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Characterization of 1:1 Random Copolymers Obtained From 6-, 7-, 11-, and 12-Carbon Amino Acids

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Abstract

Copolymers were prepared from the title amino acids by melt condensation under dry nitrogen. The resulting copolymers were characterized by solution and solid-state NMR, FTIR, DSC, and WAXD. Solution NMR spectra (at 75.5 MHz) showed multiple peaks with almost equal intensities in the carbonyl region (indicating random copolymer formation) with no evidence of end-group peaks (confirming high molecular weight). Solid-state ^{13}C (at 100.6 MHz) and ^{15}N (at 20.3 MHz) spectra of most solution cast films contained peaks consistent with the γ -form crystallites (δ_{N15} ca 89) being the predominant ordered phase. Only nylon 6-co-7 formed almost exclusive α -form on solution casting (δ_{N15} 84.5). Nylon 7-co-11 formed the α -form almost exclusively from the melt but gave a combination of α - and γ -phases (δ_{N15} 84.5 and 88.7) on solution casting. The copolymers possessed 3-component ^{13}C T_1 values ranging from 21 to 97 s for the slowest-relaxing component, indicating less-ordered domains than for the homopolymers. Absence of the amide V band near 680 cm^{-1} and the presence of a broad peak near 620 cm^{-1} in the FTIR spectra of 6-co-11, 6-co-12, 7-co-12, and 11-co-12 indicated the lack of an α -phase and presence of the γ -phase. Two peaks were seen in the FTIR spectra of the nylon 6-co-7 and 7-co-11 solution cast films near 580 and 680 cm^{-1} confirming α -crystallites. WAXD patterns of the solution cast films also confirmed the presence of the γ -phase (2θ ca 21.5°) and the α -phase (2θ ca 20.5° and 22.5°) in the various samples.

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Introduction

Our interest in random nylon copolymers derives from the behavior of homo- and copolymers of vinylidene fluoride (PVF₂) which exhibit excellent piezoelectric properties, especially for the copolymers.^{1,2,3} However, PVF₂ and derivatives are expensive and tend to lose piezoelectric activity over time and on heating.⁴ Better suited for anchoring the important polar crystal phase responsible for electrical properties in such polymers is a hydrogen bonded network.^{5,6,7} Although odd nylons do not possess the magnitude of piezoelectric response of PVF₂ polymers, their long-term stability, heat resistance, and lower cost make them attractive candidates for improved polymer-based devices.

Dipole rotation in crystalline or mesomorphic regimes that occurs in polar polymers in the presence of externally applied electric fields is key to the understanding of the poling process used to make piezoelectric polymer films.⁷ Nylon processing involves samples quenched from the melt to generate low amounts of imperfectly formed crystallites that are then poled and annealed to lock in orientation. We hypothesize that introduction of mismatched repeat unit lengths would facilitate segmental motion needed for dipole orientation. A-B type nylon copolymers, either with odd-odd or odd-even repeat unit combinations, are useful in evaluating this possibility and for determining the optimum repeat unit placement for good poling and enhanced piezoelectric behavior.

We report here the synthesis and characterization of six random nylon copolymers based on the commercially available amino acids, 6-aminohexanoic acid, 7-aminoheptanoic acid, 11-aminoundecanoic acid, and 12-aminododecanoic acid. A series of nylon 6-co-7⁸ and nylon 11-co-12⁹ copolymers with varying ratios of repeat units were

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described in more detail in other papers (with the former obtained by lactam ring-opening copolymerization). These copolymers could be dissolved in 2,2,2-trifluoroethanol and methylene chloride (3:2 by volume) and cast onto glass to give thin films. This technique should be very useful in preparing poled films in a manner similar to that used for nylon 3 polymers.⁶ We therefore carried out analysis of the crystallite types generated with this method for the group of 1:1 random copolymers described here.

Experimental

The amino acids were purchased from Aldrich Chemical Company and used as received except for 12-aminododecanoic acid which was recrystallized from boiling, deionized water (three times) before use. Methylene chloride and 2,2,2-trifluoroethanol (TFE) were reagent-grade and used as received. The copolymer polymerization method has been described elsewhere.^{8,9}

Differential scanning calorimetry (DSC) data were collected at 10° C/min under N₂ using a Perkin-Elmer DSC-7. The instrument was calibrated immediately prior to use with indium and tin standards.

Solution NMR data were collected using a Bruker AC-300 operating at 75.5 MHz for ¹³C. Concentrations of copolymer were ca 10 % w/v in a mixture of TFE and CH₂Cl₂ (3:2 by volume) with a capillary insert of D₂O for locking; no insoluble polymer was observed on dissolution, but small shards of glass (from breaking of the polymerization tubes) were removed by filtration through a cotton plug. Solid-state NMR data were collected using a Bruker MSL-200 for ¹⁵N (20.3 MHz), and a Bruker MSL-400 for ¹³C

(100.5 MHz). The acquisition parameters used have been outlined previously.⁹ The CPT1 experiment was a modification of the procedure outline by Torchia.¹⁰

FTIR data were collected using a Perkin-Elmer 1600 IR spectrometer at 2 cm⁻¹ resolution. A total of 64 scans were taken per sample with the background subtracted using the Perkin-Elmer-supplied software.

WAXD patterns were obtained using a Seimens XPD-700P polymer diffraction system using Cu K α X-rays and equipped with a two-dimensional, position sensitive area detector; background correction used the Siemens GADDSTM software package.

All spectral and thermal data were processed off-line using *Spectra Calc.*¹¹ An Array Basic program written in-house, **SC_NMR**, was used specifically to process the Bruker NMR data.

Results and Discussion

The random copolymers prepared by melt-condensation of 1:1 mole ratio mixtures of amino acids were nearly transparent except for the nylons 7-co-11 and 11-co-12 samples. Each sample was tough and required **careful** cutting (much force needed) with a razor blade in order to obtain thin samples for spectroscopic analysis. The copolymers were readily soluble in 2,2,2-trifluoroethanol and methylene chloride (3:2 by volume) up to 25 wt-% to give very viscous but pourable solutions. The films prepared by solvent casting (2 wt-%) were transparent, very flexible, and could be stretched to at least twice their original length (except the film of nylon 11-co-12). No further study on stretched films was made, however.

