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Production of Polymers from the Seed Oil of Crambe Abyssinica. IV. Polyamides Based on Tridecanedioic (Brassylic) Acid

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ABSTRACT

Brassylic acid from crambe oil was used to synthesize 613 and 1013 polyamides by conventional melt polycondensation. The physical properties were compared to those of a commercial nylon 612: the polymers were melt-spun to monofilaments whose mechanical properties and moisture isotherms were found. Wide-angle x-ray diffraction patterns were determined, and a preliminary attribution of crystal structure made.

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INTRODUCTION

Although nylon 66 and nylon 6 remain the polyamides of major commercial importance both as thermoplastics and fibers, a number of other nylons are of considerable commercial status. These generally retain the desirable attributes such as the ability to cold-draw to filaments of high tensile strength, good flow properties, relatively high melting temperatures and relatively good chemical resistance. Among these polyamides are some in which the amide chain repeat units are separated by longer aliphatic sequences as, for example, nylons 11 and 612. The availability of brassylic acid of high purity prompted us to examine this C13 diacid as a polyamide monomer. Wolff and co-workers have briefly reported some of the physical and mechanical properties of nylons 1313 [1], 13 [2], and 613 [3]. We have prepared samples of 613 and 1013 polyamides and have compared them with a commercial sample of nylon 612.

EXPERIMENTAL RESULTS

Preparation of Polyamides

Brassylic acid was prepared as before [4] and other materials were used as received. The preliminary stage of the polyamidation process is to form the diammonium salt. Thus brassylic acid (49 g, 0.200 mole) and hexane-1,6-diamine (237 g, 0.204 mole) as 10% solutions in ethanol were mixed and heated to reflux briefly with vigorous stirring and then allowed to cool and to stand overnight. The precipitated 613 salt was filtered, washed with cold ethanol, and dried at room temperature to constant weight to give a 93% yield. The salt was further purified by recrystallization from ethanol containing 3-4% water to give a product melting at 179° C (by differential scanning calorimetry). The 1013 nylon salt was prepared similarly and in rather better yield; after recrystallization from water the salt had a melting temperature of 168° C (DSC).

Polycondensation was carried out in two stages. A 30-40 g portion of the nylon salt was charged into a cylindrical reaction tube as shown in Fig. 1a. A constriction was then made in the upper part of the long neck and this tube then connected via a three-way stopcock to a vacuum line and to low pressure (approx. 5 psi) nitrogen. The contents were outgassed for 5-10 min and then filled with nitrogen; after five or six such cycles the tube constriction was sealed with the tube under vacuum. A wire mesh was placed over the wider part of the reaction

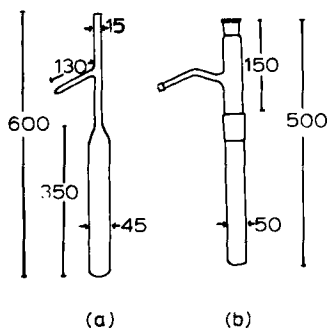


FIG. 1. Polyamidation reaction tube: (a) first stage; (b) second stage. Dimensions in mm.

tube and this then put in a vapor bath for 1-1.5 hr, the whole apparatus being positioned behind safety screens. A reaction temperature of 190°C (decahydronaphthalene vapor bath) was used for nylon 1013 and 222°C (methyl salicylate) for nylon 613.

Some of the liberated water condensed in the sealed side arm which was outside the heating bath and served as a convenient monitor of the course of reaction. After completion of the first-stage heating cycle, the sealed tube was allowed to cool to room temperature, removed from the heating bath, and cautiously opened. After smashing the glass tube the brittle, low molecular weight, polymer was transferred to a second tube (Fig. 1b). The side arm was connected through a condenser and trap to a vacuum pump. An inlet for nitrogen comprising a glass capillary tubing drawn out to a fine tip was fitted through the joint at the top so as to reach to the bottom of the reaction tube. After purging the air by alternately evacuating and flushing with nitrogen the contents were heated in a vapor bath at 222°C (nylon 1013, methyl salicylate bath) or 245°C (nylon 613, digol bath). The pressure was gradually reduced to a vacuum of 0.1-0.2 Torr during a heating period of about 1.75 hr, after which the gentle stream of nitrogen was continued as the polymer cooled. When cold, the hard polymer was smashed into small fragments. If the second stage of polymerization is allowed to continue for too long, the melt turned to a straw-yellow color, indicating some degree of degradation; such preparations were discarded.

