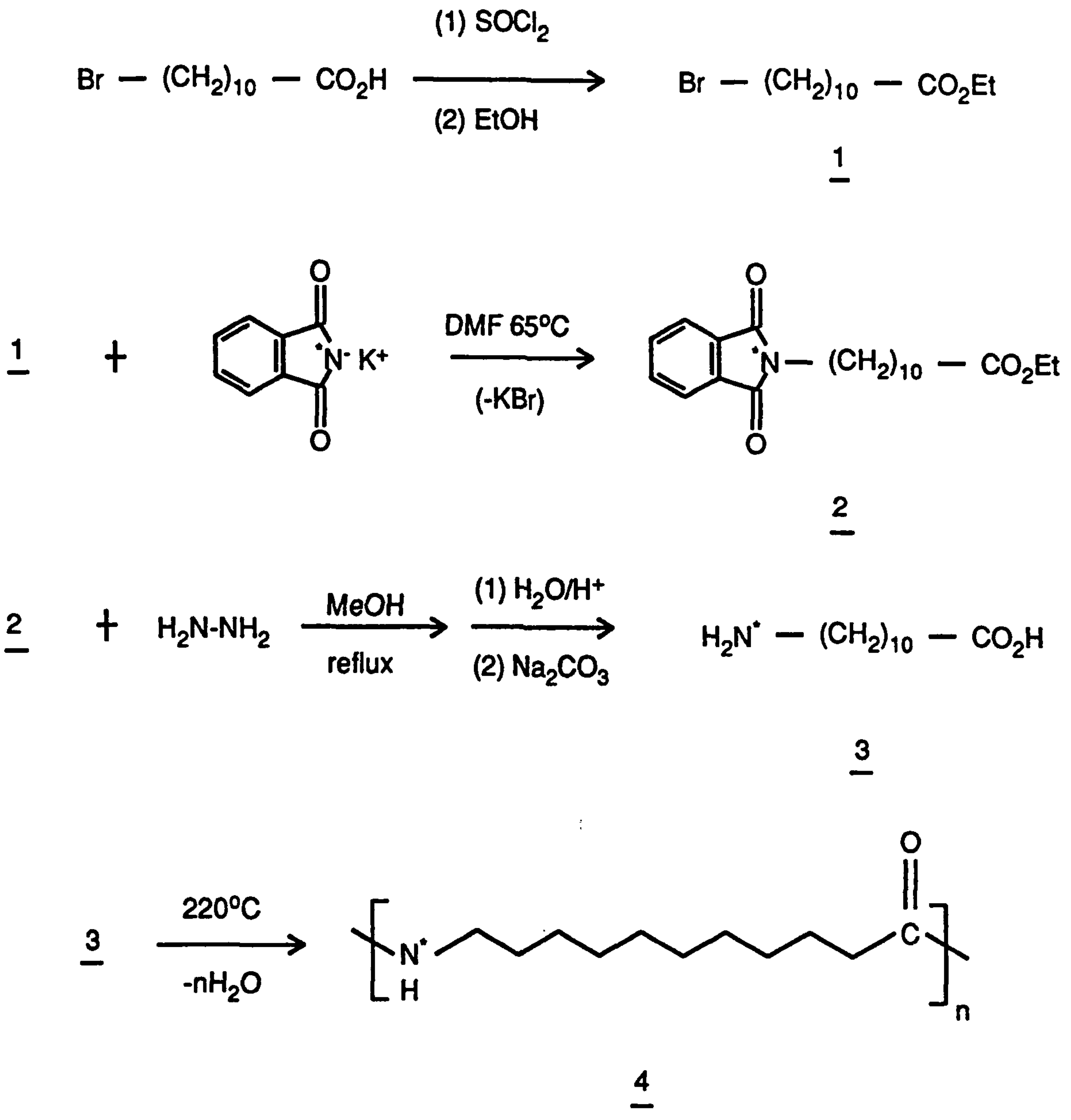
[b] This region also contains resonances for "amorphous" nylon