Solution and Solid-State NMR Analysis

The gated-decoupled solution ^{13}C NMR spectra of 6-co-11, 6-co-12, 7-co-11, and 7-co-12 in the TFE solvent mixture are shown in Figure 1; the spectra of the nylon 6-co-7 and 11-co-12 samples were published previously.^{8,9} The carbonyl region (expanded in the right column) shows multiple peaks representing the copolymer backbone composition. This is consistent with the observations made by Kricheldorf¹² that there are four (simple) sequence possibilities for such nylon copolymers that are often seen with NMR. The four peaks correspond to **A** and **B** (representing short and long amino acid residues, respectively) sequences, where **AA**, **AB**, **BA**, and **BB** represent homogeneous and heterogeneous head-to-tail arrangements. Kricheldorf also showed that perfectly alternating nylon 3-co-6 was useful in determining the carbonyl peak positions for random copolymers. He assigned the most upfield peak to the β -alanine residue, and the downfield peak to the 6-carbon fragment carbonyl. Similar results were found for alternating nylon 4-co-6, implying that the shorter aliphatic segment has the more upfield chemical shift.

If we let **A** equal hexanoic and **B** undecanoic monomer fragments, **AB** equals the hexanoic-undecanoic sequence, for example. Based on Kricheldorf's observations, the peaks in the carbonyl region of Figure 1, top trace, are assigned as follows: 176.4 ppm is **AB** (or hexanoic next to undecanoic), 176.5 is **AA**, 176.8 is **BB**, and 176.9 is **BA**. Similar assignments can be made for 6-co-12. However, the spectra for nylons 7-co-11 and 7-co-12 cannot be so readily assigned. It appears that the 7-carbon residue is too long to allow differences in sequence placement (with 11- and 12-carbon fragments) to

be observed at 75.5 MHz. The peaks are almost resolved as suggested by the downfield shoulders on the downfield peaks in the traces for 7-co-11 and 7-co-12, and by the broadening of the upfield peaks. The spectrum of nylon 6-co-7⁸ contained two equal-intensity peaks in the carbonyl region with no sequence-dependent splitting, while a single peak was seen in the spectrum for 11-co-12.^{9,12} This suggests that these repeat units are too similar in length to allow any sequence information to be observed by NMR. In summary, none of the resolved peaks in the carbonyl region was significantly greater in intensity than others indicating overall copolymer compositions consistent with 1:1 monomer feed ratios and random sequence distributions, an assumption consistent with the melt polymerization method used which should allow reversible addition and transamidation to lead to complete equilibration of the monomer sequences.

The solid-state ¹³C CPT1 NMR spectra for the solution cast films are shown in Figure 2. The chemical shifts from the CPT1 experiments are summarized in Table 1 along with values for homopolymers in various crystal forms. The CPT1 method discriminates in favor of rigid domains based on the spin-lattice relaxation time differences for the ordered and amorphous domains. The traces for nylons 6-co-11, 6-co-12, 7-co-12, and 11-co-12 are similar to each other with the main or only peaks assigned to carbons in the γ -phase based on our earlier work^{13,14} and that of others.¹⁵ The trace for 6-co-7 is clearly different from the others. Comparison of the chemical shifts (see Table 1) confirms that 6-co-7 forms almost entirely an α -like phase similar to those of the homopolymers, nylons 6 and 7, as indicated by the location of the two C_β peaks at ca 27 and 28 ppm and the combined C_N peak at 43 ppm. It is interesting that the carbon beta

to the carbonyl residue of each of the 6- and 7-carbon repeat units appears as a separate peak while the carbons immediately adjacent to the amide units overlap.

The nylon 7-co-11 spectrum in Figure 2 clearly contains multiple peaks arising from the two crystalline phases, α and γ . Figure 3 contains the CPT1 spectra for solution cast and as-polymerized polymers along with the spectral subtraction trace of the latter from the former. The as-polymerized spectrum is consistent with almost exclusive α -phase formation with the carbonyl peak at 175.0, C_N at 43.0, C_α at 36.0, the all-trans methylene chain peaks at 33.4 and 31.8 (for the two different repeat units), and C_β at 27.6 ppm. The as-polymerized trace was subtracted from that of the solution cast sample until no negative peaks appeared. This left the bottom trace in Figure 3 which contains peaks of the γ -phase for C_N at 39.4, C_α at 37.2, C_{AT} at 33.6, and C_β at 30.0 ppm.

Similar results were obtained for as-polymerized nylon 6-co-11, which appeared to contain both α - and γ -phases but with much smaller contribution from the α -form. The spectra (not shown) of the other as-obtained materials (6-co-11, 6-co-12, and 7-co-12) appeared to be those of poorly formed or disordered phases with no features specific for α or γ crystallites. The C_N peaks for these three copolymers appeared near 40.5 ppm in the CPT1 spectra which is closer to that of a pseudohexagonal phase than to those of α and γ crystal forms.⁹ Nylon 7-co-11 was the only copolymer to show such a distinct α -phase in the as-polymerized sample (see discussion below on X-ray results).

Multiple crystal domain peaks consistent with the ^{13}C results were seen in the ^{15}N CP/MAS NMR spectra of solution cast films for the copolymers (Figure 4), with the chemical shifts listed in Table 1. With the exception of nylon 6-co-7, whose main peak

position at 84.5 ppm corresponds to predominant α -phase, all samples have a main peak near 89 ppm. This latter value is consistent with the chemical shift of γ -nylon 12.¹³ The 7-co-11 spectrum contains an additional peak near 84 ppm for the α -phase,^{15,16} while the shoulder at 89 ppm in the 6-co-7 spectrum confirms the presence of γ -form crystallites for this sample. The broad amorphous peak is centered near 87 ppm in all of the spectra. Solution casting clearly provides a method of generating different crystal forms for these samples and may be useful for preparing nylon films with piezoelectric response.

