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Polymer 43 (2002) 3331–3333

polymer

www.elsevier.com/locate/polymer

Structural characterization of nylon 4 in the solid state by high-resolution solid-state ^{1}H NMR spectroscopy

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Received 18 January 2002; accepted 21 February 2002

Abstract

High-resolution solid-state ^{1}H NMR spectra of nylon 4 melt-quenched sample and single crystal sample in the solid state were measured in a wide range of temperatures from room temperature to 505 K by using solid state 300 MHz NMR with the FSLG-2 homo-nuclear dipolar decoupling method combined with high speed magic angle spinning method. From the experimental results, structural characterization on the crystalline and non-crystalline components was carried out. Further, intermolecular interaction between nylon 4 and water contained in the sample was discussed.

Keywords: Polyamide; Nylon 4; Structure

1. Introduction

Recently, structural characterization of various kinds of polyamides, that is nylons, in the solid state has been carried out by high-resolution solid-state ^{13}C and ^{15}N NMR [1–9]. These methods have given new and useful structural information on the crystalline and non-crystalline components of nylon 4, nylon 6, nylon 6,6 in addition to X-ray diffraction, infrared absorption, etc. The chemical shifts of ^{13}C and ^{15}N nuclei for polymers in the solid state have been widely used in studying the conformation and hydrogen-bonded structure, but there is little study on high-resolution solid-state NMR of protons in polymers nylon except for some polypeptides [10,11]. One of the main reasons is very large dipolar interaction with ^{1}H and quadrupolar interaction with amide ^{14}N, which leads to large broadening of the spectral line. If these dipolar and quadrupolar interactions are eliminated, high-resolution solid-state ^{1}H NMR is one of the routine methods. In previous works, we have successfully measured high-resolution solid-state ^{1}H NMR spectra of polypeptides and peptides including the amide proton by using high frequency solid state 800 MHz NMR [10] and solid state 300 MHz NMR with the FSLG-2 (frequency-switched Lee–Goldburg) homo-nuclear dipolar decoupling method combined with high speed magic angle spinning (MAS) [11].

From such a background, we aim to study structure of nylon 4 melt-quenched sample and nylon 4 single crystal sample in the solid state by using solid state 300 MHz NMR with the FSLG-2 homo-nuclear dipolar decoupling method combined with high speed MAS method as developed by us, in order to obtain further useful information about structure and dynamics of these polyamides in addition to structural knowledge obtained already by high-resolution solid-state ^{13}C and ^{15}N NMR.

2. Experimental

2.1. Materials

Nylon 4 (30 000) was kindly supplied by Toray Industries, Inc. Nylon 4 single-crystal sample and melt-quenched sample were prepared by the following procedure.

For solution crystallization of nylon 4, the nylon 4 was dissolved at 423 K in water at a concentration of 0.05% (w/v). The solution was kept at 423 K for about 10 min and was then slowly cooled to room temperature. After cooling, the solution was diluted with methanol and the deposited crystals were separated from the solution by decantation, washed with methanol, and further dried. This sample is composed of single crystals, as identified by electron microscopy. On the other hand, melt-quenched sample was obtained by the following procedure. The nylon 4 was put into a glass tube and sealed off in vacuum. The

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0032-3861/02/$ - see front matter
PII: S0032-3861(02)00164-7

glass tube was heated at 503 K and then quenched in a mixture of ice and water.

2.2. NMR measurements

High-resolution solid-state ^{1}H NMR measurements were made with a Bruker Avance DSX300 NMR spectrometer operating at 300.13 MHz with a high power accessory. The conventional 4 mm wide-bore CP/MAS probehead was used, but the sample with the volume of about 20 μl was placed at the center of an NMR rotor to enhance the radio-frequency field homogeneity. The FSLG-2 homo-nuclear decoupling with high-speed MAS method [11] was used to observe high-resolution proton spectra. The first 90° pulse with 3.0 μs pulse width was applied, of which the field strength is 83 kHz, and then the off-resonance pulse length under the FSLG-2 sequence was calculated to be 9.75 μs with the same pulse power. Thus, the offset can be calculated to be 50 kHz. In the NMR spectrometer to be used here, the frequency switching time is 0.2 μs and the sampling time in each period of the FSLG-2 sequence is 3 μs including frequency resets for the observation to obtain 512 data points. The MAS speed rate of 12 kHz is used to reduce ^{1}H–^{1}H dipolar interactions and remove hetero-nuclear dipole interactions. The typical recycle delay is 10 s and the numbers of scans is typically eight times. In addition, it is liked to say that the usual combined rotation and multiple pulse spectroscopy technique [12,13] which is sometimes used in high-resolution ^{1}H NMR experiments gave no signal for the amide proton due to very broadening because of large dipolar and quadrupolar interactions with the amide nitrogen with spin number of 1.

