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Preparation, characterization and crystalline transition behaviors of polyamide 4 14

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Abstract

A new polyamide, nylon 4 14, was synthesized and characterized in this paper. The polymer was prepared by melt polycondensation, which yielded materials of molecular weight about 15,000 g/mol. The product was characterized by means of elementary analysis, intrinsic viscosity, infrared spectrometry, ^{1}H and ^{13}C nuclear magnetic resonance, differential scanning calorimetry, and thermogravimetric analysis. In addition, the crystalline transition behavior of nylon 4 14 was carefully investigated by variable-temperature X-ray diffraction (XRD). It was found that well-melt-crystallized nylon 4 14 undergoes Brill transition at 170°C on heating. When it crystallized at high temperature from the melt, nylon 4 14 crystallized directly into a kind of α phase with two peaks in its XRD patterns, which is very different from nylon 6 6 and nylon 10 12 and similar to nylon 10 10. Upon further cooling to room temperature, nylon 4 14 preserved the triclinic structure (α phase). © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Nylon 4 14; Melt polycondensation; Brill transition

1. Introduction

Nylon is an important kind of polymer because of its unique properties. Almost all of the nylons are semicrystalline polymers that usually exhibit a relatively high modulus, good temperature resistance, excellent toughness and strength, and are also very resistant to abrasion, so they have been widely used in many fields, especially as fibers and engineering thermoplastics [1]. The attractive matrix of properties of nylons originates from strong hydrogen bonds which are formed by –NH– and –CO– in the amide groups [2]. Therefore, the properties of nylons vary with the density of the amide groups in their molecular chains. Since the discovery of nylon 6 6 by Carothers in 1934 [3,4], many nylons with different amide densities have been investigated, a number of which have been commercialized during the past 50 years. In recent years, much attention has been paid to the new nylons, especially to the synthesis of the short [5] and long [6] alkane segment nylons. In this paper, a new polyamide, nylon 4 14, was synthesized based on a short alkane diamine, butylenediamine, and a long alkane carboxylic diacid, 1,12-dodecanedicarboxylic acid. The resulting polymer was carefully characterized.

Nylons can crystallize into more than one crystal structure with different chain folding patterns or different packing modes under different conditions. It is well-known that many even–even nylons [7–10] with α structure at room temperature show a crystal to crystal transition upon heating, which is the Brill transition [11]. As a new synthesized nylon, its crystalline transition behaviors under different conditions (i.e. on heating, isothermal crystallization, and on cooling) were also systematically investigated by variable-temperature wide-angle X-ray diffraction (XRD). Nylons 2 14, 6 14, 8 14, 10 14, 12 14, and 14 14 have been synthesized simultaneously, and will be published elsewhere.

2. Experimental

2.1. Polymer synthesis

1,12-dodecanedicarboxylic acid (5.16 g, 0.02 mol) was dissolved in absolute alcohol (50 ml) at 50°C and a solution of butylenediamine (1.85 g, 0.021 mol) in absolute alcohol (30 ml) was added under vigorous stirring. The butylenediamine-dodecanedicarboxylic acid salt immediately precipitated. The mixture was stirred for another 30 min at 50°C, allowed to cool to room temperature, and the white product was collected by filtration. The salt was recrystallized from a mixture of alcohol (130 ml) and water (40 ml),

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and obtained as a white powder (5.96 g, 85%), m.p. 172.6°C.

A glass tube was charged with butylenediamine-dodecanedicarboxylic acid salt (5.20 g, 0.015 mol) and a slight excess of butylenediamine (0.013 g, 0.15 mmol) was added. The glass tube was snugly fitted into an autoclave. After the autoclave was evacuated and flushed with nitrogen and the cycle had been repeated three times, a nitrogen pressure of 10 atm was applied. The reaction was subsequently started by quickly raising the autoclave temperature to 220°C. After keeping the autoclave for 2 h at 220°C, the temperature was increased to 235°C; after 1.5 h under these conditions, the pressure was decreased (5 atm) and the autoclave was kept for 2 h. In the last step, a vacuum (~0.1 atm) was established, the temperature was increased to 245°C, and the reaction was continued for another 2 h. The autoclave was then cooled to room temperature. The resulting nylon 4 14 was obtained as a white solid (2.5 g, 85%) and pulverized in a freezing mill.