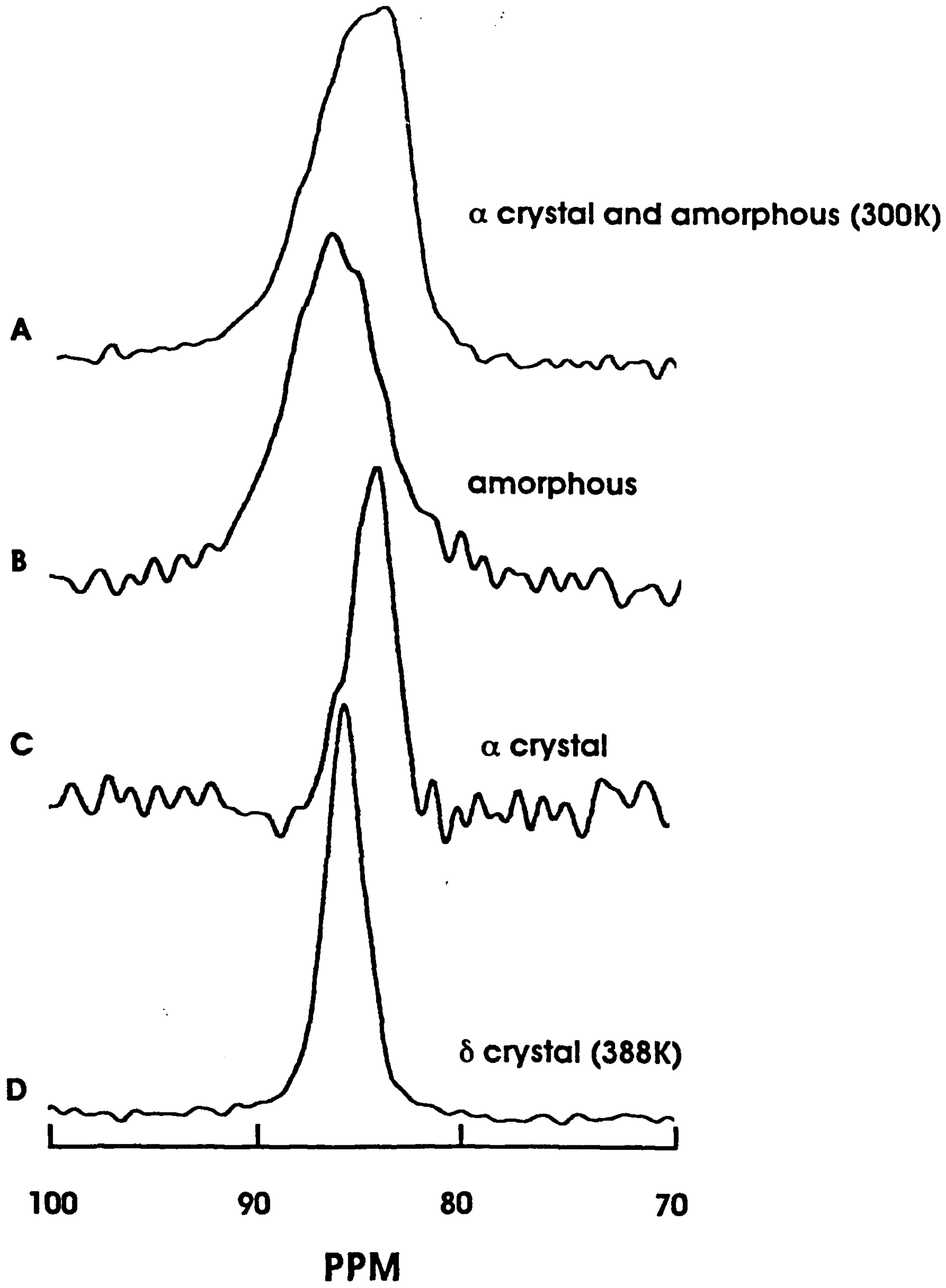
[c] T_{1N} acquisition temperature

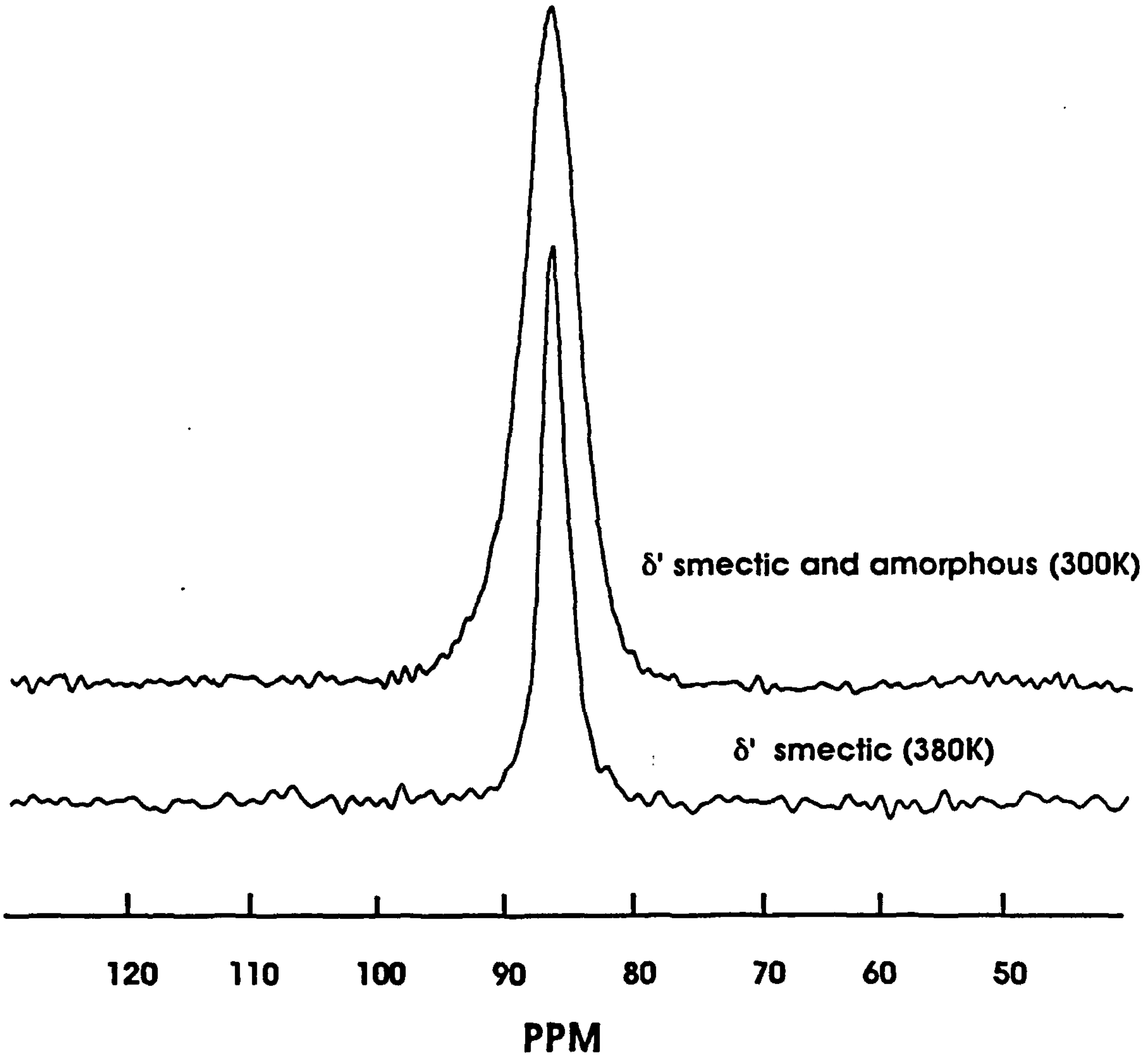
TABLE 2

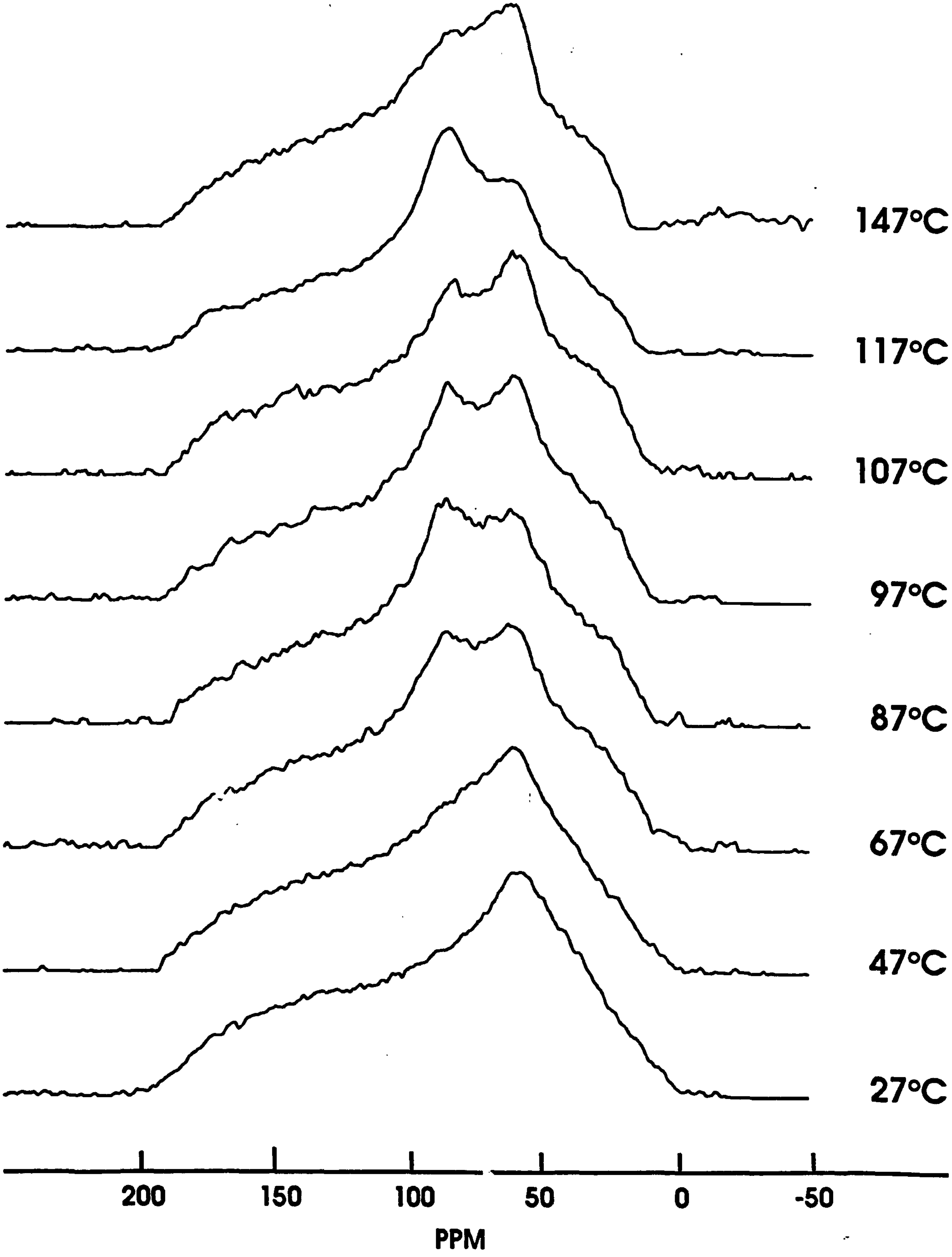
Crystalline System and Unit Cell Dimensions for Nylon 11

Crystal Modification	Crystalline System	(Chain Axis)	(Chain Packing)		Ref.
		d_{001}	d_{010}	d_{100}	
α crystal form	triclinic	12.1Å	3.62Å	4.40Å	1-4
δ crystal form	pseudohexagonal	11.3Å	4.16Å	4.16Å	6,8
δ' smectic form	pseudohexagonal	11.3Å	4.11Å	4.11Å	8

