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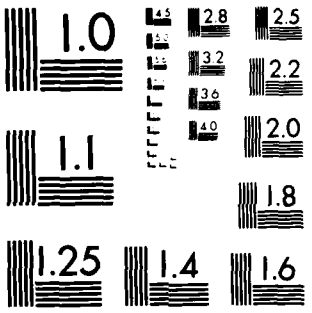

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Careful examination of the X-ray diffraction patterns from melt-crystallized Nylon 11 films showed significant discrepancies with the proposed α-form structure. These discrepancies did not disappear after annealing the samples. The temperature dependence of the d-spacings of the two strongest peaks showed further evidence that the melt-crystallized and solution cast films (α-form) possess different crystal structures. These results suggest a different crystal structure for the melt-crystallized films, and this would help explain the rather low piezoelectric response of these films and also the →

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failure to observe a rapid decrease in polarization at the transition temperature.

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Technical Report No. 5

TEMPERATURE DEPENDENCE OF THE CRYSTAL STRUCTURES OF NYLON 11

by

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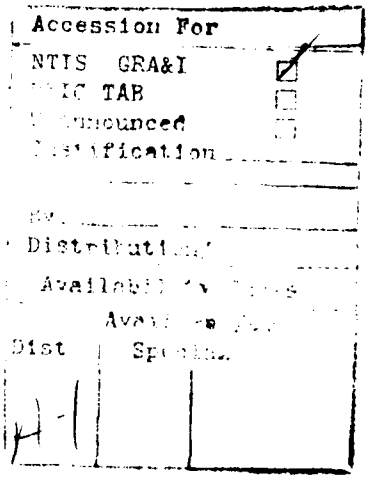

Introduction

In recent years, the piezoelectric and pyroelectric properties of Nylon 11 films have been the subject of considerable interest, but some difficulty has been encountered in understanding the relationship between the electrical properties and the structures of this polymer as reported by previous workers [1-4]. For this reason, a study of the crystal structures and crystal structure transitions in the odd Nylons, beginning with Nylon 11 has been undertaken.

In a general investigation of the structures of a series of polyamides, Kinoshita [5] concluded that fiber specimens of "series E" (which included Nylon 11) have the same crystal structures as "series A" (which included Nylon 66 and Nylon 610). The crystal structures of Nylon 66 and Nylon 610 had been determined earlier by Bunn and Garner [6]. The structure of Nylon 11 has been considered by several other workers [7-9], but since very few X-rayreflections are observed, no detailed structure analysis has been carried out. Using X-ray diffraction fiber diagrams, Slichter [10] showed that all the reflections of Nylon 11 could be indexed on the basis of a structure similar to the triclinic structure (α-form) proposed by Bunn and Garner for Nylon 66. Later, from observations of X-ray diffraction patterns of solvent cast films (trifluoroacetic acid) Sasaki [11] reported the existence of a γ-form of Nylon 11. Sasaki also reported that films cast using phenol-ethylene chlorodhydrin as a solvent showed the α-form and that well annealed melt crystallized films gave a diffraction pattern "similar" to the α-form.

More recently, Newman et al. [8], using a well annealed oriented fiber reported that they were unable to confirm Slichter's reported value for the c-parameter of the unit cell of the α-form. They proposed a modified structure of the α-form of Nylon 11 with a shortening of the c-parameter

obtained by twisting the planar zig-zag chain to achieve better packing of the hydrocarbon sequence. In addition, it was reported that melt-crystallized samples showed a transition to a pseudo-hexagonal lattice at 95°C, with this structure existing until melting occurred. In the α-form, hydrogen bonds are confined to a sheet and at any temperature, the thermal expansion perpendicular to the molecular chains in the plane of the sheet would be expected to differ from the thermal expansion perpendicular to the sheet. If it is assumed that the melt crystallized films are in the α-form proposed by Slichter, some rearrangement of the hydrogen bonding to give another structure in which the thermal expansion perpendicular to the chains is isotropic would be necessary to explain the observation that no splitting of the principal reflections of the high temperature pseudo-hexagonal phase occurs at temperatures up to the melting point. Finally, Kawaguchi et al. [12] reported three crystal modifications (α, β and γ) for Nylon 11 from a study of single crystals obtained by crystallization from different solvents.