A sample of Zytel 612 polyamide, kindly provided by Du Pont (UK) Ltd., was used as a comparison material.

Characterization

Polymer melting points were measured after annealing at 160-170° C in vacuo for 24 hr both by differential scanning calorimetry and optically. For the former, a 20-mg sample was encapsulated and heated at 16° C/min under nitrogen. The melting endotherm showed two peaks, and the maximum of the higher temperature peak was taken as the melting point. The optical melting point was measured on a Kofler hot stage fitted to a polarizing microscope and was taken as the temperature at which the last traces of birefringence disappeared. The apparent glass transition temperature was found to $\pm 2^\circ$ C by DTA examination (Du Pont 900) at 20° C/min; as T_g is more readily detected at higher amorphous contents, the samples were first melted and the melt quenched in liquid nitrogen prior to testing. Viscosities of solutions of the polymers in freshly distilled m-cresol were measured in suspended-level dilution viscometers. Number-average molecular weights were estimated by measurement of the amine and carboxylic acid end groups by use of a method [5] based on that first described by Waltz and Taylor [6]. Densities were measured on melt-spun fibers (see below) in a density-gradient column filled with carbon tetrachloride and toluene. These physical properties are recorded in Table 1.

Preparation of Fibers

Melt-spun fibers were produced by a small rod-spinning machine. About 30-35 g of polyamide was dried in vacuo at 60-70° C for 24 hr. Such careful drying was found necessary to remove the moisture which otherwise would lead to hydrolytic chain scission under spinning conditions. The dried polymer was packed into the barrel which was fitted with a melt block, a filter, and a spinneret carrying a single central hole of 0.5 mm diameter. A piston was placed over the polymer which was then heated to its softening point and compressed hydraulically for 15 min to displace air as the pieces of polyamide fused to a rod. The piston was removed, and a tightly-fitting PTFE plug inserted. After replacing the piston, the barrel temperature was raised to the spinning temperature (220° C for polyamide 1013, 230° C for 613 and 240° C for 612). The hydraulic pump was switched off as soon as molten polymer appeared through the spinneret hole and the metering pump switched to give a steady throughput of fiber. The filament was wound onto a constant-speed, surface-driven, bobbin; the take-up speed was kept as low as possible to minimize the

TABLE 1. Physical Properties of Polyamides

| Property | Nylon 613 | Nylon 1013 | Nylon 612 ^a |
|---|--------------|---------------|---------------------------|
| \bar{M}_n (end group) | 20700 | 15000 | — |
| $[\eta]$ (dl/g) ^b | 1.17 (1.12) | 0.83 | 1.05 (1.07) |
| T_m (°C) | | | |
| DSC | 205 | 187 | — |
| Optical | 207-208 | 188-189 | 219 |
| T_g (DTA) (°C) | 45-49 | 42-44 | 50 |
| Density (g/cm ³) ^c | | | |
| Unannealed | 1.047 | 1.016 | 1.062 |
| Annealed ^d | 1.062 | 1.032 | 1.082 |

^aCommercial sample Zytel 6-12 (Du Pont).

^bValue in parentheses refer to melt-spun fibers.

^cDrawn fibers.

^dAnnealed 4 hr in vacuo at ($T_m - 20$)°C.

drawing of the fiber. The natural draw ratios of the melt-spun fibers were found by extending them on an Instron tensile testing instrument.

The fibers from the melt-spinner were drawn on a laboratory drawing machine in which the desired draw ratio is set by the relative size and speed of the feed and draw rolls. Although the machine was set close to the natural draw ratio, the denier of the drawn fibers produced were not exactly as expected from calculation. This effect, which was more pronounced with 613 and 612 polyamides of high initial denier, may be caused by fiber slippage or by fiber recovery. These polymers were, therefore, hot-drawn at 80-82°C, and this procedure facilitated the drawing process and reduced the draw tension; the data in Table 2 refer to such hot-drawn samples.

