Research Article

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Crystal transition and thermal behavior of Nylon 12

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Abstract: The polyamide 12 (PA12) with different crystal forms is prepared with three crystallization paths. The crystal structures and corresponding thermal properties are systematically investigated. The results reveal that an α-form and a mixed (α + γ)-form of PA12 can be obtained by casting at 30°C and (40–80°C), respectively. Meanwhile, the γ-form of PA12 can be obtained by both casting at 90°C and slow melt cooling. However, the γ’-form is obtained only by melt quenching. Both the γ and γ’ forms of PA12 exhibit a single melting peak, whereas the α-form exhibits two melting peaks. The higher peak is attributed to the melting of γ-PA12, which originates from the melting–recrystallization of the α-PA12. It is found that the tensile properties of PA12 depend on the crystal forms. Both the γ and γ'-PA12 are strong and tough polymer materials, while α-PA12 is a strong but brittle polymer material.

Keywords: PA12, crystal transition, thermal behavior

1 Introduction

A class of linear polymers containing repeated polarity amide group (–NHCO–) in the main chain is called polyamide (PA) (1). Nylon 12 (PA12) is an important material with excellent physical properties such as toughness, abrasion resistance, and good oil resistance, which are attributed to the amide groups in the molecular and the hydrogen bonds between the adjacent molecular chains (2–6). The crystal form of PA12 is similar to those of other polyamides, which mainly contain four kinds of crystal forms: α, α’, γ, γ’ (7). The α-form can be obtained under specific conditions, such as high pressure or drawing (8,9). The α-form of PA12 can be produced by cooling above 500 MPa from the melt or by annealing the γ'-form at high pressure (above 500 MPa). The γ-form can be obtained by drawing from the melt, annealing the α-form at high temperature (above 150°C), or annealing γ’-form above 110°C. Meanwhile, the structure of the γ’-form, similar to that of the γ-form, can be obtained by quenching from the melt (10), drawing the α-form above 70°C, or drawing the γ’-form above 50°C.

The γ-form with a hexagonal structure is the most common one and can be easily obtained. It was reported that the γ-form showed only one strong reflection with the d-spacing at about 0.42 nm (11,12). The monoclinic structure has been assigned to the α-form, which exhibits two distinct peaks corresponding to d-spacing at about 0.37 and 0.44 nm (10). The γ’-form can be regarded as variant of the γ-form due to the similar structure possessed by both γ’-form and γ-form (13). It must be noted that, the thermal treatment under pressure can transform the γ’ phase into the α phase. On the contrary, the γ-form cannot be transformed into the α-form even under high pressure (14,15).

One of the main characteristics of Nylons is the strong interchain interaction that arises from the hydrogen bonding between amide groups (16,17). Long-alkane-segment Nylons have high CH3/amide ratios. The hydrogen bond structures of α and γ forms in PA12 are
depicted in Figure 1. In the γ-form, the chains are aligned parallel and the full hydrogen bonding requires some twisting of the chains. The extended CH2 zigzags of each chain are in the plane of a molecular sheet, while the amide plane is twisted out of the polyethylene plane by about 60° (18). In the α-form, the molecular chains are antiparallel, and the full hydrogen bonding between extended chains can be easily attained (5,9).

Although the crystal formation conditions of PA12 and the transformation between different crystal forms have been well researched, the crystal structure characteristics under the application environment of less than 100°C are still unclear. This report is dedicated to studying the crystal structure and thermal properties of PA12, which undergoes the isothermal crystallization in the range from room temperature to the temperature close to the melting point. The PA12 samples were prepared by three methods: solution casting at different temperatures, slow melt cooling, and melt quenching. The crystal and chemical structure, thermal properties, and mechanical properties of prepared PA12 samples were, respectively, characterized by wide-angle X-ray diffraction (WAXD), Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and tensile tests, which may provide more theoretical support for the basic research and application of PA12.

2 Experimental

2.1 Materials and sample preparation

The PA12 pellets used in this work were purchased from Sigma-Aldrich and were dried at 80°C for 24 h in a vacuum oven to eliminate the moisture before processing.

The sample of solution casting was prepared by dissolving the PA12 in the phenol/ethanol (70/30) mixture. The concentration of solution was 40 mg/mL. In order to dissolve PA12 as soon as possible, an ultrasonic cleaner was used for 1 h. The casting temperature was selected at 30, 40, 50, 60, 80, and 90°C. The sample of melt cooling was obtained by cooling naturally from 220°C to room temperature. By contrast, the sample of melt quenching was prepared by cooling down rapidly in ice–water mixture from 220°C.

