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

by

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13. ABSTRACT (Maximum 200 words)

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 ($\delta_{N15}$ ca 89) being the predominant ordered phase. Only nylon 6-co-7 formed almost exclusive α-form on solution casting ($\delta_{N15}$ 84.5). Nylon 7-co-11 formed the α-form almost exclusively from the melt but gave a combination of α- and γ-phases ($\delta_{N15}$ 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.

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# Characterization of 1:1 Random Co-Nylons Derived From 6-, 7-, 11-, and 12-Carbon Amino Acids

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## INTRODUCTION

Most AB homopolyamides are polymorphic indicating that they can exist in more than one crystalline phase, and suggesting that through chemical or thermal method,[1] the type of crystallinity can be changed. Nylon 6 forms the α-phase from solution or the melt, while treatment with aqueous potassium triiodide gives the γ-phase. Nylon 12 forms the γ-phase from the melt and the α-phase on casting from phenol/ethanol. Recently, nylon 7 was shown to form the γ-phase by casting from 2,2,2-trifluoroethanol/$CH_2Cl_2$ or by treatment similar to γ-nylon 6, although transformation into the γ-phase is not complete.[2]

Random nylon copolymers crystallize into phases similar to those of the homopolymers but are referred to as isomorphic phases.[1] Thermal analysis (DSC) gives a $T_m$ but underestimates the percent crystallinity. The crystalline phase formed from the mixture of repeat units has a ΔH different from the averages of the ΔH's for the two homopolymer crystalline phases. WAXS and density measurements give more reliable measures of crystallinity.

Of the methods mentioned above (X-ray, DSC, and density), only X-ray diffraction gives what type of crystalline phase is present, density and DSC do not. Although percent crystallinity can be obtained using solid-state NMR, it is time-consuming due to the very long $^{13}C$ spin-lattice relaxation times involved. However, other advantages are associated with solid state NMR. By taking advantage of the difference in spin-lattice relaxation times, the amorphous and crystalline phases can be independently observed. We describe here 1:1 random co-nylons focusing on the type of crystallinity developed using solid-state NMR and X-ray diffraction.

## EXPERIMENTAL

Amino acids and solvents were purchased from Aldrich Chemical Co. and used as received except for 12-aminododecanoic acid which was recrystallized from boiling water three time before use. DSC measurements were made using a Perkin-Elmer DSC-7 taken at 10 °C/min. Wide-angle X-ray diffraction measurements were made using a Seimens XPD-700P. Solution NMR measurements were made using a Bruker AC-300 operating at 75.5 MHz for $^{13}C$. Solid-state $^{13}C$ NMR measurements[3] were made using a Bruker MSL-400 operating at 100.6 MHz and $^{15}N$ measurements were made using a Bruker MSL-200 operating at 20.3 MHz. $^{13}C$ $T_1$ measurements were made using the method developed by Torchia.[4]

Typically, the copolymers were prepared from equal molar mixtures of the amino acids (about 2 g total) in a two-step heating process. The mixture was charged to a test-tube and placed under vacuum for 12 h, the tube back-flushed with dry nitrogen, and placed in a Wood's metal bath at 170 °C. The temperature was slowly increased (flowing $N_2$) until the mixture melted and held there until no more gas was evolved. The temperature was then brought to 220 °C and held there for 4 h. The cooled polymer plug was removed from the tube by crushing the tube carefully with a hammer. The polymers were obtained in greater than 97% yields. The polymers were dissolved in a mixture of 2,2,2-trifluoroethanol and methylene chloride (3:2 by volume) for NMR measurements and solution casting (10% w/v solution for NMR and 2% w/v for casting). The transparent films could be easily stretched except for nylon 11-co-12 copolymer which gave a [illegible]

## RESULTS AND DISCUSSION

The DSC data for the copolymers are shown in Table 1. It is clear that for most of the copolymers, the $T_m$ and ΔH values are higher for the solution cast samples than for the as-obtained materials. The nylon 11-co-12 as-obtained sample has a higher $T_m$ than for the solution cast sample, although the ΔH value is higher for the solution cast sample. The higher $T_m$ and ΔH values suggest that solution casting generates greater order and crystalline perfection.

**Table 1.** First-run thermal data for 1:1 random co-nylons[a]

| copolymer | $T_m$ (°C) | ΔH (J/g) |
|---|---|---|
| nylon 6-co-7 | 146 | 31 |
| | not collected | not collected |
| nylon 6-co-11 | 113 | 31 |
| | 136 | 33 |
| nylon 6-co-12 | 120 | 40 |
| | 131 | 56 |
| nylon 7-co-11 | 129 | 30 |
| | 141 | 50 |
| nylon 7-co-12 | 106 | 37 |
| | 134 | 54 |
| nylon 11-co-12 | 152 | 31 |
| | 146 | 75 |

[a] - first row per sample entry is for as-obtained material, second row is for solution cast material