The results obtained from studies of the piezelectric and pyroelectric properties of Nylon 11 were hard to understand in terms of these proposed structures. The structure proposed for the α-form is very polar and would be expected to give rise to large piezoelectric coefficients. Observations of melt crystallized films (which were presumed to be α-form) failed to confirm this [1,13-14]. Furthermore, polarization in Nylon 11 crystals is most likely associated with a reorientation of the large dipole moments of the amide group. Any significant rearrangement of the hydrogen bonds at the transition temperature ~100°C, should give rise to a rapid decrease in the piezoelectric and pyroelectric coefficients. In fact, the transition temperature might be expected to behave as a Curie point for this material. This was not observed in a stdy of the temperature dependence of the piezoelectric coefficient, d_{31},

by Scheinbeim [2].

In order to understand these electrical properties of Nylon 11 films, it was decided to examine more closely the structures of the melt-crystallized and solution cast films and the nature of the crystal transition.

Experimental

Materials

Nylon 11 was provided in powder form by Rilsan Co. in Glen Rock, N.J. The polymer was free of additives. Melt-crystallized films were made by cooling slowly (2.5°C/min) from the melt. Films were also crystallized into the α-form by casting from a 15% solution in meta-cresol at room temperature. Both the melt-crystallized and solvent cast films were found to be unoriented.

X-ray Diffraction

CuK_α radiation was used for the X-ray diffraction studies utilizing a Phillips XRG-3100 X-ray generator. High temperature data was obtained using a Phillips wide angle vertical diffractometer with the sample temperature controlled (± 0.3°C) using a resistance heater. Some data was obtained using a position sensitive detector (Tennelec PSD 1100), the sample temperature being controlled using a modified Mettler FP52 Hot Stage and a Mettler FP5 temperature controller. Flat film photographs were also used to obtain the d-spacings of weak reflections, using a CaF_2 powder as an internal standard to measure the sample to film distance.

Results

Figure 1 shows X-ray diffraction scans of the melt-crystallized film and the solvent cast film superimposed on the same figure. The general appearance of both scans is similar, consisting of three reflections which in the α-form

are indexed as (001), (100) and (010). All reflections from the solvent cast films are sharp and the general background scatter is less, which might be attributed to larger crystals and a greater degree of crystallinity. The d-spacings obtained, adding those weak reflections observed on film, are shown in Table 1. The d-spacings from the solvent cast films agreed closely with the d-spacings from the α-form, using the cell parameters given by Slichter [10]. The d-spacings obtained from the melt-crystallized film in general were similar, but differed significantly from those calculated from the α-form unit cell. These differences were significantly beyond those expected from experimental error and consistent for many different samples. The smaller angle d-spacing from the melt crystallized film (which in the α-form corresponds tothe (001) reflection) was larger: 11.95Å as opposed to 11.33Å. The d-spacing of the reflection which in the α-form indexed as (010) was 3.82Å instead of 3.72Å. The third strong reflection, in the α-form indexed as (100), had the same d-spacing (within experimental error) in both melt crystallized and solvent cast films. After annealing, the d-spacings of the melt-crystallized films did not approach those of the α-form and moreover the half-width of the reflections did not decrease significantly. The 11.95Å spacing increased to 12.50Å after annealing, that is, the discrepancy with the 11.33Å spacing increased rather than decreased.