An 11-co-12 sample enriched with ^{15}N was prepared via the Gabriel method afforded a copolymer containing 50 mol-% ^{15}N at each residue.⁹ Isotopic enrichment allows additional NMR experiments to be performed that are not feasible (with our instruments) at the natural-abundance ^{15}N level. The CPT1 experiment, which discriminates for rigid and crystalline phases, is one such experiment. The ^{15}N CP/MAS and CPT1 spectra for 11-co-12 are seen in Figure 5. The amorphous contribution has been eliminated in the bottom trace and the remaining crystalline peak is very narrow with a chemical shift consistent with γ -nylon 12. No evidence for α -phase crystallites was observed despite the facts that the α -form is preferred for nylon 11 and can easily be induced in samples of nylon 12 by precipitation.

Spin-Lattice Measurements

The ^{13}C spin-lattice relaxation values are listed in Table 2. The magnetization decays could be fit with 3-components (except for C_N of nylon 6-co-7) which is consistent

with the behavior of semi-crystalline nylons. The fast-relaxing components are assigned to the bulk amorphous fractions having T_1 's of a few hundred milliseconds. The slow-relaxing, rigid components have T_1 's of tens of seconds in this case, which are somewhat shorter than those seen for nylons 7¹⁴ and 13,13 (T_1 's of hundreds of seconds),¹⁷ but are in the same range or somewhat longer than those determined for other compositions of 6-co-7 and 11-co-12.^{8,9} The intermediate-relaxing components with T_1 's of a few seconds are assigned to constrained amorphous regions, or the interphases formed between the ordered domains and the bulk amorphous fractions. The carbon alpha (C_{α}) to the carbonyl often has the lowest T_1 values (greatest mobility) for the slow-relaxing component and it's possible that within the ordered domains, the effect of repeat unit mismatch is localized at or near these carbons allowing more vibrational or librational motion.

FTIR Analysis

The FTIR spectra of the solution cast films of the copolymers are shown in Figure 6. The films were cast and dried at ambient temperature in order to induce no thermal history that might change their crystalline content. The region shown in Figure 6 (between 800 and 500 cm^{-1}) contains two peaks specific for the known nylon polymorphs, the amide V and VI modes near 690 and 580 cm^{-1} , respectively, seen for α -crystals. The former peak is not seen for γ -crystals (γ -nylon 12,¹⁸ for example) while the latter peak shifts to ca 620 cm^{-1} . The dotted-line marks the position for the amide V peak not seen for the copolymers which show only γ -phase by NMR. In contrast, nylons 6-co-7 and 7-

co-11 have broad peaks in this region as well as additional peaks near 580 cm^{-1} for the amide VI mode which confirm γ form crystals.¹⁸

WAXD Analysis

The wide-angle X-ray powder diffraction patterns are seen in Figure 7, left column for as-polymerized samples and right column for solution cast films. The broad diffraction patterns for the as-polymerized samples of 6-co-7, 6-co-11, and 7-co-12 are similar in appearance to melt-quenched films of nylon 12¹⁹ and nylon 13,13¹⁷ which possess very little long-range order (low crystallinity). Nylons 6-co-12 and 11-co-12 appear to have fairly well-ordered γ -phases and 7-co-11 has a very ordered α -phase, consistent with the solid-state NMR results. Solution casting produced improved ordered phases for all of the samples as indicated by sharp single peaks at $2\theta = 21.5$ for the γ -form samples or two peaks at $2\theta = 20.1$ - 20.6 and 22.5 - 22.6 for samples with α crystallites.

Three points should be emphasized. First, solvent casting greatly increased the γ -content of nylons 6-co-11, 6-co-12, 7-co-12 and 11-co-12. Second, nylon 6-co-7 was essentially amorphous in the as-obtained sample but developed highly ordered α -crystals on solvent casting with no evidence of γ -phase. Third, the nylon 7-co-11 was highly α -crystalline in the as-obtained state but contained both α - and γ -crystallites in the solution cast film. These results are in good agreement with the NMR data, although some of the peaks for the smaller amounts of crystal phases are seen by NMR but not clearly observed by WAXD.

Thermal Analysis

The first-run DSC data on the solvent cast films were taken at 10 °C/min and are shown in Table 3. The glass transition temperatures for the as-obtained samples were all below 25 °C, which is consistent with the T_g behavior of other nylon copolymers,⁹ although no T_g was observed for 11-co-12. Melting points were also reduced from the homopolymer values as were the ΔH values. The second DSC heating run for these copolymers showed crystallization exotherms with peak maxima near 66 °C, and associated ΔH values nearly equal to the ΔH for melting. Only the nylon 11-co-12 sample showed no crystallization exotherm but did show a reduced melting endotherm. For example, on the second run, nylon 7-co-12 showed a crystallization peak centered at 66 °C ($\Delta H = -24$ J/g) and a melting peak at 120 °C ($\Delta H = 26$ J/g). Crystallization occurred over a narrow range while the melting transition was nearly 50 °C wide. Although the copolymers differ in backbone composition, it is very interesting that they show similar glass transition temperatures and second-run DSC behavior.

Conclusions

Peaks observed in the solid-state ^{13}C and ^{15}N NMR spectra confirm the presence of crystalline and amorphous phases in the samples and allow qualitative determination of the presence and the relative amounts of each. It has been shown that solution casting of the (mostly) amorphous nylon copolymer samples obtained by melt polymerization generates predominately γ -crystalline phases, except for 6-co-7 and 7-co-11 samples. Solution casting of the amorphous nylon 6-co-7 sample produced mainly α -phase (with a small amount of γ -form) while the nylon 7-co-11 sample, which was highly

α -form in the as-obtained sample, displayed mostly γ -phase peaks (along with those of small amounts of α -phase) after solvent casting. This last sample's behavior mimics that of nylon 7 which prefers the α -phase but will form the γ -phase under the same solution casting conditions.¹⁴ Peaks in the FTIR spectra and X-ray powder patterns confirmed the α - and γ -phases present in the copolymer solution cast samples. The latter clearly showed increases in crystalline order in all the samples on solvent casting with four of the samples showing only γ -crystallites and the nylon 6-co-7 and 7-co-11 samples displaying only α -, and both α - and γ -forms, respectively. DSC data indicated lower T_m 's and enthalpies than the homopolymers (first-run data) with remarkably similar glass transitions and second-run melting and crystallization behavior. The nylon 11-co-12 sample was unique in not displaying a T_g under any conditions nor a crystallization endotherm.

