Residual Monomer in Synthetic Fibers

NMR Spectroscopy Method Provided the Identity of the Residual Monomer

Background

Synthetic polymers, like plastic fibers, often contain low levels of residual monomers. Monomers are typically reactive and toxic, especially compared with properties of synthetic fibers. The presence of residual monomer can affect the odor of the product as well as the mechanical properties. Analysis of residual monomers can be used to assess the likely building blocks of the polymer. The residual monomer content also indicates the effectiveness of the polymerization reaction, and purification steps. Residual monomer analysis is commonly performed by Polymer Solutions Incorporated for evaluating polymers at every stage of their life-cycles. Liquid chromatography, gas chromatography, and nuclear magnetic resonance (NMR) spectroscopy are some of the methods we use for that determination. In this case study, the NMR spectroscopy method is described.

The Approach

The fiber strand was dissolved in a 50:50 mixture, on a volume basis, of 1,1,1-trifluoroethanol (TFE) and deuterated chloroform (CDCl3) for analysis by proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectroscopy. The sample dissolved easily in this solvent mixture to give a transparent, but orange-colored solution.

The Analysis

Figure 1 shows the ^{1}H NMR spectrum for the sample. The large signals at 4.9 ppm and 3.8 ppm are due to the TFE solvent. The signals at 6.48 ppm, 3.15 ppm, 2.14 ppm, 1.55 ppm, 1.46 ppm, and 1.27 ppm are due to nylon-6. The small signals at 2.41 ppm and 1.76 ppm are due to caprolactam monomer. Additional support for the presence of caprolactam monomer are the partially resolved caprolactam signals observed as shoulders on the peaks at 6.48 ppm, 3.15 ppm, and 1.55 ppm. No signals other than nylon-6, caprolactam, and solvent were observed in the sample spectrum. The lack of additional 1H NMR signals allowed us to rule out the presence of comonomers. The lack of comonomers, in turn, verified that the fiber strand was a homopolymer, not a copolymer or polymer blend.
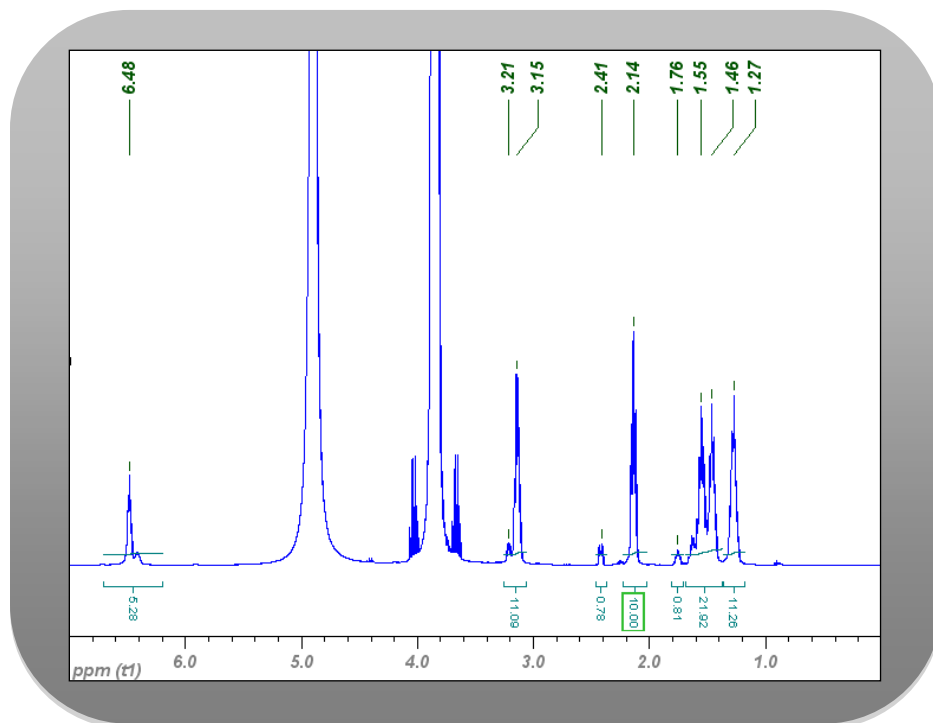

Figure 1. The proton nuclear magnetic resonance (^{1}H NMR) spectrum recorded for a dissolved strand of fiber.

Figure 2 shows the carbon nuclear magnetic resonance (^{13}C NMR) spectrum of the dissolved polymer sample. The intense peaks at 125 ppm and 62 ppm are due to TFE solvent. The large signals at 77 ppm are due to CDCl$_3$ solvent. The signals at 177 ppm, 39 ppm, 36 ppm, 29 ppm, 26 ppm, and 25 ppm are due to nylon-6. The smaller signals at 182 ppm, 43 ppm, 36 ppm, 30 ppm, and 23 ppm are due to caprolactam monomer. No other signals that would indicate the presence of a copolymer were detected in the sample. The lack of additional ^{13}C NMR signals allowed us to again rule out the presence of comonomers. The lack of comonomers, based on the ^{13}C NMR spectrum, substantiated the determination that the fiber strand was a homopolymer, not a copolymer or polymer blend.
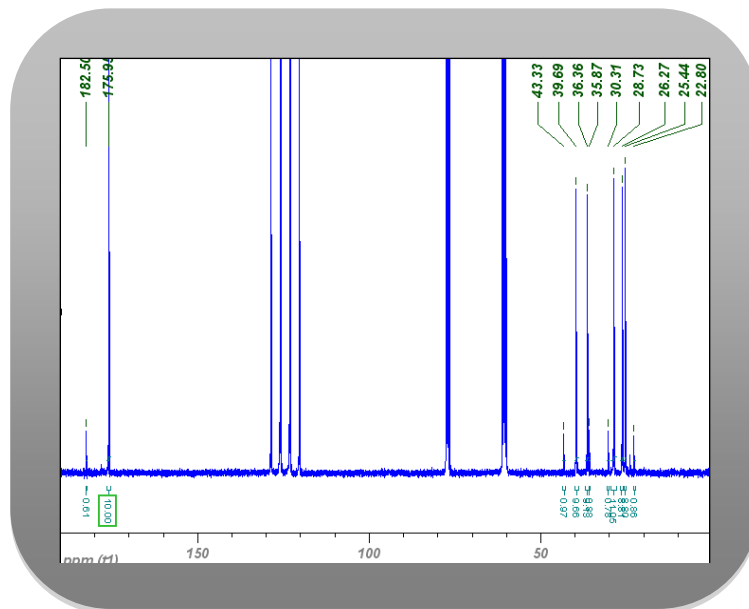

Figure 2. The carbon nuclear magnetic resonance (^{13}C NMR) spectrum recorded for a dissolved strand of fiber.

Conclusions

The NMR spectroscopy method was able to provide the identity of the residual monomer as well as its concentration in a strand of fiber. It was also important to determine if any comonomers were present in the fiber strand. Comonomers, if detected, would indicate that the fiber was a copolymer or blend. To verify the initial determination made using proton NMR spectroscopy additional analysis was performed using carbon NMR spectroscopy. The spectra were obtained at room temperature in the solution state. Values of 7.24 and 7.78 weight percent caprolactam were found, respectively. This monomer verifies that the fiber itself was poly(caprolactam), also known as polyamide-6 or Nylon-6.