These factors tended to confirm the supposition that the melt-crystallized film might not be the α-form. Further evidence that the melt-crystallized and solution cast films possess different crystal structures was obtained by measuring the temperature dependence of the d-spacings of the two strongest peaks. As shown in Fig. 2a, the intensity of the (010) reflection of the solution cast (α-form) film gradually decreases with increasing temperature and is no longer observed at temperatures above

~140°C. At the same time, the peak position gradually shifts to lower values of 2θ as temperature increases. The (100) reflection also decreases somewhat in intensity with increasing temperature, but is still observed at temperatures above 140°C. This peak position gradually shifts to higher values of 2θ with increasing temperature. However, the two peaks do not merge into a single peak at any temperature. In Fig. 2b the temperature dependence of the corresponding Bragg reflections of a melt crystallized sample is shown. While both peaks decrease somewhat in intensity with increasing temperature, the relative intensities remain approximately constant. In addition, they move towards each other and finally merge into the single peak characteristic of a pseudo-hexagonal structure at ~100°C. The difference in behavior between the solvent cast and melt crystallized films is also shown in Fig. 3, which plots the d-spacings from the two films as a function of temperature. To ensure that the peaks from the melt crystallized film merged, indicating the formation of a true pseudo-hexagonal structure as suggested in Fig. 3 (as opposed to slowly crossing each other above the transition temperature, which would arise from different lattice expansions in different directions), we also measured the combined half-width of the reflections from room temperature to ~170°C. The results of these measurements are presented in Fig. 4, which shows a rather rapidly decreasing half-width (increasing magnitude of the slope of $\Delta 2\theta$ vs. T) with increasing temperature up to 95°C. At this temperature, the magnitude of the slope of $\Delta 2\theta$ vs. T discontinuously decreases and then remains constant with increasing temperature.

Discussion and Conclusions

The origin of the observed temperature dependence of the crystal structures of the polyamides in general and thir relationship to hydrogen bonding has been studied by many workers. For Nylon 66, Brill [15] and Schmidt et al. [16] suggested that a transition from the triclinic cell with the hydrogen bonded sheet structure to a pseudo-hexagonal cell was associated with rotation about the chain axis and a dynamic three-dimensional network of hydrogen bonds. Slichter [17] and Starkweather [18] reported that the α-structure of Nylon 66 and Nylon 610 transformed to a triclinic (pseudo-hexagonal) form at high temperature. On the basis of N.M.R. studies Olf et al. [19] suggested the possibility that hydrogen bonds were free to rotate by 60° increments to break up the α-form sheet structure above the transition temperature. Finally, Itoh [20] reported that the hydrogen bonded sheets of Nylon 66 and 610 were maintained at temperatures up to the melting temperature and excluded even the existence of a high temperature hexagonal phase. He attributed the coincidence of the d-spacings of the two principal reflections from these polymers at elevated temperatures to anisotropic thermal expansion. By careful measurements of the d-spacings using doubly oriented samples, he reported that at temperatures close to the melting point the two reflections merged and separated again.

For Nylon 11, on the basis of our results we propose that the melt-crystallized films do not have the α-form structure despite the general similarity of their diffraction patterns to the solution cast α-form diffraction patterns. The solvent cast α-form Nylon 11 films do not show the transition observed in the melt-crystallized films. The existence of a crystal structure in the melt-crystallized films different from the α-form but with a similar diffraction pattern at room temperature might explain some of

the apparently contradictory results obtained by various workers for other polyamides [16-18,20]. This can be illlustrated by comparing the results obtained by Starkweather et al. [18] and Itoh [20] for Nylon 66.

Starkweather using a sample obtained by slow-cooling from the melt observes a reversible transition at 175-180°C. The diffraction peak associated with the high temperature pseudo-hexagonal form sharpened and increased in intensity with increasing temperature up to 250°C. The peak remained sharp up to the melting point (272°C). This was similar to the behavior observed for melt crystallized Nylon 11. On the other hand, Itoh using a doubly oriented sample obtained by cooling quickly from the melt followed by drawing, pressing and then annealing at 230°C observed that the d-spacings of the two principal reflections associated with the triclinic structure approached each other coincidently at 200°C and separated again at high temperatures before melting. Although a doubly oriented sample was not used by Starkweather (or in the present work on Nylon 11) the sharpening of the reflection associated with the pseudo-hexagonal phase at temperatures above the transition temperatures would appear to exclude the possibility of this behavior for these films.