3. Polymer characterization

The resulting nylon 4 14 was characterized by means of intrinsic viscosity, infrared (IR) spectrometry, ^{1}H and ^{13}C nuclear magnetic resonance (NMR), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). IR spectrum was determined on a Perkin–Elmer Paragon 1000 PC Fourier transform IR spectrometer. Trifluoroacetic acid was used as the solvent for NMR measurements. ^{1}H NMP and ^{13}C NMR spectra were recorded with a Bruker AVANCE 500 at 500 and 150 MHz, respectively. The intrinsic viscosity was determined in dichloroacetic acid in an Ubbelohde viscometer at 25°C. A Perkin–Elmer Pyris-1 differential scanning calorimeter calibrated for temperature with indium was used to record the thermal properties of nylon 4 14. TGA was performed on a Perkin–Elmer TGA7 thermobalance with the heating rate at 20°C/min.

4. Wide-angle X-ray diffraction

A film of Nylon 4 14 about 1 mm thick for the XRD measurement was pressed between two glass slides at 240°C in a hot stage, and then annealed in an oven at 160°C for 5 h.

The wide-angle XRD measurements were performed using a Rigaku III Dmax 2500 diffractometer with Cu radiation (35 kV, 25 mA). The equipment was fitted with a high-temperature attachment. The sample was placed in a platinum block sample holder and heated at 5°C/min to the desired temperature and held for 2 min before data collection. The development of the crystalline structure during isothermal crystallization was studied by scanning the sample at regular time intervals. After the crystallization was completed, the sample was cooled to room temperature and the change in the crystal structure was recorded by scanning at different temperatures during cooling.

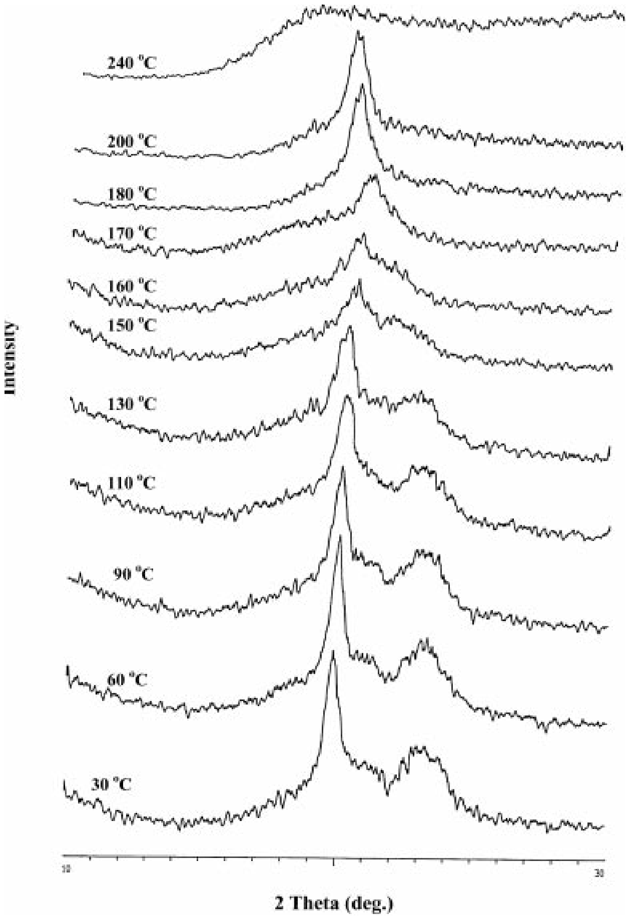

Fig. 1. XRD patterns of nylon 4 14 obtained on heating from room temperature (25°C) to melting temperature (240°C).

