studies of E–P copolymers do not aid in the elucidation of the mechanism of stereospecific catalysis in α-olefin polymerization.

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Structure of Poly(hexamethylene oxamide) [Nylon 62][+]

Y. Chatani,[†] Y. Ueda,[†] H. Tadokoro,[†] W. Deits,[‡] and O. Vogl[*][‡]

Department of Polymer Science, Osaka University, Toyonaka, Osaka, Japan,
and Polymer Science and Engineering Department, University of Massachusetts,
Amherst, Massachusetts 01003.

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ABSTRACT: Poly(hexamethylene oxamide) [Nylon 62] of reasonable molecular weight was prepared by a modification of the Sokolov technique for the preparation of oxamides. This polymer could be stretched and a fiber diagram of the polymer could be obtained. Nylon 62 has a structure similar to that of the α form of Nylon 66.

Polyoxamides are generally high-melting materials which decompose to some extent below their melting point especially when the aliphatic portions of the diamine of the polyoxamides[1,2] are short. As a consequence, polyoxamides have not reached commercial importance inspite of their interesting overall properties. Recently regular copolyamides based on the oxamide linkage have shown promise as materials for desalination membranes.[3–9]

Polyoxamides of reasonable molecular weight cannot be easily prepared by the normal polymerization techniques for polyamides.[1,10,11] Although several oxalic acid derivatives have been used for polyoxamide preparation, polyoxamides normally obtained had an inherent viscosity not exceeding an η of 0.3. Only the method utilizing oxalyl chloride gives polymers of substantially higher molecular weight. The specific technique is a gas liquid interfacial polymerization technique first devised by Sokolov[12–15] in which oxalyl chloride diluted with nitrogen is bubbled into an aqueous solution of the diamine. The relationship between the yield and viscosity of various polyoxamides as a function of the reaction temperature, the diamine concentration in water, the concentration of the gaseous oxalyl chloride in the inert gas, and the height of the aqueous phase was investigated. The high reactivity of oxalyl chloride in aqueous solution leads readily to its hydrolysis but the relatively low solubility of oxalyl chloride and also the high reaction temperature which reduces the solubility of the oxalyl chloride favors polymerization. The relationship between reactant and concentration (both gaseous and liquid) was found to be qualitatively similar to that found in liquid–liquid type interfacial polymerizations; consequently it was expected to be possible to prepare, by this gas/liquid interfacial technique, samples of high enough molecular weight Nylon 62 for the determination of its crystal structure.

Structure determinations of Nylon 6,[16,17] Nylon 66,[18] and more recently wholly aromatic polyamides[19] have been carried out. Nylon 6 crystallizes in three forms, the α,[16] β,[16] and γ form.[17] The α form is monoclinic, has eight monomeric units per unit cell, and has a fiber period of 17.2 Å. The β form is difficult to analyze, as the β-type specimens all contain a high percentage of the α form. The γ form is again monoclinic but has a twisted molecular structure with 0.3 Å shorter fiber period than that of the α form. Nylon 66[18] also has an α and β form; the α form is triclinic and has one polymer chain per unit cell, while the β form is monoclinic with two chains per unit cell. Both forms have a fiber period of 17.2 Å. Poly(*p*-phenyleneterephthalamide) and poly-*p*-benzamide are fully extended,[19] while poly(*m*-phenyleneisophthalamide)[20] is twisted with a fiber period about 1 Å shorter than that of the fully extended structure. The characteristic tensile moduli[21] features of these aromatic polyamides were also interpreted in terms of these structures.

It was the purpose of this paper to prepare Nylon 62 of reasonable molecular weight and to fabricate the polymer into samples which could be drawn and for which good x-ray fiber diagrams could be obtained. Identification of the spacing would be suitable for the calculation of the unit cell of Nylon 62 and for fully characterizing the crystal structure of the polymer.

[+] Regular Copolyoxamides. 6.

[†] Onsaka University.

[‡] University of Massachusetts.

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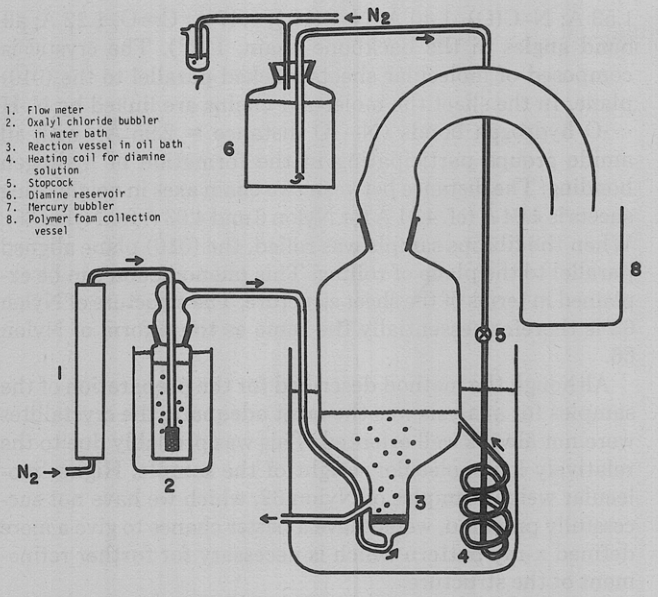

Figure 1. Schematic drawing of continuous gas–liquid interface polycondensation apparatus.