Finally, it should be noted that for the case of melt crystallized films of Nylon 11, the observed X-ray diffraction peaks may indicate a hydrocarbon subcell associated with the paraffinic sections of the polymer, and not from the proposed sheet structure as is commonly assumed. At nigh temperatures, the single strong and sharp X-ray reflection characteristic of the pseudo-hexagonal phase may simply be associated with a rotator phase of the paraffinic sections.

The existence of a crystal structure in the melt-crystallized films which is different from the highly polar α-structure would also help explain the rather low piezoelectric response of these films and the failure to observe a rapid decrease in polarization at the transition temperature. Further studies are underway to determine the actual crystal structure of the melt-crystallized material and to generalize our investigations to other polyamides.

Acknowledgements

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Figure Captions

Figure 1 Superimposed X-ray Diffraction Scans of Nylon 11 at Room Temperature.

Figure 2 The Temperature Dependence of X-ray Diffraction Peaks of Nylon 11 (a) m-Cresol cast (α-form), (b) Melt Crystallized.

Figure 3 The Temperature Dependence of Interplanar Spacings of Nylon 11.

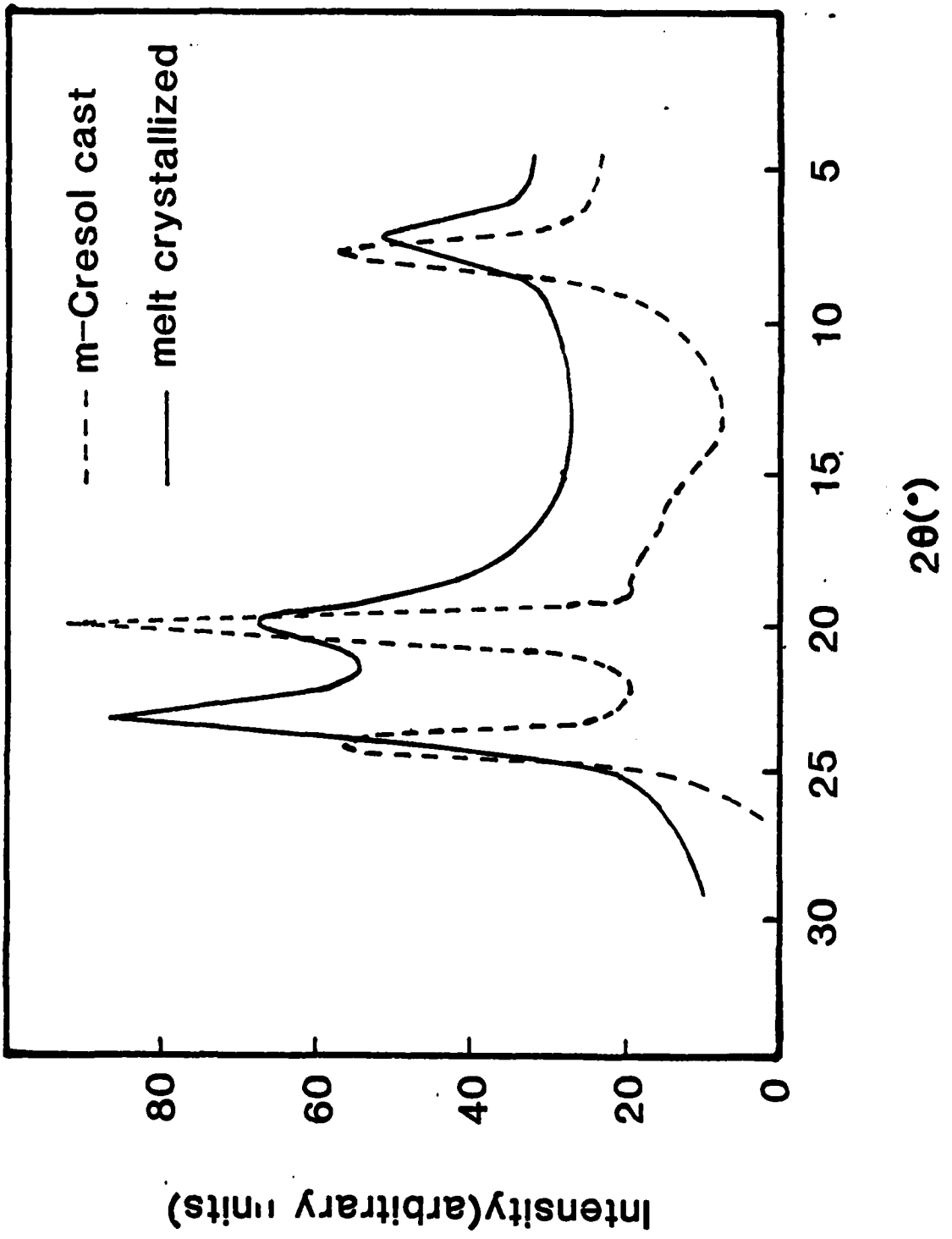
Figure 4 The Temperature Dependence of X-ray Diffraction Line Width of Melt Crystallized Nylon 11.