The carbonyl region in solution $^{13}C$ NMR spectra of polyamides has been used to determine sequence information for many random and alternating copolyamides.[5] Based on these results, the carbonyl region indicates that the copolymers are random. Four peaks of nearly equal intensity appear in the spectra for the 6-co-11 and 6-co-12 polymers. If one of the peaks were more intense than the others, this would indicate a preference for alternation or block formation. Nylon 6-co-7 shows two equal intensity peaks suggesting that no blockiness is present, but no other sequence information is available due to the similarity of the repeat units.[6] Nylon 11-co-12 shows a single, symmetric peak in the carbonyl region, providing even less sequence information.[7]

The solution cast copolymers tend to crystallize into the γ-phase as indicated by the $^{13}C$ and $^{15}N$ NMR chemical shifts. The peaks for the carbons adjacent to the nitrogen ($C_N$) and beta to the carbonyl ($C_\beta$) appear near 39.8 and 30.3 ppm, respectively, for 6-co-11, 6-co-12, 7-co-12, and 11-co-12. This is consistent with the peak positions of γ-nylon 6[8] and γ-nylon 12.[9] However, nylons 6-co-7 and 7-co-11 show different behavior. The 6-co-7 polymer remains α-like when cast from solution with $C_N$ at 43 ppm and $C_\beta$ near 27 ppm. The 7-co-11 polymer forms both α- and γ-phases, with two peaks seen for $C_N$ (at 42.9 ppm and 39.4 ppm) consistent with the α- and γ-phases, respectively.

The solid-state $^{15}N$ CP/MAS NMR spectra of the solution cast samples of 6-co-11, 6-co-12, 7-co-11, and 7-co-12 are shown in Figure 1. The spectra for 6-co-11, 6-co-12, 7-co-12, and 11-co-12 (spectrum not shown) contain a sharp peak near 89 ppm, consistent with the γ-phase, and a broad peak centered near 87 ppm for the amorphous domains. The $^{15}N$ spectrum of the 7-co-11 polymer contains multiple resonances with a sharp peak at 88.7 ppm and a distinct shoulder near 84.5 ppm, consistent with γ- and α-phases, respectively. The spectrum for nylon 6-co-7 has a sharp peak at 84.5 overlapped by a broad amorphous peak [illegible] ppm. This sample contains only α-phase domains no matter what the sample history. Chemical shift values from $^{13}C$ CP/MAS and $^{15}N$ CP/MAS spectra for solution cast samples are shown in Table 2.

Table 2. CPT1 chemical shift data (ppm) for 1:1 random copolymers

| sample | CO | $C_N$ | $C_\alpha$ | $C_{\beta'}$ | $C_\beta$ | NH[a] |
|---|---|---|---|---|---|---|
| 6-co-7 | 173.5 | 43.0 | 36.3 | 30.3 | 28.0<br>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 α<br>39.4 γ | [b] | 33.5 | 27.9 | 84.5<br>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 |

a - data from CP/MAS experiments
b - peaks not cleanly separated

The $^{13}C$ spin-lattice relaxation times taken at 100.6 MHz for the 6 copolymers are shown in Table 3. The magnetization decays were fit to three components indicating the presence of a mobile amorphous phase with relaxation times of hundreds of milliseconds, a constrained amorphous or interphase region with relaxation times of several seconds, and a rigid phase relaxing on the order of tens of seconds. The $T_1$ value of the slow-relaxing component of these copolymers is similar to that of solution cast nylon 7 (eg. $C_N$ $T_1$ of 80 s) which formed well-ordered domains of γ- and α-crystallites.[2]

Table 3. Random copolymer $^{13}C$ spin-lattice relaxation data (in sec)

| sample | $C_N$ | $C_\alpha$ | $C_{\beta'}$ | $C_\beta$ |
|---|---|---|---|---|
| 6-co-7 | 0.7<br><br>15.5 | 1.0<br>9.8<br>24.4 | 0.6<br>4.6<br>32.0 | 0.4<br>2.2<br>21.2 |
| 6-co-11 | 0.3<br>3.5<br>34.9 | [illegible]<br>1.2<br>28.8 | 0.6<br>7.3<br>57.9 | 0.4<br>5.4<br>43.1 |
| 6-co-12 | 0.4<br>5.2<br>55.5 | 0.4<br>2.5<br>35.5 | 0.9<br>10.0<br>71.0 | 0.5<br>8.3<br>72.6 |
| 7-co-11[a] | 1.1<br>4.5<br>62.7 | 0.4<br>3.2<br>45.5 | 0.6<br>5.1<br>49.4 | 0.3<br>2.3<br>51.8 |
| 7-co-12 | 0.8<br>8.0<br>96.7 | 0.5<br>3.8<br>61.0 | 0.4<br>5.7<br>53.4 | 0.4<br>3.4<br>41.9 |
| 11-co-12 | 0.4<br>4.2<br>33.7 | 0.3<br>1.2<br>25.4 | 0.9<br>7.0<br>44.4 | 0.4<br>5.0<br>33.2 |

a - data for α-phase

The WAXS patterns are shown in Figure 2. Most of the scattering patterns for the as-obtained polymers contain peaks centered near 2θ=21.1 which are very broad, indicating low levels of order. Peak maxima in the patterns of the solution cast samples shift to 2θ=21.5 and the peaks narrow, consistent with solution casting resulting in higher order compared to the as-obtained samples. For example, the scattering patterns of the 11-co-12 samples were deconvoluted to give two peaks. The sharpest peak appeared at 2θ=21.4 and 21.6 for as-obtained and cast samples, respectively, with the latter 25% larger than the former.