Mechanical Properties of Fibers

The tensile properties of the monofilaments were found by extending 50 mm samples at 25 mm/min on an Instron tester; ten specimens of each fiber were tested, and the results are quoted to the

TABLE 2. Mechanical Properties of Melt-Spun Monofilaments

| Polyamide | Initial denier | Young's modulus (g/den) | Yield stress (g/den) | Yield strain (%) | Tenacity at break (g/den) | | | Elongation at break (%) |
|---|----------------|-------------------------|----------------------|------------------|---------------------------|--------------|--------------|-------------------------|
| | | | | | Initial denier | Final denier | Final denier | |
| Undrawn fibers | | | | | | | | |
| 612 | 154 | 8.4 ± 0.7 | 0.30 ± 0.01 | 8.3 ± 1.2 | 1.0 ± 0.1 | 6.1 ± 0.8 | 513 ± 53 | |
| 613 | 353 | 14.7 ± 2.2 | 0.50 ± 0.04 | 10.8 ± 1.7 | 0.7 ± 0.1 | 4.0 ± 0.8 | 450 ± 40 | |
| 1013 | 18 | 18.7 ± 5.0 | 0.40 ± 0.06 | 3.8 ± 0.3 | 1.0 ± 0.2 | 4.0 ± 0.8 | 311 ± 26 | |
| Drawn fibers (relaxed overnight) | | | | | | | | |
| 612 | 42 | 36.4 ± 0.9 | 3.0 ± 0.04 | 10.9 ± 0.3 | 4.4 ± 0.2 | 6.5 ± 0.4 | 48 ± 6 | |
| 613 | 83 | 30.9 ± 0.9 | 3.6 ± 0.04 | 13.4 ± 0.3 | 4.0 ± 0.1 | 5.0 ± 0.2 | 26 ± 2 | |
| 1013 | 5.0 | 31.7 ± 3.1 | 2.8 ± 0.05 | 9.4 ± 0.7 | 3.3 ± 0.4 | 4.6 ± 0.8 | 38 ± 15 | |
| 66 | — | 40-60 | — | — | 4.6 ± 5.8 | — | 26-32 | |
| Drawn and annealed fibers | | | | | | | | |
| 612 | 37 | 38.9 ± 1.8 | 3.9 ± 0.1 | 16.0 ± 0.6 | 4.8 ± 0.2 | 6.7 ± 0.4 | 39 ± 5 | |
| 613 | 81 | 36.4 ± 0.9 | 3.5 ± 0.1 | 11.5 ± 0.2 | 4.1 ± 0.1 | 5.1 ± 0.1 | 24 ± 1 | |

95% confidence limit. The values for Young's modulus, tenacity at break, and yield stress are given in the traditional textile units of grams/denier. In order to obtain an accurate estimate of the Young's modulus from the initial slope of the stress-strain curve the recorder chart was run eight times as fast as the Instron crosshead. Table 2 summarizes the data for undrawn and drawn filaments and also for drawn fibers which had been annealed at $(T_m - 30)^\circ\text{C}$ for 20 hr. For comparison some literature values [7] for nylon 66 textile grade fiber are also listed.

Moisture Regain

Some of the more important characteristics of polyamides, especially in fiber form, are closely related to their behavior in varying atmospheric conditions, and many properties are affected by the amount of moisture absorbed by the polymer. The moisture regain, defined as the mass of water absorbed at equilibrium by unit mass of dry polymer, but expressed as a percentage, was found as follows. Fibers which had been drawn to their natural draw ratio were dried at 105°C in vacuo for 24 hr; weighed samples were then placed in sealed desiccators containing various salt solutions known to provide a range of relative humidities [8] and reweighed at approximately 12 hr intervals until equilibrium was attained (usually about 36 hr). The dependence of the regain on relative humidity is shown in Fig. 2, which also shows literature [9] data for nylon 66.

X-Ray Diffraction

Wide-angle x-ray examinations were made of drawn fibers which had been annealed under tension for 4 hr at the specified temperatures. Nickel-filtered radiation from a copper target ($\text{CuK}\alpha$) was incident normal to the fiber axis. The fiber-plate distance was approximately 60 mm; an accurate estimate was found by dusting the surface of the fiber sample with finely ground sodium chloride and calculating from the Debye-Scherrer rings superimposed on the fiber diagram. The interplanar spacings corresponding to the observed equatorial and meridional reflectors were calculated from Bragg's equation and are given as Table 3.