Overall, this work shows that the combination of spectroscopic methods with X-ray diffraction gives a more complete picture of the type and relative amounts of ordered phases occurring in nylons. Sample treatments, especially solvent casting from TFE- CH_2Cl_2 , radically changed the degree of order and can induce formation of less-favored crystal phases.

Finally, Table 4 allows several conclusions to be drawn about the ability of each repeat unit to influence type and degree of crystallinity. While three of the homopolymers prefer the α -form crystals from the melt, the nylon 12 units induce amorphous or γ -form crystals in the copolymers with nylon 6, 7 and 11 units in as-polymerized samples. However, all four homopolymers can be induced to form some γ -phase while predominant γ -form develops for nylons 7 and 11 on solvent casting. All of the 1:1 copolymers formed

mostly or exclusively γ -crystallites on solvent casting with only the nylon 6-co-7 sample showing a mixture of crystal forms favoring α . Nylon 6, 7 and 11 units can induce some α -phase, especially in combination with each other. In fact, the 6-co-7 and 7-co-11 samples give mainly or only α -crystals from solution casting and the melt, respectively.

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Table 1. ^{13}C CPT1 chemical shifts of solution cast films of the random nylon copolymers (^{15}N values in last column from CP/MAS spectra).

Copolymer	CO	C_N	C_α	C_AT	C_β	NH
6-co-7	173.5	43.0	36.3	30.3	28.0 26.8	84.5
6-co-11	173.0	39.9	36.8	33.6	30.4	89.0
6-co-12	172.9	39.8	36.9	33.6	30.3	89.1
7-co-11	173.2	42.9 39.4	- -	33.5	27.9 -	84.5 88.7
7-co-12	173.1	39.9	36.8	33.7	30.4	89.1
11-co-12	173.1	39.7	36.8	33.6	30.3	88.9
α -nylon 6	173.2	43.3	36.4	30.1	26.3	84.3
γ -nylon 6	173.0	39.9	37.8	30.1	30.1	89.5
α -nylon 7	173.6	43.1	35.6	31.7	28.2	84.5
α -nylon 11	173.7	42.5	35.8	33.4	27.5	84.2
γ -nylon 12	173.3	39.6	36.8	33.5	30.2	89.1

Table 2. T_{1C} values obtained with 2- or 3-component exponential fits of the relaxation data using the Bruker-supplied Pascal program, SIMFIT.

Copolymer	C_N	C_α	C_{AT}	C_β
6-co-7	0.7	1.0	0.6	0.4
	15.5	9.8	4.6	2.2
	-	24.4	32.0	21.2
6-co-11	0.3	0.1	0.6	0.4
	3.5	1.2	7.3	5.4
	34.9	28.8	57.9	43.1
6-co-12	0.4	0.4	0.9	0.5
	5.2	2.5	10.0	8.3
	55.5	35.5	71.0	72.6
7-co-11 (α -form peaks)	1.1	0.4	0.6	0.3
	4.5	3.2	5.1	2.3
	62.7	45.5	49.4	51.8
7-co-12	0.8	0.5	0.4	0.4
	8.0	3.8	5.7	3.6
	96.7	61.0	53.4	41.9
11-co-12	0.4	0.3	0.9	0.4
	4.2	1.2	7.0	5.0
	33.7	25.2	44.4	33.2

Table 3. DSC data for random copolymers including the T_m onset temperature, the maximum in the melting peak (T_m peak) and the melting enthalpy (ΔH in J/g).

Copolymer	T_m onset ($^{\circ}\text{C}$)	T_m peak ($^{\circ}\text{C}$)	ΔH (J/g)
6-co-7	132	149	26
6-co-11	136	145	33
6-co-12	131	139	57
7-co-11	141	147	50
7-co-12	135	142	53
11-co-12	146	153	65

Table 4. Comparison of the preferred (from the melt) and induced (by solvent casting from TFE-CH₂Cl₂) crystals found for the homo- and copolymer nylons (underline indicate main form observed in mixtures).

nylon polymer	melt crystallized	solution cast
6	α	α
7	α	$\alpha + \underline{\gamma}$
11	α	$\alpha + \underline{\gamma}^a$
12	γ	$\underline{\alpha} + \gamma^b$
6-co-7	amorphous	$\underline{\alpha} + \gamma$
6-co-11	amorphous	$\alpha + \underline{\gamma}$
6-co-12	γ	γ
7-co-11	α	$\alpha + \underline{\gamma}$
7-co-12	amorphous	γ
11-co-12	γ	γ

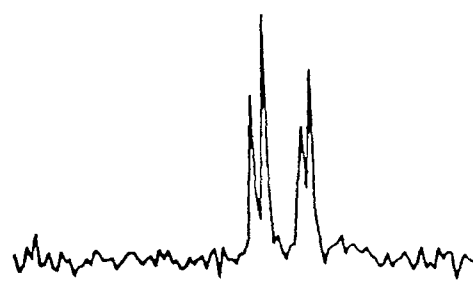
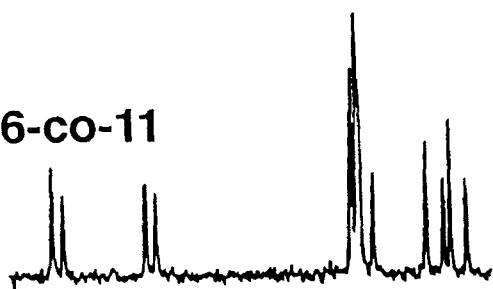
^afilm cast from trifluoroacetic acid