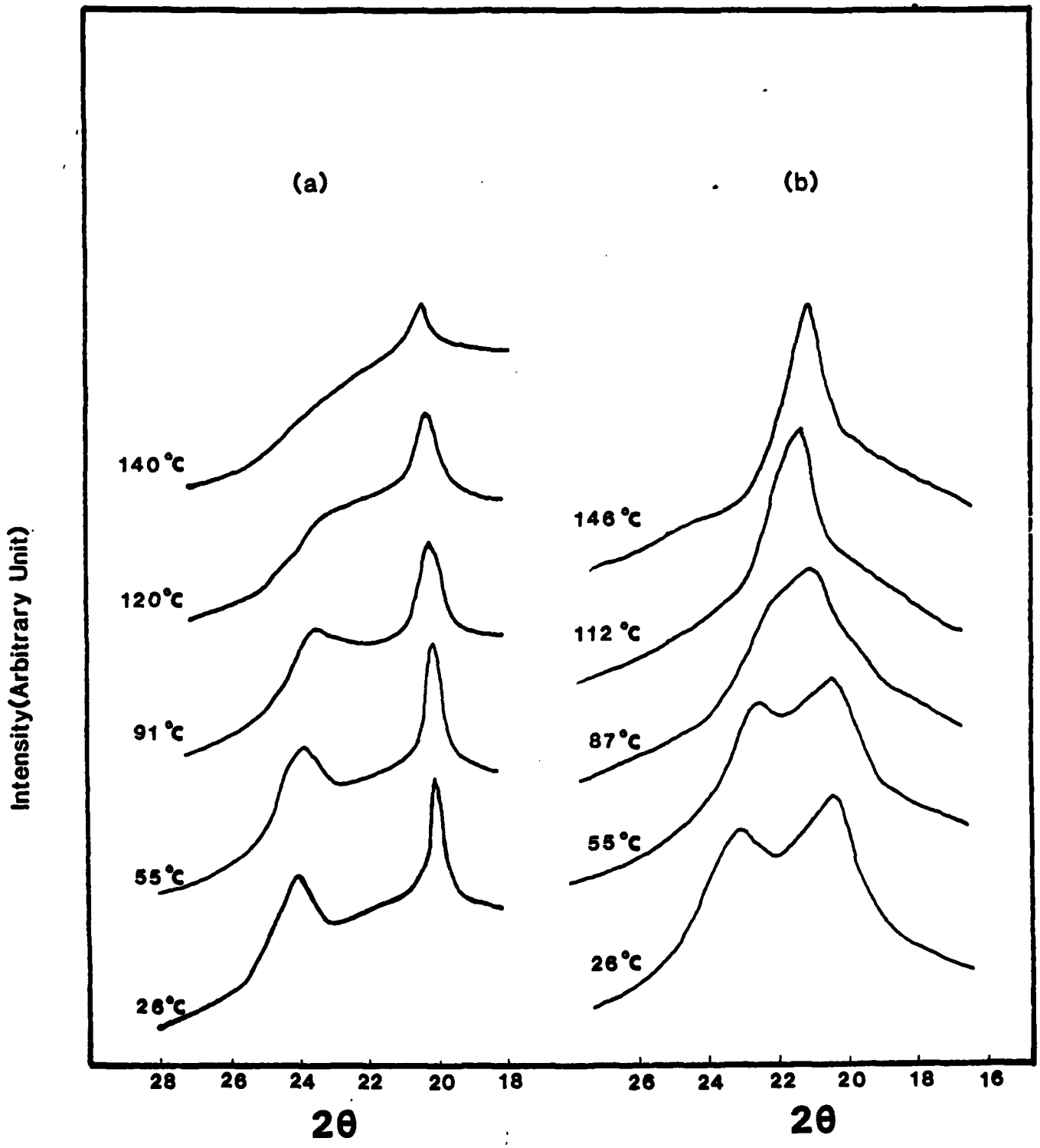
Table Caption

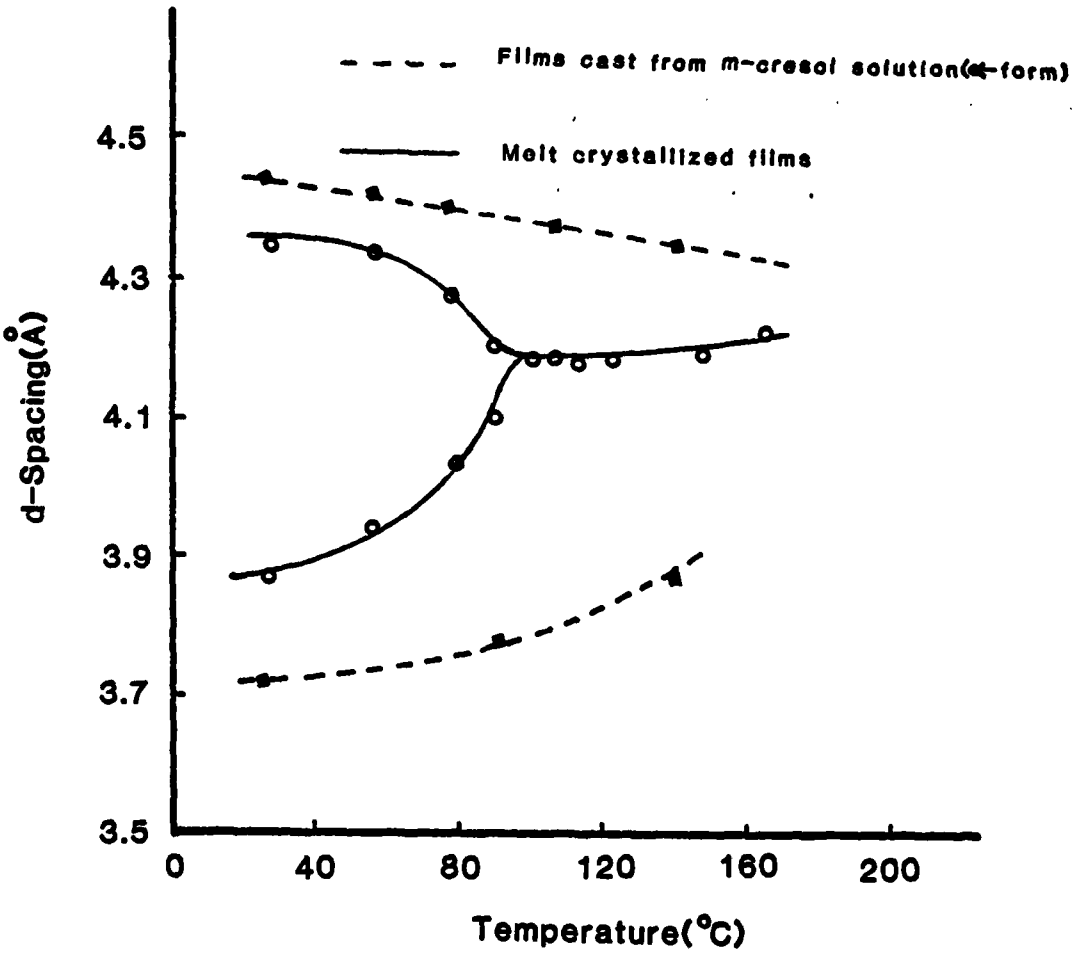
Table 1 Interplanar Spacings from Nylon 11 Melt-Crystallized and Solvent-Cast Films.