Because of the strong equatorial reflections with d spacings of the magnitude expected for parallel extended chain molecules of this type [10] it may be assumed that the chain axes (c axis) are perpendicular to the equatorial plane of the x-ray diagram and that this plane contains

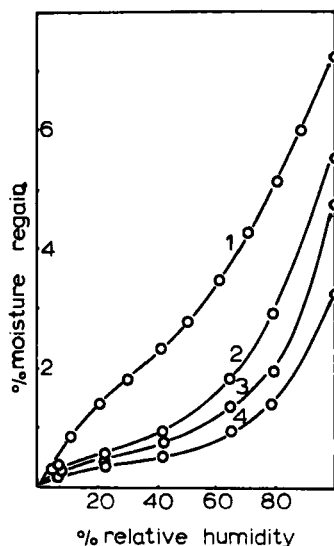


FIG. 2. Moisture regain of polyamide fibers at various relative humidities: (1) nylon 66; (2) nylon 612; (3) nylon 613; (4) nylon 1013.

the parallelogram set of (hko) reflections. The c axis length is calculated from the layer line reflections. Construction of the cell base projected on to the plane normal to the c axis is made from the location of the equatorial reflections, taking into consideration the indexing found in previous examination of polyamides [11, 12].

Unit cell dimensions given in Table 4 are of c , the axis in the fiber direction, and a' , b' the projected unit cell base dimensions, and γ' , the supplement of the angle between them; calculation of the density of fully crystalline polymer is made from the unit cell volume. Estimates of the amorphous densities were made by using values for the group contribution of molar volume [13] and the percentage crystallinity found by incorporating the measured density of fibers annealed at 200°C in the unrelaxed state.

DISCUSSION

Brassylic acid forms diammonium salts with the selected diamides, and polycondensation to polyamides of typical molecular weights is normal.

TABLE 3. Interplanar (d) Spacings of Polyamides

| Polyamide | Reflections | d spacing (nm) | | | | Index |
|------------|-------------|-----------------|---------|--------|--------|-------|
| | | Annealed 150° C | 170° C | 180° C | 200° C | |
| Nylon 613 | Equatorial | | 0.436 | | 0.435 | (010) |
| | | | 0.379 | | 0.396 | (100) |
| | | | 0.241 | | 0.243 | (110) |
| | Meridional | | 2.365 | | 2.124 | (001) |
| | | | 1.228 | | 1.296 | (002) |
| | | | — | | 1.048 | |
| | | 0.819 | | 0.834 | (003) | |
| | | — | | 0.690 | | |
| | | 0.506 | | 0.514 | | |
| | | | | 0.421 | | |
| Nylon 1013 | Equatorial | | | | | (010) |
| | | | 0.417 | | 0.426 | (100) |
| | | | (0.417) | | 0.391 | (110) |
| | Meridional | | 0.240 | | 0.239 | (002) |
| | | | 1.474 | | 1.586 | (004) |
| | | | 0.750 | | 0.767 | (006) |
| | | 0.504 | | 0.512 | | |
| Nylon 612 | Equatorial | | | | | (010) |
| | | | | | 0.443 | (100) |
| | | | | | 0.376 | (110) |
| | Meridional | | | | 0.238 | (001) |
| | | | | | 2.268 | (002) |
| | | | | | 1.163 | (003) |
| | | | 0.795 | (007) | | |
| | | | 0.341 | | | |