^bprecipitated from phenol-ethanol mixture

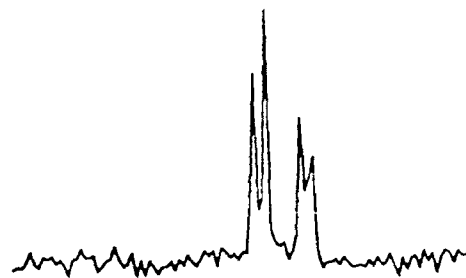
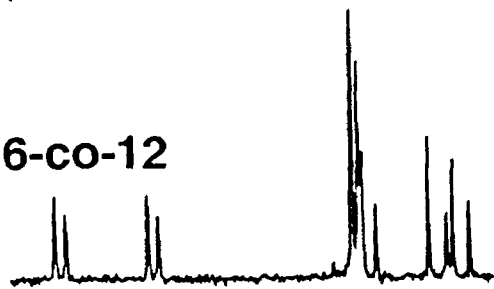
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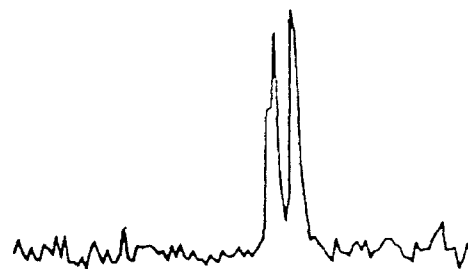
N6-co-11



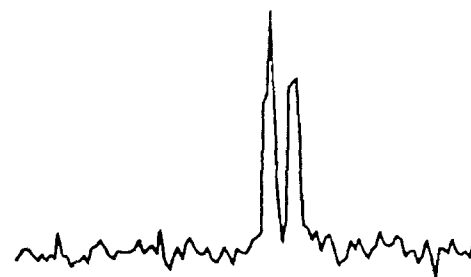
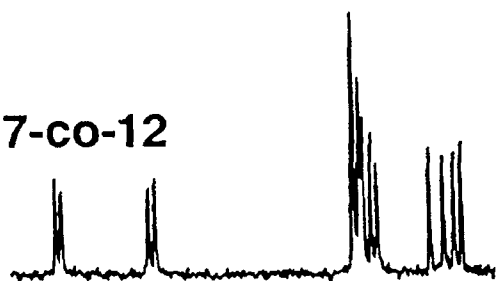
N6-co-12