5. Results and discussion

5.1. Synthesis and characterization

Melt polymerization gives nylon 4 14 in an 85% yield. Elemental analysis: calculated for $C_{18}H_{34}N_2O_2$: C, 73.93%; H, 11.78%; N, 6.60%; O, 7.69%. Found: C, 73.93%; H, 11.84%; N, 6.63%; O, 7.58%. The measured intrinsic viscosity (0.60–0.80 dl/g) corresponds to a molecular weight range of 1.1×10^4–1.8×10^4 if the viscosimetric equation of nylon 6 6 [12] is applied for the calculation. The IR spectrum of nylon 4 14 shows characteristic amide and methylene absorption bands: 3301(N–H stretching), 3063 (overtone of N–H in plane bending), 2919 (C–H bending), 1635 (amide I), 1542 (amide II), 1273 (amide III), 946 (amide IV), 690 (amide V). The chemical shifts of the intense signals observed in the ^{1}H and ^{13}C NMR spectra are in full agreement with the anticipated chemical composition. Furthermore, no sign branching or irregularity is

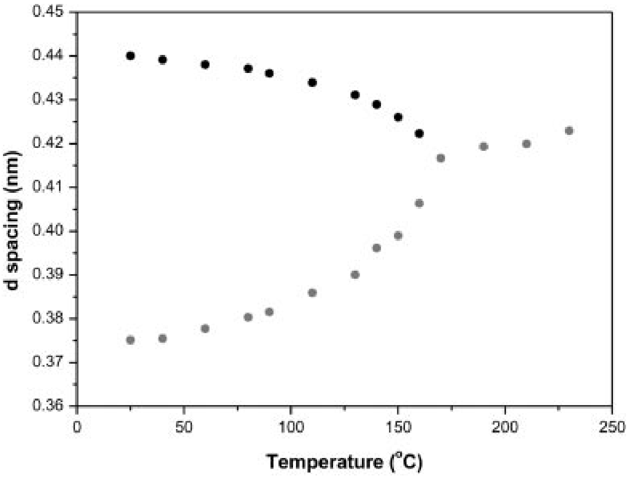

Fig. 2. Changes in diffraction spacings as functions of temperature.

detected in its NMR spectrum. The melting point was also determined by DSC to be 230°C which, not surprisingly, is slightly below the melting temperature reported for nylon 6 6 (252°C) and higher than that of nylon 10 10 (203°C). TGA shows the initial decomposition temperature is 420°C and the maximum decomposition temperature at 470°C, which are almost the same as those of nylon 6 6 [13].

5.2. Crystalline transition behaviors

The XRD patterns taken as a function of temperature for nylon 4 14 are shown in Fig. 1. The crystal structure of nylon 4 14 shows typical triclinic form [14] (α phase) with two strong reflections at room temperature, which are the characteristic projected inter-chain and inter-sheet diffraction signals at spacing 0.44 and 0.37 nm, respectively. With increasing temperature, these two reflections converge and merge into one peak at 170°C, which is the Brill transition temperature (T_B) for nylon 4 14. The transition behavior indicates the formation of the high-temperature pseudo-hexagonal γ modification [15]. The T_B of nylon 4 14 is a little higher than that of nylon 10 12 [16] (at about 120°C) and nylon 10 10 [17] (at about 135°C), and lower than that of nylon 6 6 [18] (at about 180°C). The changes in the spacings of the characteristic 100 and 010/110 diffraction signals as the functions of temperature are shown in Fig. 2. The 100 spacing (d_{100}), i.e. the distance between 100 planes, which is strongly fixed by the hydrogen bonds and hence is less sensitive to temperature variation, shows a slight decrease during the transition. On the contrary, $d_{010/110}$ (the inter-sheet distance) shows a dramatic increase with temperature and equals the value of d_{100} at the transition temperature. Above T_B, the d spacing slightly increases due to the normal thermal expansion.