2.2 WAXD

The crystal structures were measured with a D8 DISCOVER diffractometer operated at 50 kV and 1,000 mA. The X-ray sources were nickel-filtered Cu Kα radiation (λ = 1.5418 Å). The WAXD data were collected from 3 to 32°. The specimens were fixed on the equipment with a hot stage and a hot-stretching stage.

2.3 DSC

The DSC (NETZSCH) thermograms of PA12 samples were measured from 5 to 220°C under nitrogen with a heating rate of 5°C/min.

2.4 FTIR

FTIR spectroscopy measurements were carried out with a Bruker TENSOR II FTIR spectrometer. The equipment was operated in transmission mode with 64 scans per sampling at a resolution of 4 cm⁻¹ in the wavenumber range between 4,000 and 400 cm⁻¹.

2.5 Tensile test

A dumbbell-shaped specimen was cut from the premade PA12 film. The tensile tests of tailored specimens were
conducted on a UTM6104. All tests were carried out at room temperature with a speed of 10 mm/min according to GB/T 1040.2-2006.

3 Results and discussion

3.1 The different crystal forms and crystal transition analysis

The 2D-WAXD patterns and the corresponding 1D-WAXD curves of PA12 with three different crystallization processes are shown in Figures 2 and 3, respectively. The d-spacings of the three PA12 forms calculated from Figure 3 are summarized in Table 1.

The sample obtained by solution casting at low temperature (30°C) shows a weak diffraction (002) at about 6.2° and two strong diffractions (200) and (010) at 20.2° and 23.1° (Figure 3a), corresponding to the triclinic α-form crystal (19). For the sample prepared by melt cooling (Figure 3b), two strong diffractions (020) and (001) and one weak diffraction (040) exist, belonging to the pseudohexagonal γ-form crystal. Two diffractions of (020) and (001) corresponding to the γ'-form can be observed in the sample prepared by melt quenching (Figure 3c). It can be seen clearly that the diffraction peak (040) of γ'-PA12 is more obvious than that of γ-PA12. In addition, the diffraction ring of γ-form is sharper than that of γ'-form, indicating the lower crystallinity of γ'-form that may be caused by the rapid freezing of the molecular chain and imperfect crystallization during melt quenching.

The 2D-WAXD patterns and the corresponding 1D-WAXD curves of PA12 at different casting temperatures are, respectively, shown in Figures 4 and 5. With the casting temperature increasing, the (200) and (010) planes gradually become blurred, and two new diffraction peaks of (001) and (020) planes appear (Figure 4). This change can be clearly seen in Figure 5. Only α-form

![Figure 2: The 2D-WAXD patterns of PA12 (a) α-form sample prepared by solution casting at 30°C, (b) γ-form sample prepared by melt cooling, and (c) γ'-form sample prepared by melt quenching.](image)

![Figure 3: The WAXD patterns of PA12 of (a) α-form sample prepared by solution casting at 30°C, (b) γ-form sample prepared by melt cooling, and (c) γ'-form sample prepared by melt quenching.](image)

![Table 1: The d-spacings of three different crystallization processes of PA12](table)
exists when the casting temperature is 30°C and the diffraction peaks from left to right are (002), (200), and (010), respectively. With the increase in casting temperature, the diffraction peaks (020) and (001) of γ-form appear and the intensity gradually increases, while the intensity of the diffraction peaks (200) and (010) of α-form gradually decreases, suggesting the existence of the mixed (α + γ)-form when the casting temperature is over 30°C. When the temperature increases to 80°C, a small amount of α-form still exists although the peaks are not visible, which is evidenced by the DSC results in Figure 7. At 90°C, only γ-form exists and the diffraction peaks from left to right are (020), (040), and (001), respectively. It can be concluded that it is difficult for the α-form to transform to the γ-form below the glass-transition temperature ($T_g$) of PA12 (around 50°C). However, this process can be accelerated by the segment motion beyond $T_g$.

The phenomenon of crystalline evolution of PA12 casting at different temperatures suggests the influence of molecular motion on crystallization. Solution crystallization mainly includes the following three steps (20). First, the solvent enters the polymer by diffusion. Then, the intermolecular force is broken by the interaction between the solvent and polymer, and the mobility of the segment is improved. Finally, if the interaction between the polymer and the solvent is sufficiently strong, the polymer molecular chain may undergo rearrangement into the crystal state. It is supposed that the formation of α-form takes place when the temperature is below $T_g$ (the glass-transition temperature of PA12 is around 50°C), and the rapid volatilization of solvent and high temperature above $T_g$ are beneficial to the appearance of the more stable γ-form (21).