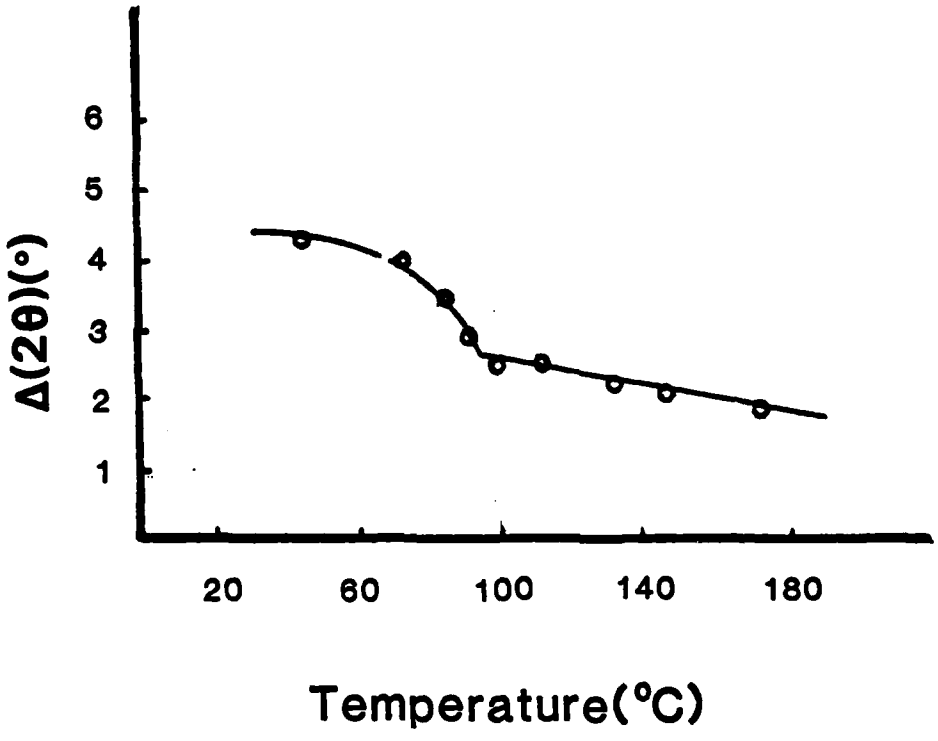
TABLE 1

Films Cast from m-cresol solution (α-form)			Melt Crystallized Films
d_{cale}	d_{obs}(Å)	(hkℓ)	d_{obs}(Å)
11.2	11.33	(001)	11.95
5.60	5.54	(002)	
4.34	4.44	(100)	4.40
3.68	3.72	(010)	
3.71		(110)	2.40
			2.20


m-Cresol cast
melt crystallized
Intensity(arbitrary units)
0
20
40
60
80
5
10
15
20
25
30
2θ(°)


(a)
(b)
140°C
120°C
91°C
55°C
26°C
146°C
112°C
87°C
55°C
26°C
Intensity(Arbitrary Unit)
28 26 24 22 20 18
26 24 22 20 18 16
2θ
2θ


Films cast from m-cresol solution(α-form)
Melt crystallized films
d-Spacing(Å)
4.5
4.3
4.1
3.9
3.7
3.5
0
40
80
120
160
200
Temperature(°C)


Δ(2θ)(°)
6
5
4
3
2
1
20
60
100
140
180
Temperature(°C)