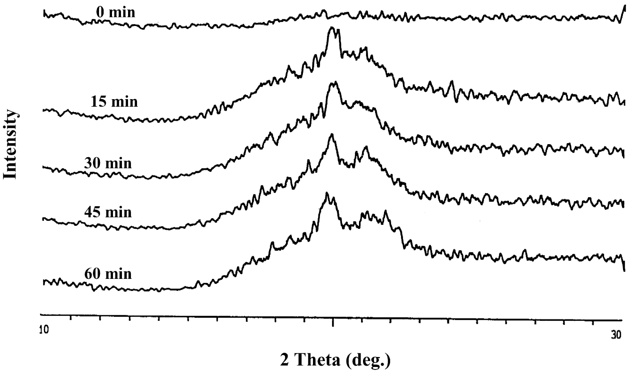

Fig. 3. XRD patterns of nylon 4 14 obtained during isothermal crystallization at 215°C.

After Brill transition was recorded on heating, the temperature was further increased to above the melting temperature of the sample, then cooled to 215°C for isothermal crystallization. Fig. 3 gives the XRD patterns obtained during isothermal crystallization at regular time intervals. The melted amorphous sample crystallized slowly with crystallization time, so the crystallization peaks developed gradually because of the small super cooling. The diffraction pattern shows two distinct crystalline peaks at $2\theta = 20.45°$ and $2\theta = 20.98°$, which correspond to the d spacings at 0.436 and 0.423 nm, respectively. The two peaks in the diffractograms indicate that the crystalline form is a kind of α phase. However, the high-temperature α structure is much different from the room temperature α phase because the two d spacings are very close. The fact that nylon 4 14 crystallizes directly into a kind of α phase at high temperature is similar to the crystallization behavior of nylon 10 10 [16] and nylon 6 12 [19]. However, it differs from nylon 6 6 [19] and nylon 10 12 [20] which always crystallize into a γ phase when crystallized at high temperature and then transform into α triclinic structure on cooling. The room temperature structure of nylon 4 14 is similar to the triclinic structure of nylon 6 6, but nylon 4 14 has a much different molecular structure since there are alternative short and long alkane segments between the amide groups. Therefore, the reason for the different crystallization behaviors

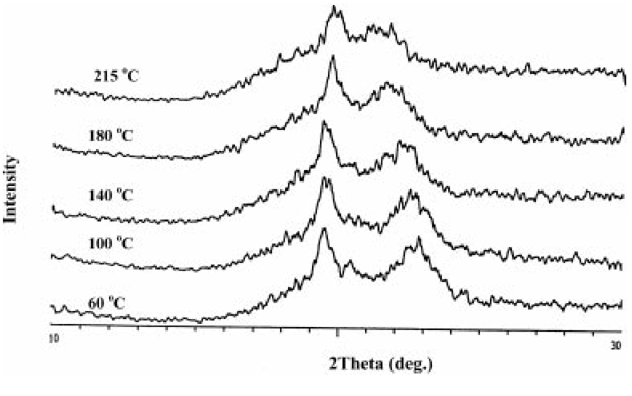

Fig. 4. XRD patterns of nylon 4 14 obtained on cooling from the isothermal crystallization temperature (215°C) to room temperature.

may be the effect of the motion of methylene segments between amide groups. It is commonly accepted that the crystalline transition is caused by the local melting of the methylene segments [20–22]. So it may be the different segment lengths and segment mobilities that bring about the different crystallization and transition behaviors. The intensity of the two peaks also increased with crystallization time (Fig. 3), as is expected because the crystallinity increased and the crystal became perfect. On cooling from the crystallization temperature, the two peaks are preserved, but start to move away from each other as shown in Fig. 4. Finally, the *d* spacings corresponding to the two peaks reach 0.37 and 0.44 nm, respectively, which is the typical reflection of the α phase structure of nylons.

6. Conclusions

A new nylon based on a short alkane diamine and a long alkane diacid was synthesized by melt polycondensation. The molecular weight of the synthesized nylon was about 15,000 g/mol. IR, NMR, DSC, and TGA were used to characterize the product. Variable-temperature XRD studies on crystallization transition show that the well-crystallized α form nylon 4 14 undergoes Brill transition at about 170°C. Much different from the crystallization behavior of nylon 6 6 and nylon 10 12, nylon 4 14 crystallizes directly into a kind of α crystal form if it is isothermally crystallized at high temperature, then the structure is transformed into the normal α form on cooling to room temperature.

Acknowledgement

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