N7-co-11



N7-co-12



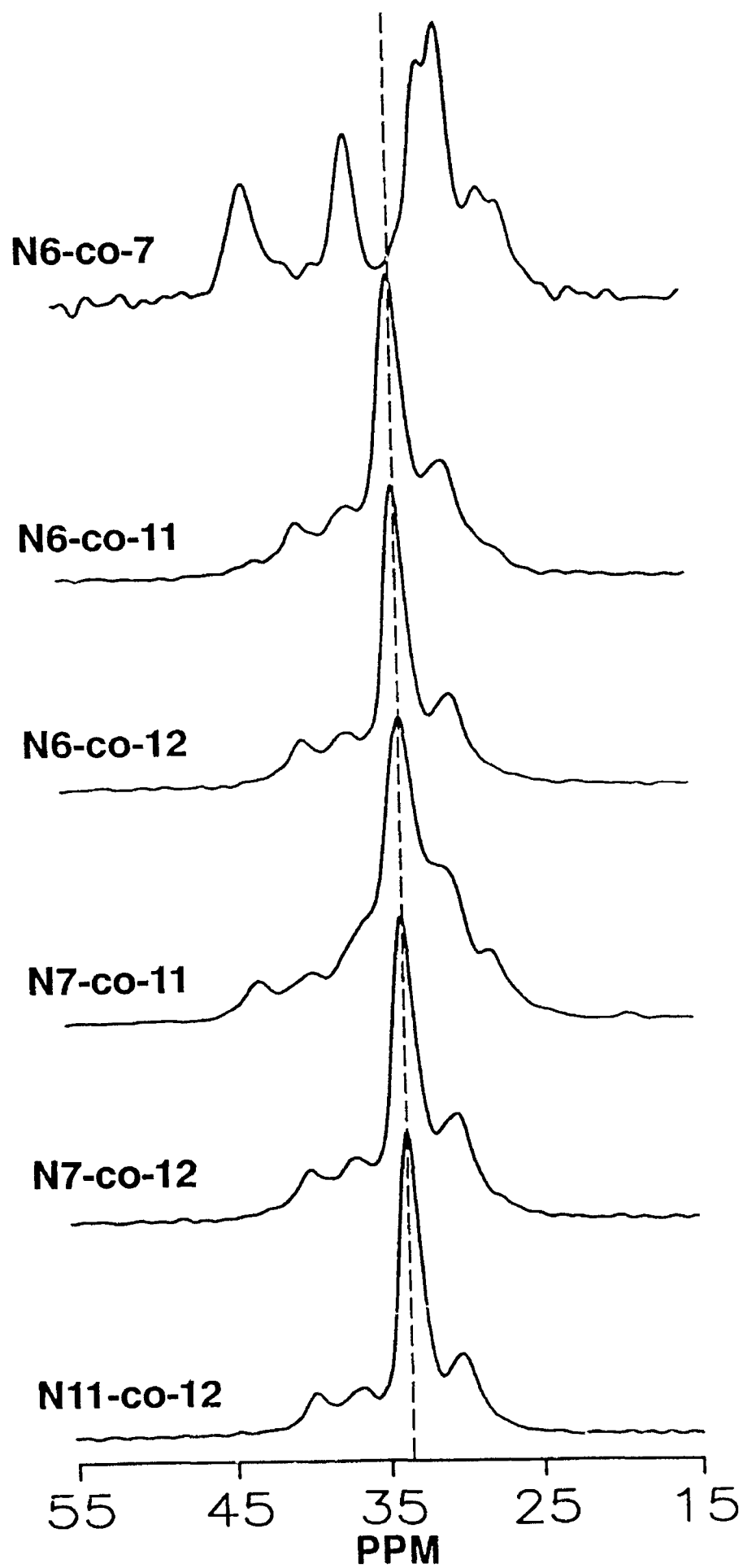
42 38 34 29 25

PPM

179 178 177 176 175

PPM

Figure 1



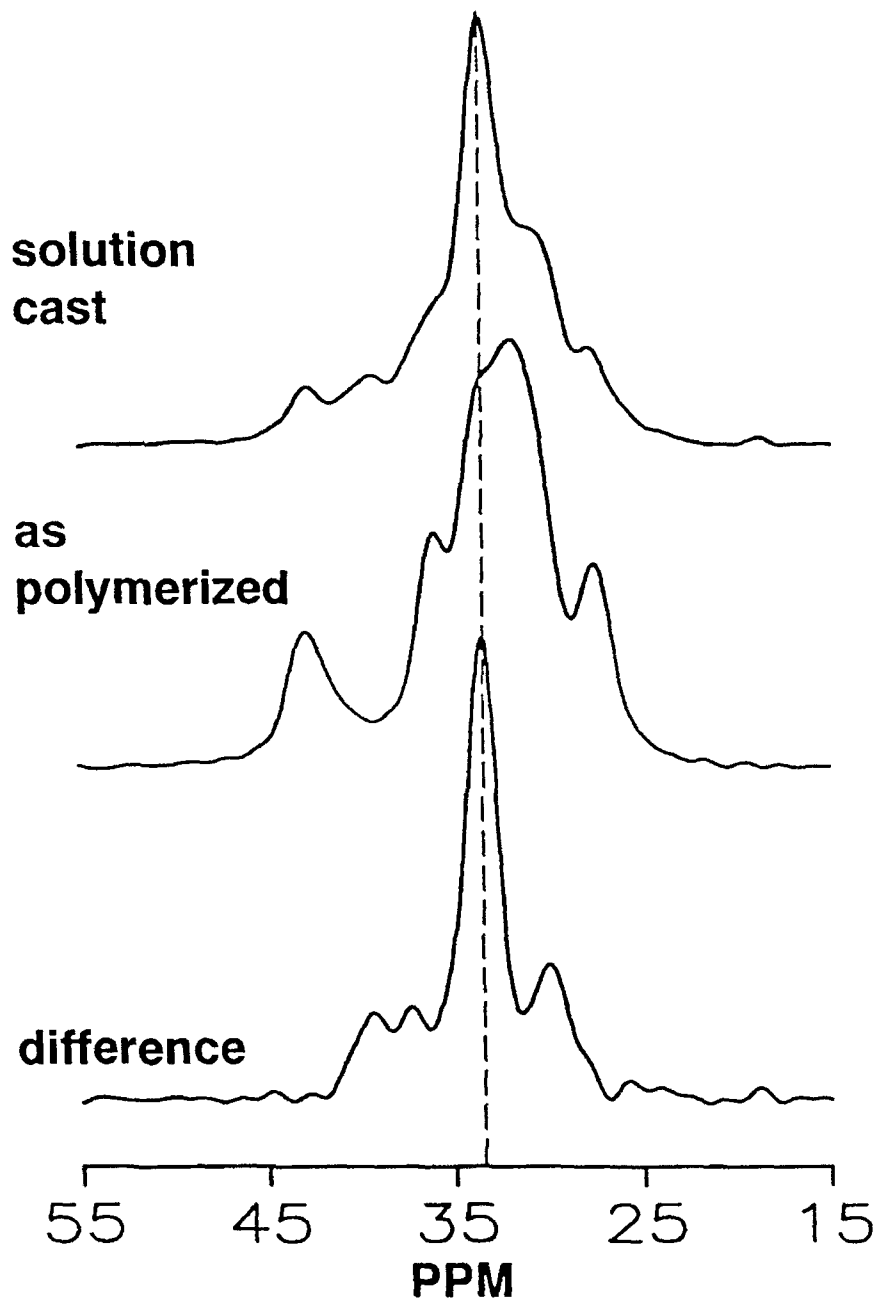