Copolymers 6-co-7 and 7-co-11 are different from the others. Nylon 6-co-7 forms an α-phase in as-obtained and solution cast films, although the former is more defective than the latter based on the scattering patterns. Nylon 7-co-11 forms an α-phase as-obtained and both crystalline phases upon solution casting similar to what was seen for nylon 7.[2] The γ-phase dominates the scattering pattern of the solution cast sample (greater intensity of the peak at 2θ=21.5).

## ACKNOWLEDGEMENTS

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## REFERENCES

1. Puffr, R.; Kubanak, V. "Lactam Based Polyamides" CRC Press, Boca Rotan, FA, Vol. 1, 1992
2. Johnson, C. G.; Mathias, L. J. *Polymer*, accepted for publication
3. $^1H$ 90°-pulses were ca 4.5 μs, contact times were 1 ms, acquisition times were 50 ms, and recycle delays were 3 s for $^{13}C$ and $^{15}N$ experiments.
4. Torchia, D. A. *J. Magn. Reson.* 1978, *30*, 613
5. Kricheldorf, H. S.; Hull, W. E. *J. Polym. Sci. Part A* 1978, *16*, 2253
6. Cypcar, C. C.; Johnson, C. G.; Mathias, L. J. *American Chemical Society Polymer Preprints* 1993, *33(1)*, 501
7. Johnson, C. G.; Mathias, L. J. *J. Polym. Sci. Part A*, manuscript submitted.
8. Hatfield, G. R.; Glans, J. H.; Hammond, W. B. *Macromolecules* 1990, *23*, 1654.
9. Mathias, L. J.; Johnson, C. G. *Macromolecules* 1991, *24*, 6114

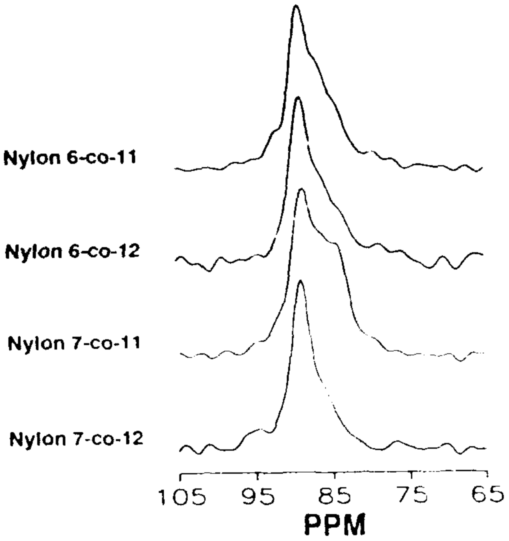

**Figure 1.** Solid-state $^{15}N$ CP/MAS NMR spectra of 1:1 random copolymers taken of solution cast films. Main peaks appear near 89 ppm, consistent with the γ-phase (α-phase is near 84 ppm).

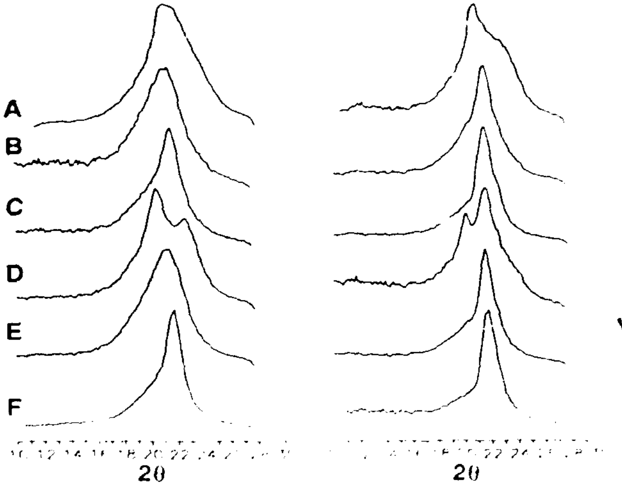

**Figure 2.** Wide-angle X-ray diffraction patterns for 1:1 random copolymers: A) nylon 6-co-7, B) nylon 6-co-11, C) nylon 6-co-12, D) nylon 7-co-11, E) nylon 7-co-12, and F) nylon 11-co-12. Left column is for as-obtained sample, while the right column is for solution cast films.

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