TABLE 4. X-Ray Crystallographic Data and Derived Properties

| Polymer | Annealing temperature (°C) | Crystal habit | a' (nm) | b' (nm) | c (nm) | γ' | V (nm ³) ^a | Density (g/cm ³) | | Crystallinity X (%) |
|---------|----------------------------|---------------------------|---------|---------|--------|-----------|-----------------------------------|------------------------------|--------------------|---------------------|
| | | | | | | | | ρ_c | ρ_a | |
| 612 | 200 | Triclinic | 0.424 | 0.500 | 2.384 | 117.5° | 0.448 | 1.150 ₇ | 1.023 ₃ | 49 |
| 613 | 170 | { Monoclinic Triclinic | 0.416 | 0.479 | 2.455 | 114.3° | — | — | — | — |
| 1013 | 200 | Monoclinic | 0.446 | 0.489 | 2.502 | 117.3° | 0.485 | 1.111 ₄ | 1.016 ₅ | 50 |
| | 150 | Hexagonal | 0.482 | 0.482 | 2.926 | 120.0° | | | | |
| | 180 | Monoclinic | 0.447 | 0.480 | 3.060 | 117.3° | 0.575 | 1.095 ₀ | 0.994 ₆ | 40 |

^a Unit cell volume.^b ρ_c , crystalline density; ρ_a , amorphous density.

As expected, the C 13-based nylons both have lower melting points and densities than the C 12 sample; the supposed glass transition temperature seems relatively independent of chain composition (Table 1). These polyamides are readily melt-spun to monofilaments whose tensile properties are recorded in Table 2; in comparing the properties of the fibers it must be remembered that the samples have somewhat different extents of crystallinity. The polar amide groups which repeat regularly along the chain associate to form dipolar layers and these interactions may be expected to govern the physical and mechanical properties. This effect is partially reflected in the present results by the initial moduli and, more clearly, in the tenacities. Heat treatment of the fibers increases the modulus and tenacity while decreasing the elongation at break. These changes may be attributed to the higher crystallinity of the annealed samples, as evidenced by the higher densities, although some relaxation of structure in the drawn but unannealed samples may have been a contributory effect.

The interpretation of the isotherms of moisture sorption by polymers has been the subject of much speculation. Typically, polar polymers such as proteins, cellulose and polyamides exhibit S-shaped isotherms like those of Fig. 2, usually accompanied by extensive hysteresis on desorption. Such isotherms may result from the combination of an initial, Langmuir type, adsorption followed by the sharp upswing in sorption arising from some kind of multilayer formation, solution by the sorbate or capillary condensation [14, 15]; a more recent treatment refers to the formation of transient pores during the adsorption of the first monolayer [16]. The initial (low relative humidity) portion of the sorption may be attributed to the progressive hydration of the higher affinity sites of the sorbant which, in the present case, may be identified as the chain amide groups.

The curves of Fig. 2, when replotted in the form of the BET equation [17], are linear between relative humidities of approximately 5 to 40%. The application, commonly made, of the BET equation, which was derived on the basis of a model quite different to the sorption process of water in a polar polymer, is difficult to justify; certainly it is inappropriate to derive an apparent surface area from the analysis. However, as seen in Table 5, the three polyamides reach a sorption equivalent to a monolayer, that is, satisfaction of the most active sorption sites, at similar relative humidities; all have similar values of the c constant of the BET equation, which is a measure of the net enthalpy of sorption.

The quantities C_M and C_S of Table 5 are calculated on the assumption that amide groups in crystalline regions are not available for sorption and by using the crystallinity data of Table 4. The value of C_S is in the region of one water molecule shared between two amide

TABLE 5. Analysis of Water Vapor Isotherms

| Polymer | c | Monolayer region (%) | Monolayer RH (%) | C_M (mole/mole) ^a | C_S (mole/mole) ^b |
|---------|------|----------------------|------------------|--------------------------------|--------------------------------|
| 6.12 | 16.4 | 0.53 ₀ | 19.8 | 0.068 | 0.699 |
| 6.13 | 17.7 | 0.47 ₂ | 19.2 | 0.065 | 0.649 |
| 10.13 | 16.4 | 0.32 ₂ | 19.8 | 0.044 | 0.448 |

^aWater per mole of accessible amide groups at monolayer RH.

^bWater per mole of accessible amide groups at 100% RH.

groups as proposed by Puffr [18] for the higher polyamides. The values of C_M are similar to that reported by McLaren and Rowen [14] for nylon 66.

X-ray diffraction studies of polyamides have shown that the structure is one composed of sheets of extended chains in which the amide groups are hydrogen-bonded in planes [10]. Generally, the even polyamides have the amide planes tilted with respect to the chain axis, whereas with odd polyamides the planes are normal to the fiber axis.