Figure 3

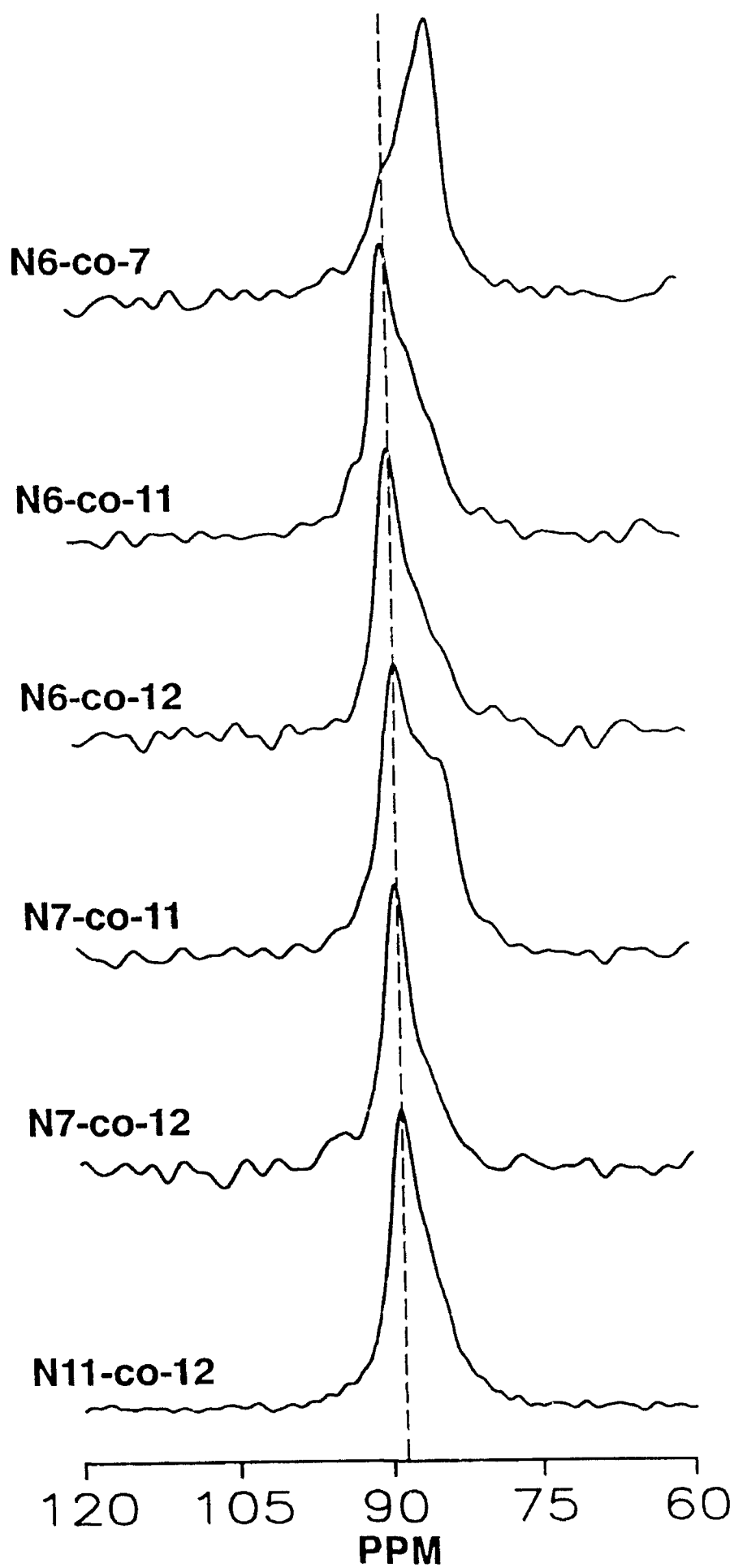
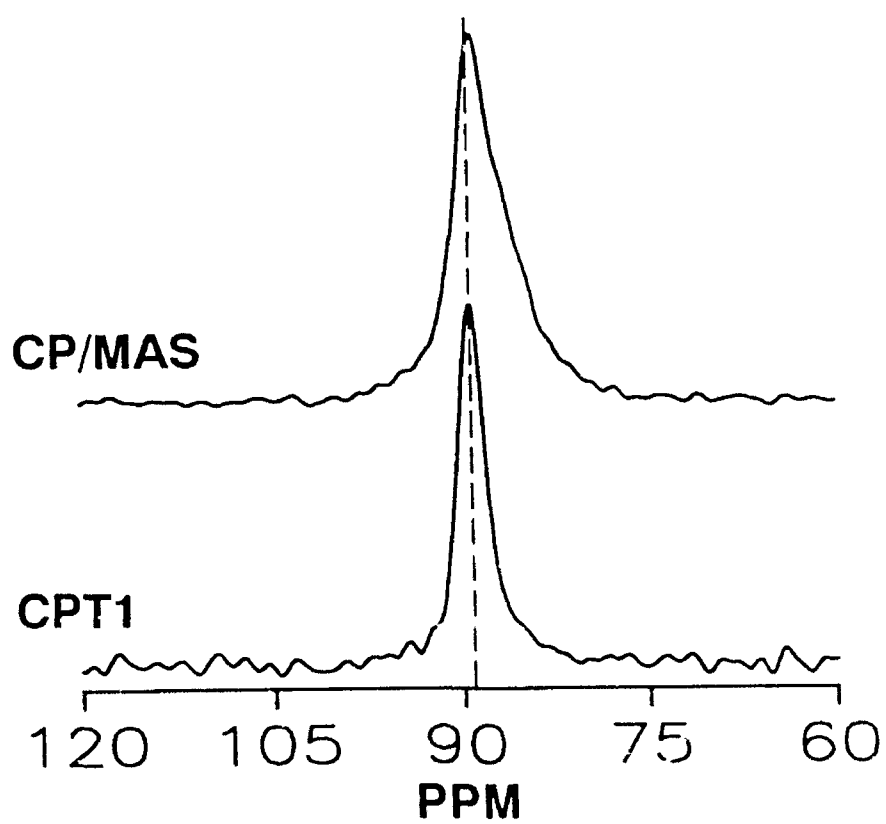
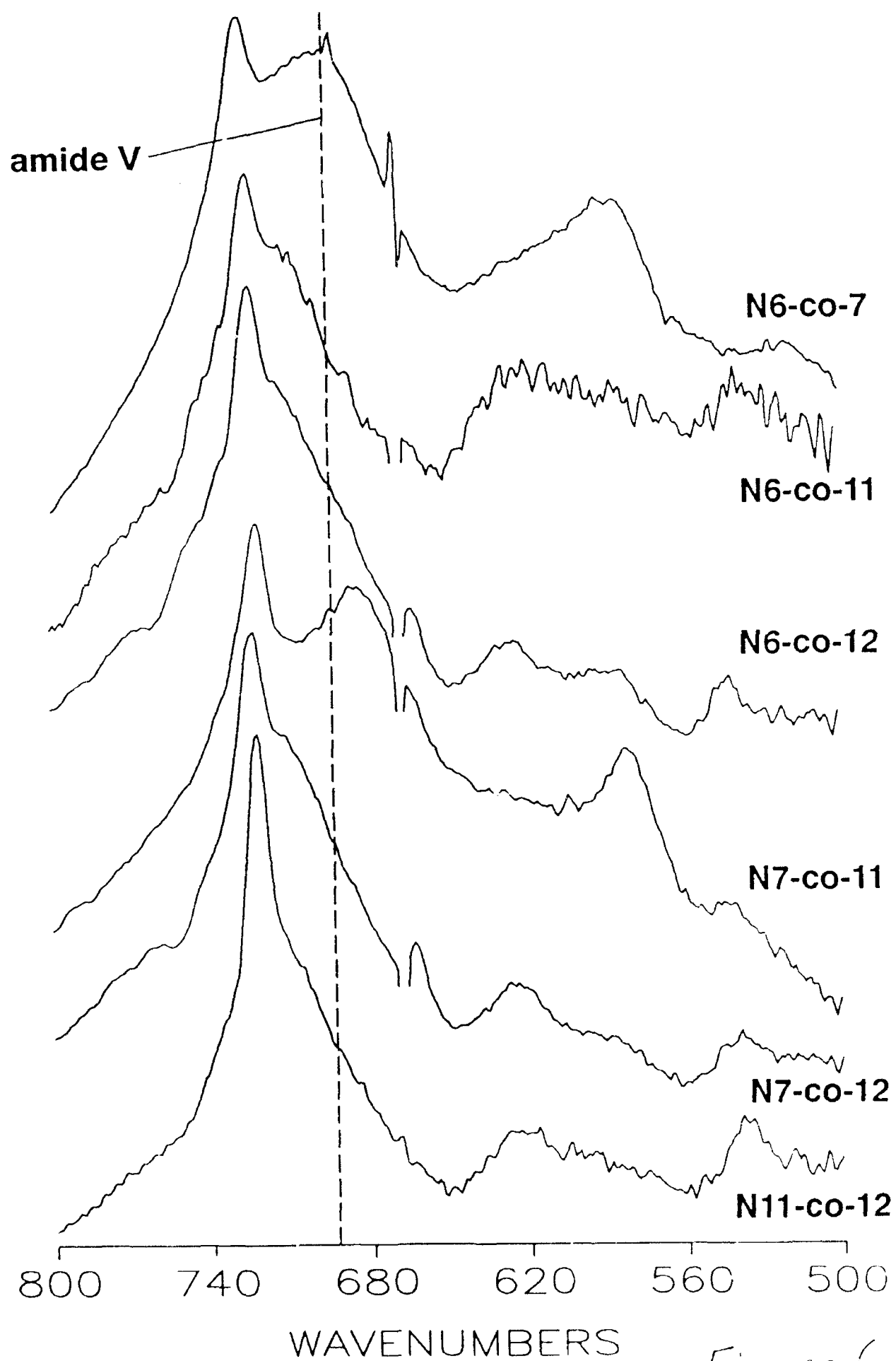