The ^{1}H chemical shifts were calibrated relative to external DSS (3-trimethylsilyl-1-propanesulfonic acid sodium salt) and the experimental scaling factor for chemical shift in the obtained spectrum is experimentally adjusted by using the single pulse glycine spectrum, which is observed at a frequency of 800 MHz and at a MAS speed of 35 kHz [10].

3. Results and discussion

Fig. 1 shows high-resolution solid-state ^{1}H NMR spectra of nylon 4 melt-quenched sample in the wide temperature range from room temperature to 487 K and at room temperature reached by cooling slowly from 487 K together with chemical structure by using the FSLG-2 homo-nuclear decoupling with high-speed MAS method. Six peaks appear at 8.0, 7.7, 4.7, 3.1, 2.2 and 1.7 ppm from downfield to upfield at room temperature. All of the peaks are numbered from downfield. Peaks 1 and 2 can be straightforwardly assigned to the amide proton. Further, peaks 4, 5 and 6 can be straightforwardly assigned to CH_2(a), CH_2(c) and CH_2(b) protons, respectively. Peak 3 at 4.7 ppm moves largely upfield with an increase in temperature and disappears at 487 K. Such a large upfield shift is characteristic for the hydroxyl proton hydrogen-bonded. The peak intensity is largely reduced at room temperature reached by cooling slowly from 487 K. From these experimental results, peak 3 may be assigned to water contained in the nylon 4 sample. In the spectra, the water signal is enhanced as compared with the other signals, which come from the polymer because the mobility of the former is much higher than that of the latter.

Next, we are concerned with spectral behavior of the amide proton and CH_2 protons by changing temperature. Peaks 1 and 2 move to upfield with an increase in temperature. This means that the strength of hydrogen-bonding for the NH group is reduced. At 473 K, peak 2 disappears completely. From these experimental results, it is suggested that there are two kinds of the NH groups. One is that the NH group forms hydrogen bond with the amide carbonyl groups, and another is that the NH group forms hydrogen bond with water. The latter decomposes by evaporation of water at higher temperature and the corresponding NH group forms hydrogen bond with the amide carbonyl

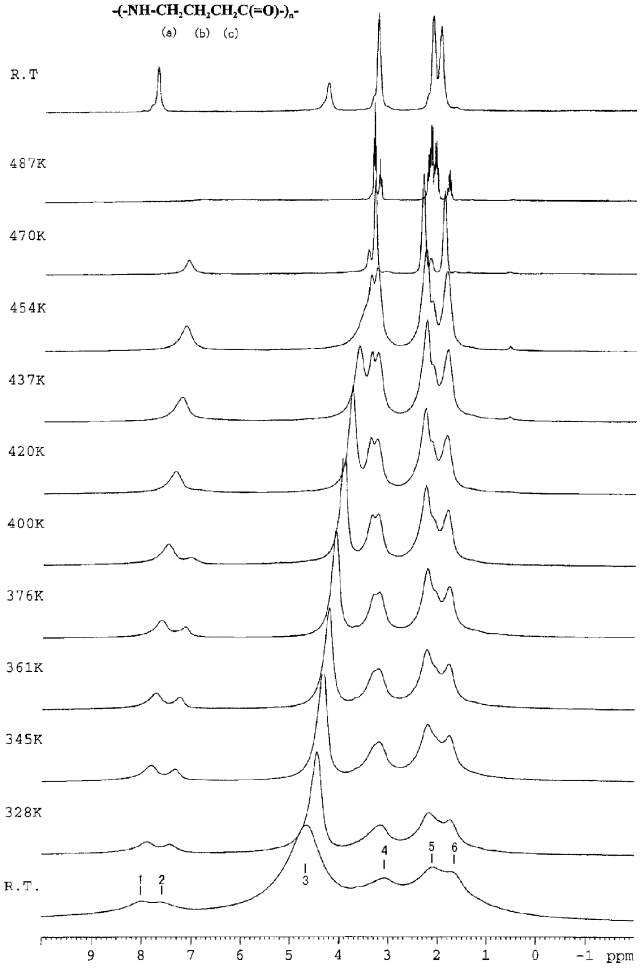

Fig. 1. High-resolution solid-state ^{1}H NMR spectra of nylon 4 melt-quenched sample in the wide temperature range from room temperature to 487 K and at room temperature reached by cooling slowly from 487 K together with chemical structure as measured by FSLG-2 homo-nuclear decoupling with high-speed MAS method.