3.2 Thermal properties

The DSC curves of PA12 obtained from three different crystallization processes are shown in Figure 6. It can be
observed that γ-form and γ’-form have only one melting endothermic peak. Interestingly, the α-form exhibits double melting endothermic peaks (Figure 6a), indicating the existence of either a mixed crystal structure of PA12 or a process related to melting–recrystallization during heating. It has been reported that α-form undergoes crystal transformation during the heating and melting process. After the α-form melts at 168.5°C, the molecular chain recombines and recrystallizes into the γ-form. Then the γ-form melts at 177°C, resulting in multiple melting behaviors (22). It can be calculated that the melting enthalpy of α-form, γ-form, and γ’-form is, respectively, 52.7, 51.6, and 43.4 J/g, and the crystallinity of those forms is 21.5%, 21.1%, and 17.7%, respectively. In conclusion, the α-form has a lower melting point than the γ-form and tends to transform into the γ-form during the heating process, which brings about the multiple melting behaviors in DSC.

Figure 7 shows the DSC thermograms of PA12 that are cast at different temperatures. The ratio of the melting enthalpy of the first melting endothermic peak at different casting temperatures is shown in Table 2. It can be observed that there are two melting endotherms in α and (α + γ) forms, hereafter identified as peak I (left) and II (right). The area of peak I decreases with an increase in casting temperature, whereas that of peak II increases. There are still two melting endotherms when the casting temperature rises to 80°C, indicating that a small amount of α-form still exists. At the casting temperature of 90°C, there is only one melting endotherm (peak II), suggesting that only γ-form is left. The above experimental results confirm the supposition that the α-form crystallization of PA12 takes place predominantly when the casting temperature is below $T_g$, while the more stable γ-form tends to appear above $T_g$ (23,24).

### Table 2: The ratio of enthalpy of fusion of the first melting endothermic peak of PA12 at different casting temperatures

| Casting temperature (°C) | 30 | 40 | 50 | 60 | 80 | 90 |
|---------------------------|----|----|----|----|----|----|
| The ratio of enthalpy of first melting endothermic peak (%) | 65.1 | 61.3 | 57.2 | 40.4 | 1.7 | 0 |

#### 3.3 Fourier transform infrared (FTIR) spectroscopy

The FTIR absorption spectra of PA12 from three different crystallization processes are demonstrated in Figure 8. The hydrogen-bonded N—H stretching at 3,299 cm$^{-1}$ in γ-PA12 and γ’-PA12 shifts to 3,315 cm$^{-1}$ in α-PA12 form. The moderate amide B bond at 3,098 cm$^{-1}$ in γ-PA12 and γ’-PA12 shifts to 3,092 cm$^{-1}$ with weak intensity in α-PA12 (25). The amide II band (C—N stretching vibration plus CO—NH bending) appears at 1,561 cm$^{-1}$ in γ-PA12, 1,557 cm$^{-1}$ in γ’-PA12, and 1,545 cm$^{-1}$ in α-PA12. The amide VI band (C=O out-of-plane bending) at 626 cm$^{-1}$ in γ-PA12 and γ’-PA12 shifts to 577 cm$^{-1}$ in α-PA12. The amide V band (N—H out-of-plane bending) at 680 cm$^{-1}$ is observed in α-PA12 but not in the γ and γ’ forms (21,26,27).

The FTIR diagrams of PA12 at different casting temperatures are shown in Figure 9. The characteristic peaks have some deviation in the different crystal forms.
The sample cast at 30°C shows the absorption bands at 680 and 577 cm\(^{-1}\), which are attributed to the \(\alpha\)-form. On the contrary, the absorption band at 624 cm\(^{-1}\) belonging to the \(\gamma\)-form does not appear. The sample cast at 90°C shows the characteristic bands of the \(\gamma\)-form. Samples cast at temperatures from 40°C to 80°C show the mixed patterns of \(\alpha\) and \(\gamma\) forms. The amide V band (N–H out-of-plane bending) at 680 cm\(^{-1}\) is observed in \(\alpha\) and \((\alpha + \gamma)\) forms but not in the \(\gamma\)-form. The amide VI band (C=O out-of-plane bending) at 626 cm\(^{-1}\) in \(\gamma\)-PA12 shifts to 577 cm\(^{-1}\) in \(\alpha\)-PA12, and the \((\alpha + \gamma)\)-form exhibits the amide VI band at 626 and 577 cm\(^{-1}\).