Figure 4

Figure 5





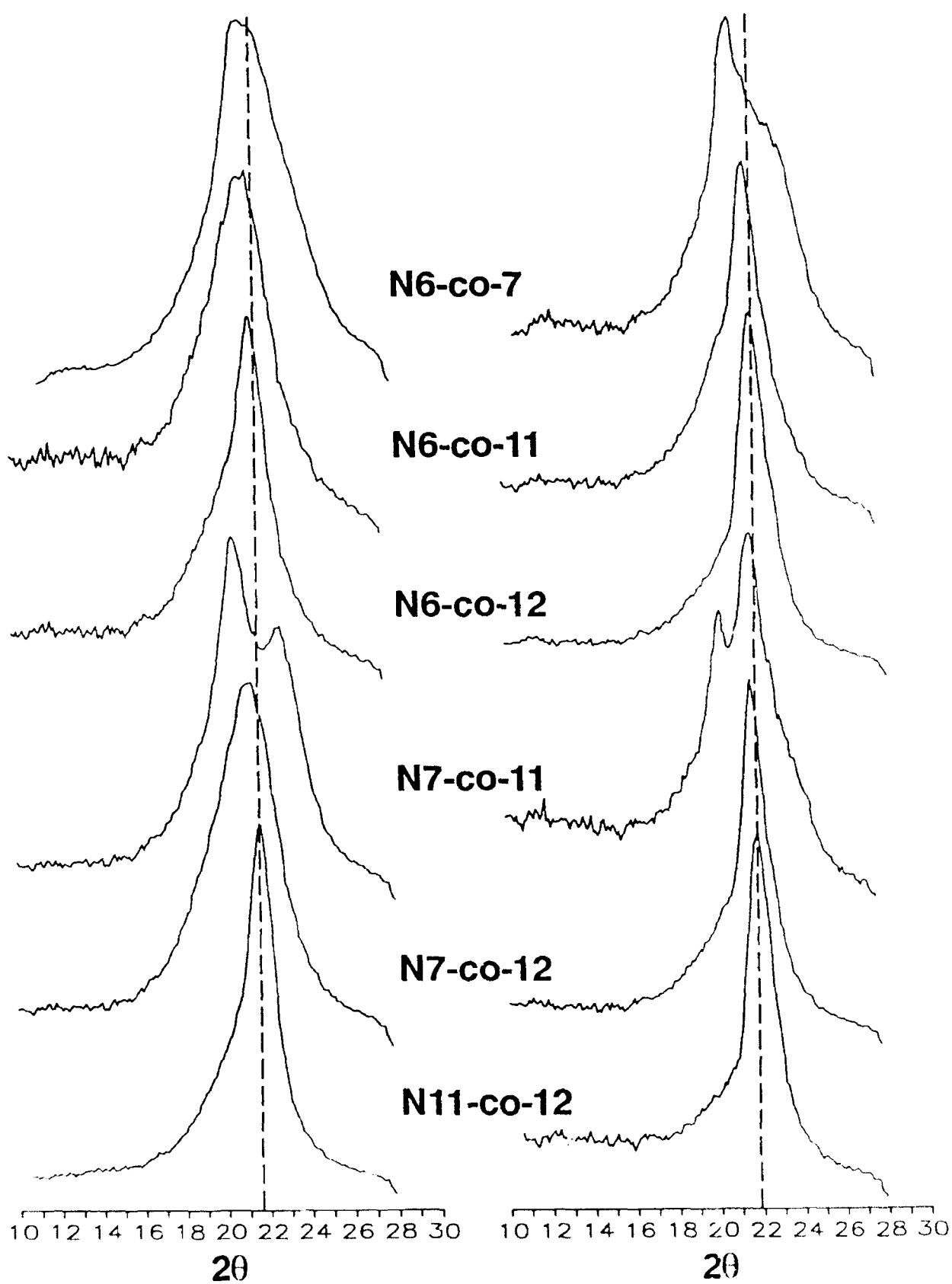


Figure 7