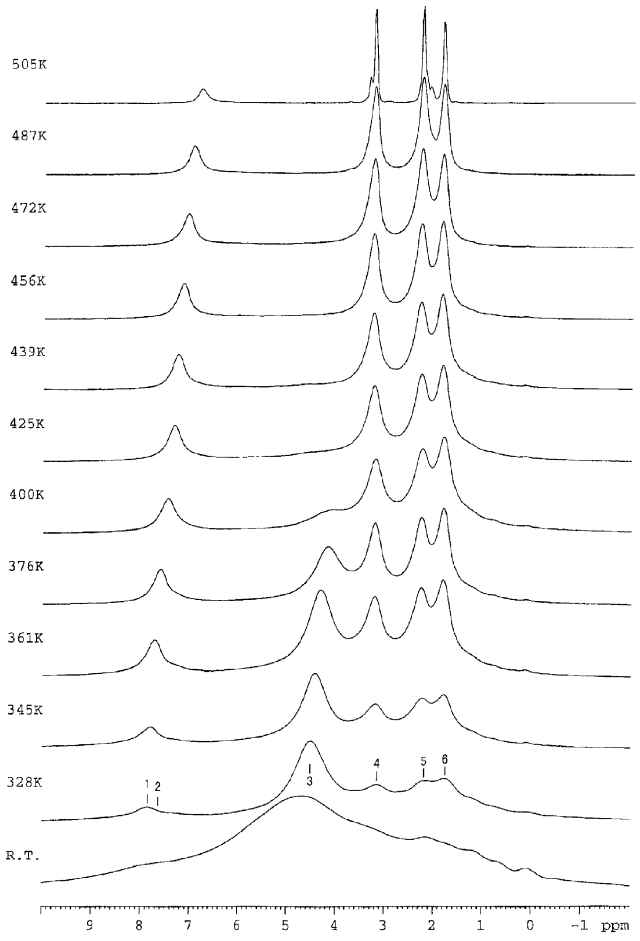

Fig. 2. High-resolution solid-state ^{1}H NMR spectra of nylon 4 single crystal sample in the wide temperature range from room temperature to 505 K as measured by FSLG-2 homo-nuclear decoupling with high-speed MAS method.

group. As the sample reached at room temperature by cooling slowly from 487 K, peak 2 does not appear at 7.7 ppm.

On the other hand, we look carefully at the CH_2 peaks as referred to the high-resolution solid-state ^{13}C NMR experiments reported previously [1,2]. The melt-quenched nylon 4 sample has the crystalline and non-crystalline components. Correspondingly, each of the CH_2 carbons has two peaks assigned to the crystalline and non-crystalline components. The CH_2(b) proton has a single peak (peak 6) in the wide temperature range, but the other CH_2(a) (peak 4) and CH_2(c) (peak 5) protons have two splitting peaks. These peak intensities are changed by temperature change. The intensities of the downfield peak for the CH_2(a) proton and the upfield peak for CH_2(c) proton as assigned to the crystalline component are gradually decreased by temperature elevation and then disappear at 487 K. On the other hand, the upfield peak for the CH_2(a) proton and the downfield peak for CH_2(c) proton are assigned to the non-crystalline component. When the sample was cooled slowly at room temperature from 473 K, it was crystallized. For this, the CH_2(a) proton and CH_2(c) proton for the crystallized sample have a single peak at room temperature as shown in the top spectrum.

Fig. 2 shows high-resolution solid-state ^{1}H NMR spectra of nylon 4 single crystal sample in the wide temperature range from room temperature to 505 K. At room temperature the ^{1}H NMR spectrum is much broader compared with those at higher temperature. At 328 K five peaks appear clearly at 8.0, 4.7, 3.3, 2.2 and 1.7 ppm from downfield to upfield at room temperature. All of the peaks can be assigned according to the above assignment for the melt-quenched sample. As for the amide proton, an intense peak 1 appears at 8.0 and a very weak shoulder peak 2 appears at upfield. The water peak moves to upfield with an increase in temperature and the intensity is reduced. At 425 K the peak disappears completely. The water peak disappears at lower temperature by about 45 K compared with the melt-quenched nylon 4. The intermolecular interaction with water is much more weak compared with the case of the melt-quenched nylon 4. The CH_2(a) and CH_2(c) protons have a single peak. This is different from the melt-quenched sample. This means that the degree of crystallinity for the single crystal sample is much higher than that for the melt-quenched sample.

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