### 3.4 Mechanical properties

The mechanical properties of the three crystal forms of PA12 are shown in Table 3. The tensile strength of \(\gamma\)-PA12 is 44.1 MPa, and the elongation at break is 446%. Moreover, the tensile strength of \(\gamma\)-PA12 is 63.9 MPa, and the elongation at break is 618%. The high tensile strength and large elongation at break mean that the \(\gamma\)-PA12 and \(\gamma'\)-PA12 are strong and tough polymer materials. However, the tensile strength and the elongation at break of \(\alpha\)-PA12 are only separately 25.2 MPa and 18%, indicating that the \(\alpha\)-PA12 is a strong but brittle polymer material. The mechanical properties of \(\gamma\)-PA12 are better than those of \(\gamma'\)-PA12, which are mainly attributed to the most stable \(\gamma\)-form obtained by cooling slowly from the melt, where the molecular chains are closely arranged and the crystallinity is higher. The result is consistent with the conclusion that the \(\gamma\)-form is the most stable crystal phase for PA12 (28).

### 4 Conclusions

PA12 samples with different crystal forms prepared by solution casting, slow melt cooling, and melt quenching were investigated by WAXD, DSC, FTIR, and tensile test. It is found that the \(\gamma\)-form crystal of PA12 can be obtained by both slow melt cooling and casting at 90°C, whereas the \(\gamma'\)-form crystal of PA12 belonging to a metastable structure of the \(\gamma\)-form can be obtained by melt quenching. The \(\gamma\)-form and \((\alpha + \gamma)\)-form crystals of PA12 are, respectively, obtained by casting at 30°C and higher temperatures (from 40°C to 80°C). The \(\alpha\)-form of PA12 has a lower melting point than the \(\gamma\)-form and tends to transform into the \(\gamma\)-form on heating to the temperature near the melting point. The amide VI band (C=O bending) at 626 cm\(^{-1}\) in \(\gamma\)-PA12 and \(\gamma'\)-PA12 shifts to 577 cm\(^{-1}\) in \(\alpha\)-PA12. The amide V band (N–H bending) at 680 cm\(^{-1}\) is observed in \(\alpha\)-PA12 but not in \(\gamma\) and \(\gamma'\) forms. The tensile strength, elastic modulus, and elongation at break of \(\gamma\)-PA12 and \(\gamma'\)-PA12 are much larger than those

![Figure 8: The FTIR diagrams of PA12 (a) \(\alpha\)-form sample prepared by solution casting at 30°C, (b) \(\gamma\)-form sample prepared by melt cooling, and (c) \(\gamma'\)-form sample prepared by melt quenching.](image)

![Figure 9: The FTIR diagrams of PA12 at different casting temperatures.](image)

### Table 3: The mechanical properties of three different forms of PA12

| Sample | Tensile strength (MPa) | Elastic modulus (MPa) | Elongation at break (%) |
|--------|------------------------|-----------------------|-------------------------|
| \(\gamma\)-PA12 | 63.9 | 411.8 | 618 |
| \(\gamma'\)-PA12 | 44.1 | 325.7 | 446 |
| \(\alpha\)-PA12 | 25.2 | 308.5 | 18 |

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of α-PA12, in which the γ-PA12 and γ’-PA12 show strong and tough feature, whereas α-PA12 shows strong and brittle feature. It reveals that the different crystal forms of PA12 have different responses to the tensile properties. Therefore, it is possible to fabricate PA12 with advanced mechanical performance by tailoring the crystal forms.