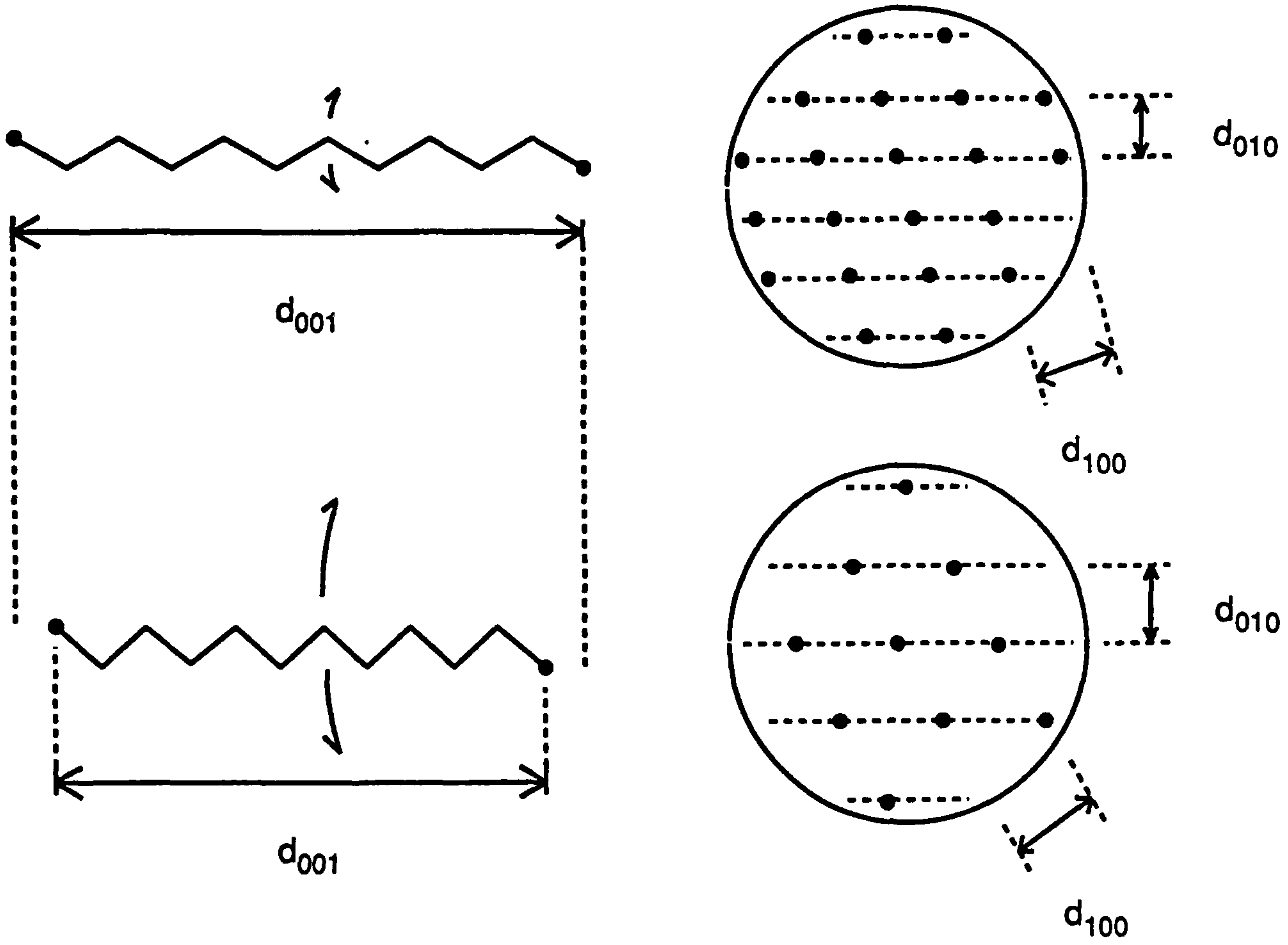

Br — (CH2)10 — CO2H
(1) SOCl2
(2) EtOH
Br — (CH2)10 — CO2Et
1
1
+
O
N- K+
O
DMF 65°C
(-KBr)
O
N— (CH2)10 — CO2Et
O
2
2
+
H2N-NH2
MeOH
reflux
(1) H2O/H+
(2) Na2CO3
H2N* — (CH2)10 — CO2H
3
3
220°C
-nH2O
N*
H
O
C
n
4


α crystal and amorphous (300K)
A
amorphous
B
C
α crystal
δ crystal (388K)
D
100
90
80
70
PPM

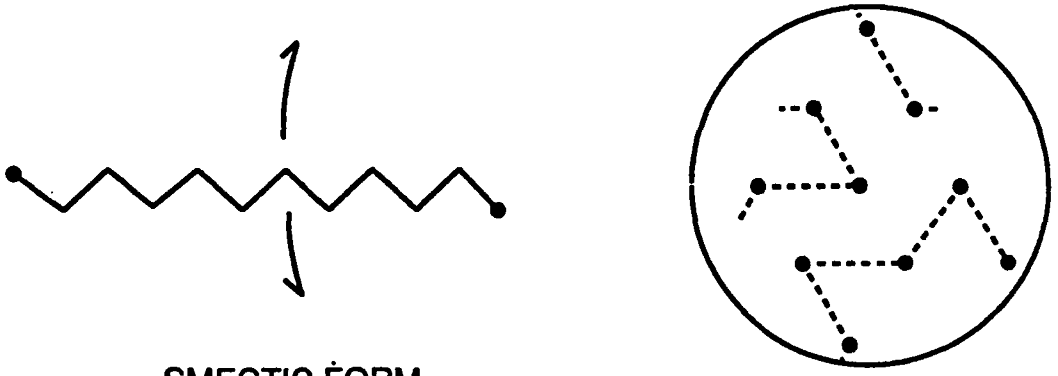

δ' smectic and amorphous (300K)
δ' smectic (380K)
120
110
100
90
80
70
60
50
PPM


147°C
117°C
107°C
97°C
87°C
67°C
47°C
27°C
200
150
100
50
0
-50
PPM

LOW TEMPERATURE FORM



HIGH TEMPERATURE FORM



SMECTIC FORM