

NOTE

SYNTHESIS OF ^{15}N LABELLED NYLON 6

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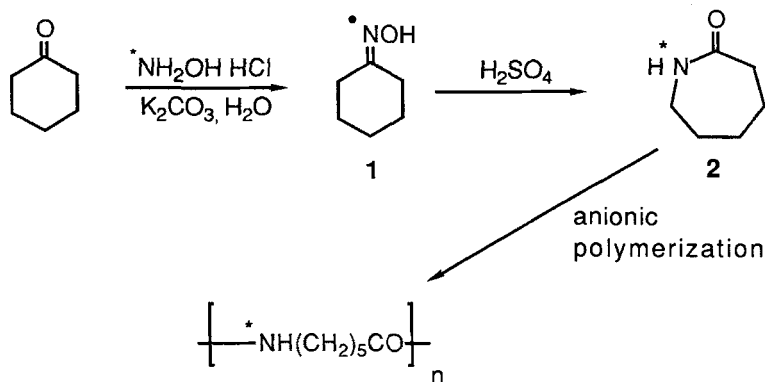
Summary

The synthesis of ^{15}N labelled nylon 6 by anionic polymerization of ϵ -caprolactam is described. Labelling of this commercially important polymer should greatly enhance investigations of its morphology by techniques such as NMR, IR, and Raman spectroscopies.

Keywords: ^{15}N labelled, cyclohexanone oxime, ϵ -caprolactam, nylon-6.

Introduction

Nylons are an important class of polymeric materials. However, in spite of extensive studies, many questions remain concerning the morphology of one of these polymers, Nylon 6.¹ An important and growing field of application for solid-state NMR has been elucidating the morphology of polymers.^{2,3} The morphology of solid Nylon 6 has been recently analyzed by natural abundance ^{15}N NMR.⁴ This study was marred, however, by a low signal to noise ratio which perhaps obscured important information available in the spectrum. In addition, IR studies relying on isotope exchange have proven fruitful in determining band assignments and providing morphological information.⁵ These motives have led us to synthesize ^{15}N labelled nylon-6 by the route shown in Scheme 1. The overall yield of this synthesis is quite high and provides material useful for the study of this commercially important polymer.



Scheme 1

Experimental

Hydroxylamine hydrochloride (^{15}N labelled, 98%) was obtained from ICON Services Inc. (Summit NJ) and used as received. Cyclohexanone was used as received from Aldrich Chemicals (99.8%, Milwaukee, WI). Acetylcaprolactam (Aldrich 99%) was distilled prior to use. Melting points were

obtained on a Hoover melting point apparatus and are uncorrected. Solution-state ^{15}N NMR spectra were obtained on a Varian XL 400 NMR spectrometer operating at 40.6 MHz under NOE suppressed conditions. Spectra are referenced to an external $^{15}\text{NH}_3$ standard. Gel permeation chromatography was performed on trifluoroacetylated samples of the polymer at room temperature in a Waters 501 chromatographic system with two Phenogel 10 μm linear columns and a chloroform flow rate of 1 ml/min. The UV absorbance was monitored at 260 nm with a Laboratory Data Control SpectroMonitor II. The chromatogram from a 100 μl injection of a 0.1% concentration was interpreted with Nelson 3000 software using universal calibration against polystyrene where

$$M_{\text{nylon}} = 0.225 M_{\text{polystyrene}}^{1.008}.$$

The exponent was determined from the viscosity measurements of Weisskoff ⁶ in tetrahydrofuran while the coefficient was selected to give consistency with other previously characterized nylon 6 samples.

Synthesis of ^{15}N Labelled Cyclohexanone Oxime (1)

A mixture of 3.92 g (56.4 mmol) of ^{15}N labelled hydroxylamine hydrochloride and 5.41 g (55.1 mmol) of cyclohexanone in 10 ml of water was treated dropwise with a saturated solution of 3.04 g (28.7 mmol) of sodium carbonate. The resulting precipitate was filtered and dried over phosphorus pentoxide to give 5.70 g (91% yield) of a white solid: MP 88-88.5 $^{\circ}\text{C}$; ^{15}N NMR (CDCl_3) δ 329.2 (lit. δ 327.6 measured vs HNO_3 and converted ⁷).

Synthesis of ^{15}N Labelled ϵ -Caprolactam (2)

A sulfuric acid solution was prepared by diluting 2.5 ml of concentrated sulfuric acid with 0.5 ml of water. This solution was added to 2.44 g (21.6 mmol) of the oxime (1). This mixture was heated gently until the reaction began (very fast and exothermic). The residue was cooled in an ice bath with some ice added to the solution. Concentrated ammonium hydroxide was added to neutralize the mixture. The aqueous solution was extracted with chloroform (5 x 30 ml). The organic phase was dried (MgSO_4), decolorized (carbon), reduced and dried under vacuum to give a quantitative yield of lactam. The crude lactam was distilled (Kugelrohr, 1.5 mmHg, 145-155 $^{\circ}\text{C}$) to give 2.33 g (95% yield) of a white solid: MP 69-70 $^{\circ}\text{C}$; ^{15}N NMR (CDCl_3) δ 116.6 (lit. δ 117.6 measured vs HNO_3 and converted ⁸).

Anionic Polymerization of ϵ -Caprolactam (2)

A well dried sample of caprolactam (2.00 g, 17.7 mmol) was charged in to a dry side arm test tube fitted with an internal thermocouple under argon. Sodium (7 mg, 0.3 mmol) was added and the tube heated in a heating block to 140 $^{\circ}\text{C}$ during which time the sodium melted and dissolved in the lactam. When the temperature had equilibrated, 55 μl (0.39 mmol) of acetylcaprolactam was added with shaking. After a few minutes the solution began to thicken and an exotherm was noted. The tube was left at 140 $^{\circ}\text{C}$ for 30 min. The resulting polymer plug was broken up to give 2.06 g of a yellow material. This was ground up in a mill and extracted with water for 24 hrs to remove residual monomer. The sample was dried to give 1.87 g (91% yield) of polymer. Anal. calc. for $\text{C}_6\text{H}_{11}\text{NO}$: C, 63.69; H, 9.80; N, 12.37. Found: C, 62.15; H, 9.65; N, 12.19. GPC: M_w , 14,900; polydispersity of 2.8. ^{15}N NMR ($\text{CF}_3\text{CH}_2\text{OH}$) δ 122.7 (lit. δ 122.6 ⁹).

Acknowledgments

We would like to thank the following people at Allied-Signal for their assistance: R. Brambilla for the solution-state NMR work; M. McDonnell for the GPC results; R.D. Sedgwick and M.K. Akkapeddi for their support of this project; A. Levy and J. Dege for several fruitful discussions.

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