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References
(1) Kinoshita Y. An investigation of the structures of polyamide series. Macromol Chem Phys. 1959;33(1):1–20.
(2) Marchildon K. Polyamides—still strong after seventy years. Macromol React Eng. 2011;5(1):22–54.
(3) Wang LH, Calleja FJB, Kanamoto T, Poter RS. The characterization and properties of Nylon 13,13. Polymer. 1993;34(22):4688–91.
(4) Prieto A, Iribarren I, Muñoz-Guerra S. Structural studies of Nylon 13, 13. J Mater Sci. 1993;28(15):4059–62.
(5) Jiang T, Liu M, Fu P, Wang YD, Fang YL, Zhao QX. Melting behavior, isothermal and nonisothermal crystallization kinetics of Nylon 1111. Polym Eng Sci. 2009;49(7):1366–74.
(6) Cui X, Li W, Yan D. Investigation of odd–odd nylons based on undecanedioic acid. 2: Crystal structures. Polym Eng Sci. 2005;45(12):1673–9.
(7) Mathias LJ, Johnson CG. Solid-state NMR investigation of Nylon 12. Macromolecules. 1991;24(13):6114–22.
(8) Ramesh C. Crystalline transitions in Nylon 12. Macromolecules. 1999;32(17):5704–6.
(9) Kamal T, Park SY, Park JH, Chang YW. Structural evolution of poly(ether-b-amide) elastomers during the uniaxial stretching: An in situ wide-angle X-ray scattering study. Macromol Res. 2012;20(7):725–31.
(10) Aharoni SM. n-Nylons: their synthesis, structure and properties. Chichester: John Wiley & Sons; 1997; Chapters 1.3 and 2.12.
(11) Li L, Koch MHJ, de Jeu WH. Crystalline structure and morphology in Nylon-12: a small- and wide-angle X-ray scattering study. Macromolecules. 2003;36(5):1626–32.
(12) Wang D, Shao C, Zhao B, Zhao BJ, Bai LG, Wang X, Yan TZ. Deformation-induced phase transitions of polyamide 12 at different temperatures: an in situ wide-angle X-ray scattering study. Macromolecules. 2010;43(5):2406–12.
(13) Murthy NS. Hydrogen bonding, mobility, and structural transitions in aliphatic polyamides. J Polym Sci Part B (Polym Phys). 2006;44(13):1763–82.
(14) Hiramatsu N, Haraguchi K, Hirakawa S. Study of transformations among α, γ and γ’ forms in Nylon 12 by X-ray and DSC. Japanese J Appl Phys. 1983;22(2R):335.
(15) Hiramatsu N, Hashida S, Hirakawa S. Formation of α form Nylon 12 under high pressure. Japanese J Appl Phys. 1982;21(4R):651.
(16) Botta A, de Candia F, Palumbo R. Glass transition in aliphatic polyamides. J Appl Polym Sci. 1985;30(4):1669–77.
(17) Cannon CG. The infra-red spectra and molecular configurations of polyamides. Spectrochim Acta. 1960;16(3):302–19.
(18) Arimoto H, Ishibashi M, Hirai M, Chatani Y. Crystal structure of the γ-form of Nylon 6. J Polym Sci Part A Gen Pap. 1965;3(1):317–26.
(19) Fernández CE, Bermúdez M, Versteegen RM, Meijer EW, Vancso GJ, Muñoz-Guerra S. An overview on 12-polyurethane: synthesis, structure and crystallization. Eur Polym J. 2010;46(11):2089–98.
(20) Desai AB, Wilkes GL. Solvent-induced crystallization of polyethylene terephthalate. J Polym Sci Polym Symp. 2010;46(1):291–319.
(21) Ishikawa T, Nagai S, Kasai N. Effect of casting conditions on polymorphism of Nylon-12. J Polym Sci Polym Phys Ed. 1980;18(2):291–9.
(22) Ishikawa T, Nagai S, Kasai N. Thermal behavior of α-Nylon-12. J Polym Sci Polym Phys Ed. 1980;18(6):1413–19.
(23) Ishikawa T, Sugiura A, Hamada T, Nagai S, Yasuoka N, Kasai N. Change of fine texture of Nylon 12 by drawing. Nippon Kagaku Kaishi. 1973;9:1744–51.
(24) Gordon GA. Glass transition in nylon. J Polym Sci Part A-2 Polym Phys. 1971;9(9):1693–702.
(25) Miyazawa T. The characteristic band of secondary amides at 3100 cm⁻¹. J Mol Spectros. 1960;4(1):168–72.
(26) Simak VP. Spektroskopische untersuchungen der kristallinen modifikationen von polyamid-6. Appl Macromol Chem Phys. 1973;28(1):75–85.
(27) Abu-Isa I. α-γ transition in Nylon 6. J Polym Sci Part A-1 Polym Chem. 1971;9(1):199–216.
(28) Gogolewski S, Czernawska K, Gastorek M. Effect of annealing on thermal properties and crystalline structure of polyamides. Nylon 12 (polylaurolactam). Colloid Polym Sci. 1980;258(10):1130–6.