The wide-angle diffraction patterns obtained in the present study permit a preliminary attribution of the crystal structure of these polyamides.

The diffraction pattern from 612 resembles closely that from nylon 66 and even-even polyamides generally [21]. The prominent diagonal reflections situated on the layer lines arise from the tilted planes of amine groups [10, 19, 20]; streaks along the layer lines near the meridian are to be attributed either to some β crystal form [10] or with more disordered and incompletely developed α structures [22]. The x-ray diffraction patterns of even-even polyamides are successfully interpreted by the triclinic structure first given by Bunn and Garner [10]; the data of Table 4 show the c axis repeat distance to be about 0.1 nm less than that of the fully extended value of 2.485 nm [19].

The x-ray diffraction pattern of nylon 613, after annealing at 170°C, is like that of nylon 612 except that strong meridional reflections are also formed; this strong meridional pattern is shown by polyamides with an odd number of methylene units with structure in which the planes of amides are perpendicular to a chain axes. The existence of both strong meridional and diagonal reflections in 613 might be due to polymorphism of crystal structure similar to that reported for nylon 6

[19, 20] and nylon 6.8 [23]. However, when the 613 polyamide was annealed at 200°C and then shock-cooled, the x-ray pattern lost the diagonal reflections and became similar to that of odd-numbered series of polyamides previously reported to be monoclinic. It is generally accepted [10] that polyamides seek structures in which the coupling between amide groups on neighboring chains is maximized. Kinoshita [19], noting a shortening of the fiber repeat distance by an approximately constant amount from that of the fully extended chain, suggested a pleated structure for the odd-numbered polyamides. In this, the amide groups conformation is adjusted for hydrogen-bond formation so that, viewed edge-on to the hydrogen-bonded sheets, the chains have a stepped arrangement. The stepped pattern forces adjacent sheets to lock together with the hydrogen bonds on the same level; this, together with the rectangular periodicity of hydrogen bonding within each sheet leads to an overall monoclinic symmetry. Kinoshita's x-ray patterns of odd polyamides show off-equatorial reflections as found here; these may arise [12] from the slight chain curvature between the hydrogen-bonded units since the Fourier transform of such chains has off-equatorial wide-angle reflections.

Kinoshita's model fits the high-temperature annealed nylon 613 but is less successful with the sample annealed at 170°C. In the latter the angle subtended at the origin by the main wide-angle reflections is much greater than the angle that the inner layer line reflections subtend. This indicates a tendency towards off-equatorial diffraction and probably relates to a structure basically like Kinoshita's but somewhat distorted in a random way and so allowing some packing in the α and β modes as described by Bunn and Garner [10]. This sample has a c axis unit cell dimension which is 0.155 nm less than that of the fully extended chain, or a contraction of 5.9%.

There is a possibility that the observed fiber axis periodicity is not measuring the c repeat distance at all but that these reflections represent high orders of the chain fold periodicity which are enhanced in intensity because of their resonance with the monomer repeat distance. To test this possibility, a small-angle x-ray diffraction diagram was taken for the nylon 613 annealed at lower temperature. Although the fold period of 10.15 nm is approximately four times the wide-angle repeat distance, the small-angle reflection was so broad that it could not control the spacing of higher orders so well as to be responsible for the observed wide-angle pattern and so the contraction of the polyamide chain seems to be a real feature of the structure.

The chain packing of nylon 1013 is also dependent on the thermal history of the fiber. The sample annealed at 150°C is apparently of hexagonal symmetry, whereas that annealed at 180°C is monoclinic. Of the former case a considerable degree of directional disorder of the hydrogen bond is implied, although the c axis dimension is still

shortened with respect to the fully extended chain length; chain kinks are thus still present and lead to some off-equatorial reflections. The higher temperature annealed sample can be accommodated by Kinoshita's model although it is noticeable that the a and b dimensions (with monoclinic and hexagonal structures the projected and real dimensions are identical) are much more nearly equal than usually found, and this might imply a version of the hexagonal structure found at the lower annealing temperature.

CONCLUSION

Brassylic acid from crambe oil can be employed for the formation of higher nylons of lower moisture uptakes and melting temperatures than are usually found with polyamides. The x-ray evidence suggests that the crystalline form may be particularly dependent on annealing temperature.

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