Experimental Section

Materials. Hexamethylenediamine (Aldrich Chemical Co., Inc.) (HMD) was distilled at 136–138 °C (94 mm) prior to use.

Oxalyl chloride (Aldrich Chemical Co., Inc.) obtained in sealed ampules was used without purification. Only freshly opened ampules were used.

Sodium carbonate (Fisher Chemical Co.) was used without purification.

Procedures. For convenient continuous operation of the preparation of Nylon 62 the polycondensation procedure and the apparatus proposed and used by Sokolov[11] was modified (eq 1). All parts of the

$$H_2N{-}(CH_2)_6{-}NH_2 + ClCOCOCl \longrightarrow {-}[HN{-}(CH_2)_6{-}NHCOCO]_n{-} \quad (1)$$

Nylon 62

operation were made by Pyrex glass and were connected with thick-walled plasticized PVC tubing.

Synthesis. An aqueous solution of 465 g (4.00 mol) of HMD and 848 g (8.00 mol) of sodium carbonate in 20 L of water was prepared in a large glass container. During the polymerization reaction this solution was added to the diamine reservoir as needed. The oil bath around the reactor vessel was adjusted to 95 °C and the water bath around the oxalyl chloride container was kept at 17.5 °C.

The aqueous diamine solution was introduced into the reactor vessel after first preheating the solution to 95 °C by passing it through the heating coil. A flow rate of 2.0 L/h was maintained by adjusting the stopcock and measuring the volume of the solution leaving the reactor per unit time (Figure 1).

The polymerization reaction was started by allowing dry nitrogen to bubble through the oxalyl chloride and into the warm aqueous diamine solution at a rate of 95–100 cm^3/min. The gaseous oxalyl chloride was dispersed in the reactor by passing it through a "coarse" (70–100 μm pore diameter) fritted glass filter. Polymer formation was noticeable within a few minutes as a white foam floating on top of the diamine solution. As the reactor filled with polymer foam it was passed by way of a large "U-tube" into a collection vessel. The reaction was continued for approximately 10 h until all of the diamine solution had passed into the reactor. A total of 90.0 g of oxalyl chloride was used. The moist polymer foam was washed repeatedly with large portions of water in a 1 gallon Waring blender. The resultant white fiberous material was washed twice with methanol, filtered, and dried at room temperature for 48 h at 20 mm. The polymer (27.9 g, 31% based on oxalyl chloride) was precipitated twice from a trifluoroacetic acid solution into water and gave an off-white powder.

DSC studies of Nylon 62 showed an endotherm presumably the T_g of the "solvent quenched" material at 250 °C and a melting point at 332 °C (heating rate of 20 °C/min). A film of Nylon 62 was cast from a solution of 0.30 g of polymer in 6.0 mL of trifluoroacetic acid. The infrared spectrum (film) showed absorptions at 2860 (symmetric stretching of CH$_2$), 2930 (asymmetric stretching of CH$_2$), and near 3300 with a minor peak near 3100 (NHCO stretching), 1620 (CO stretching), and 1520 cm^{-1} (NH bending). The ^{1}H NMR spectrum (CF$_3$COOH) showed δ 8.40 (NHCO, 2), 3.2–3.7 (CH$_2$NHCO, 4), 1.1–1.9 (CH$_2$, 8). The inherent viscosity of a 1.0% H$_2$SO$_4$ solution of this polymer was 0.64 dL/g. Anal. Calcd for $(-C_8H_{14}N_2O_2-)_n$: C, 56.45, H, 8.29; N, 16.46. Found: C, 55.47; H, 7.97; N, 15.78; Ash, 0.31.

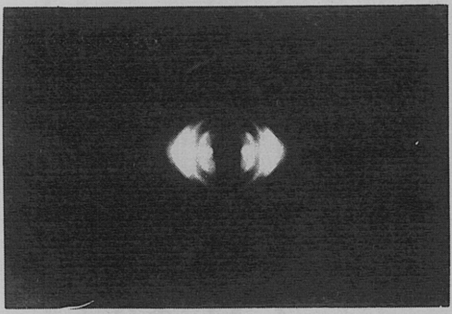

Figure 2. X-ray diffraction pattern of oriented Nylon 62.

Sample Preparation. A concentrated H$_2$SO$_4$ solution of Nylon 62 (20 wt %) was extruded into water through an injector needle to form a fibrous coagulated sample. After washing out residual H$_2$SO$_4$ with water, the sample was stretched three times on a heater, followed by annealing 2 h in Wood's alloy at 230 °C.

Characterization of Polymer. The thermal behavior of the polymer was studied on a Perkin-Elmer differential scanning calorimeter DSC-1B at a heating rate of 20 °C/min (sample size 7.0 mg). The infrared spectra were determined on a Perkin-Elmer Infrared Spectrophotometer 727. The spectra were measured on a film cast from a 5 wt % polymer solution in CF$_3$COOH. The ^{1}H NMR spectra were measured on a Perkin-Elmer R-32 (90 MHz) spectrometer in a 5% polymer solution in CF$_3$COOH. The viscosity of the polymer was measured on a 1.0 wt % solution of polymer in sulfuric acid in a Cannon-Fenske viscometer at a temperature of 30 °C. The x-ray diffraction patterns were obtained with a cylindrical camera of 35 mm radius (Figure 2).

The elemental analysis was carried out by the Microanalysis Laboratory of the University of Massachusetts.

Results and Discussion

Poly(hexamethylene oxamide) [Nylon 62] of reasonable molecular weight was prepared by modification of Sokolov's technique for the preparation of polyoxamides by passing a gaseous mixture of oxalyl chloride through an aqueous solution of hexamethylene diamine. This gas phase interfacial polycondensation suffers from some drawbacks, however. The most important one is that the output of the system is rather low. In order to increase the output per unit time as well as to provide for a continuous operation, we have assembled an apparatus with some important modifications. The gaseous oxalyl chloride/nitrogen mixture was passed into the aqueous phase of hexamethylenediamine through a fritted glass filter which produced many very small bubbles and consequently a large interfacial surface area for the reaction. This method produced a polymer foam which floated on top of the aqueous phase and consisted of microballoons of polymer. The polymer appears to be somewhat oriented and is quite tough. As in the original method,[12–14] the length of the aqueous phase and the rate of introduction of the oxalyl chloride/nitrogen mixture was also critical.

In order to provide for a continuous operation, the reactor was constructed for fresh diamine solution to enter continuously while maintaining a constant volume of solution. This was effected by installing a diamine solution reservoir with a stopcock to control the flow rate and an inlet and exit port on the reactor. The polymer was washed thoroughly in a high-speed 1-gallon Waring blender which not only washed the polymer but also helped to break up the microballoons of polymer and collapse them in order to obtain a material of

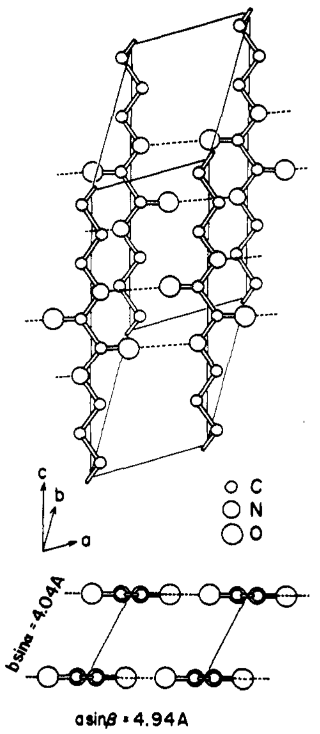

Figure 3. Crystal structure of Nylon 62. Broken lines indicate NH···O hydrogen bonds.

Table I
Crystal Structure Data

Triclinic, $P\bar{1}$
$a = 5.15$ Å, $b = 7.54$ Å, c (fiber axis) = 12.39 Å
$\alpha = 32.4°$, $\beta = 73.5°$, $\gamma = 61.9°$
One chain per unit cell
Calculated crystal density = 1.31 g/cm^3
Observed density = 1.246 g/cm^3

manageable volume as the initial material was of very low bulk density.

The molecular weight of Nylon 62 produced by the batch type and continuous reactor appeared to be of comparable molecular weight as judged by the inherent viscosity.

The crystal data of Nylon 62 are shown in Table I. The crystal structure is shown in Figure 3. The x-ray analysis revealed a fully extended molecular chain with one chain per unit cell (cf. the calculated fiber period is 12.37 Å when the following bond lengths and bond angles are assumed: C–C, 1.53 Å; N–C(O), 1.40 Å; N–C(H$_2$), 1.47 Å; C=O, 1.22 Å; all bond angles in the backbone chain, 112°). The crystal is composed of molecular sheets stacked parallel to the (010) plane. In the sheet the molecular chains are linked by N–H···O hydrogen bonds (N···O distance = 2.95 Å), with all amide groups participating in the formation of hydrogen bonding. The distance between two chain axes in neighboring sheets is 4.04 Å (cf. 4.01 Å for Nylon 6 and 4.03 Å for Nylon 66). When the fibrous sample was rolled, the (010) plane aligned parallel to the plane of rolling. This phenomenon can be explained in terms of the sheet structure. The structure of Nylon 62 is therefore essentially the same as the α form of Nylon 66.

Although the method described for the preparation of the samples for analysis was the most adequate, the crystallites were not always well oriented. This was probably due to the relatively low molecular weight of the sample. Higher molecular weight samples of Nylon 62, which we have not successfully prepared, would have a better chance to give a more defined x-ray pattern which is necessary for further refinement of the structure.

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