

# Crystallization and Crosslinking of Polyamide-1010 under Elevated Pressure

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**ABSTRACT:** The structure and thermal properties of polyamide-1010 (PA1010), treated at 250°C for 30 min under pressures of 0.7–2.5 GPa, were studied with wide-angle X-ray diffraction (WAXD), infrared (IR), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). Crystals were formed when the pressures were less than 1.0 GPa or greater than 1.2 GPa. With increasing pressure, the intensity of the diffraction peak at approximately 24° was enhanced, whereas the peak at approximately 20° was depressed. The triclinic crystal structure of PA1010 was preserved. The highest melting temperature of the crystals obtained in this work was 208°C for PA1010 treated at 1.5 GPa. Crosslinking occurred under pressures of 1.0–1.2 GPa. Only a broad diffraction peak centered at approximately 20° was observed on WAXD patterns, and no melting and crystallization peaks were found on DSC curves. IR spectra of crosslinked PA1010 showed a remarkable absorption band at 1370 cm<sup>-1</sup>. The N—H stretching vibration band at 3305 cm<sup>-1</sup> was weakened. Crystallized PA1010 had a higher thermal stability than crosslinked PA1010, as indicated on TGA curves by a higher onset temperature of decomposition. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2522–2527, 2002

**Key words:** polyamide-1010 (PA1010); crystallization; crosslinking; high pressure; annealing

## INTRODUCTION

High pressure is an extremely physical measure that can change the distance between atoms efficiently. It can help people to understand physical phenomena and material properties of atmospheric pressure at a deep level and find new phenomena, new laws, and new materials pro-

duced under high pressure. Wunderlich<sup>1</sup> first introduced high pressure to the crystal growth of polymers in 1962. He found that fully chain-extended crystal grew when polyethylene crystallized under 0.5 GPa and that the crystal was up to 3.0 μm thick. This kind of crystal showed excellent mechanical properties in comparison with general polymeric crystals formed under ambient pressure. Since then, the study of polymers crystallized or annealed under high pressure has attracted much attention.<sup>2–5</sup>

Gogolewsky and Pennings<sup>6–10</sup> extensively investigated the structure and thermal properties of polyamides crystallized under high pressure in the 1970s. For polyamide-6,<sup>6,8,11</sup> pressure gave rise to an increase in the crystallite dimensions

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and a decrease in the distance between crystal planes, but the crystal form was preserved. The highest melting temperature ( $T_m$ ) and heat of fusion ( $\Delta H_m$ ) found for pressure-crystallized samples were 256°C and 37 cal/g, respectively. The higher  $T_m$  and  $\Delta H_m$  values were attributed to the growth of chain-extended crystal during the crystallization of polyamide-6 under pressure. Chain extension may be achieved by a transamidation reaction<sup>6</sup> between the —CO—NH— groups of the broken folds of adjacent lamellae.

For polyamide-11,<sup>9</sup> chain-extended crystal was obtained by pressure-induced crystallization from the melt or by annealing of the folded-chain crystals. The highest  $T_m$  and  $\Delta H_m$  values were found to be 226°C and 35 cal/g, respectively. Moreover, the crystal structure of folded-chain crystals of polyamide-11 was preserved in high-pressure crystallization and annealing experiments. However, crystallization from the melt or annealing over 320°C at 10 kbar resulted in crosslinking of the polymer.

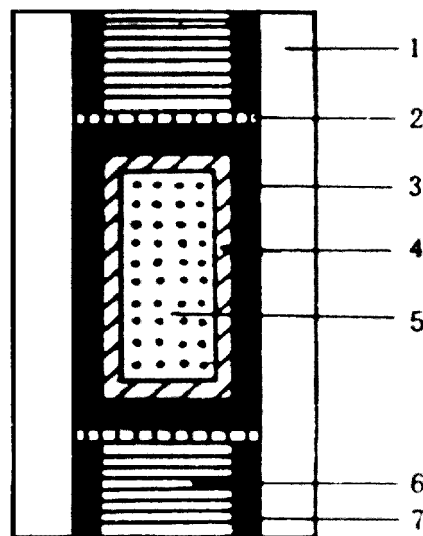
As for polyamide-12,<sup>10</sup> crystallization and annealing under pressure led to a partial transformation of the pseudohexagonal or monoclinic crystal structure to an  $\alpha$  modification.  $\Delta H_m$  was enhanced from 16 to 32 cal/g and  $T_m$  was increased from 179 to 209°C with annealing under 4.9 kbar at 260°C for 336 h. Under the same conditions used for polyamide-11, annealing caused efficient crosslinking of polyamide-12.

Polyamide-1010 (PA1010) is one of the most important polyamide engineering plastics specifically produced commercially in China. In addition to a combination of high strength, toughness, and abrasion resistance that it has in common with other polyamides, it features lower moisture absorption and, therefore, higher dimensional stability. The crystal structure and thermodynamic parameters of PA1010 have been investigated.<sup>12–15</sup> However, the structure and thermal behavior of PA1010 crystallized under high pressure are still debated. In this work, the structure of PA1010 samples treated at 250°C under various pressures for 30 min were studied with wide-angle X-ray diffraction (WAXD) and infrared (IR). The thermal properties were investigated with differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

## EXPERIMENTAL

### Materials and Sample Preparation

The PA1010 used in this work was a granular commercial product of Jilin Chemical Corp. (Jilin City,



**Figure 1** Cross section of the high-pressure cell assemblage: (1) pyrophyllite cylinder, (2) molybdenum foil, (3) graphite heater, (4) h-BN capsule, (5) starting material, (6) pyrophyllite, and (7) steel current.

China). The viscosity-average molecular weight was  $1.34 \times 10^4$ . The PA1010 pellets were dried in a vacuum oven at 80°C for 24 h before use and then extruded into a glass tube on a Brabender single-screw extruder (Germany) at 200°C. The inner diameter of the glass tube was 6.0 mm. The surface of molded PA1010 strips was smooth, and the strips were machined into  $\Phi 6 \times 8$  mm cylinders, which well fit the cell in the high-pressure apparatus.

### Treatment under High Pressure

High-pressure experiments were carried out on a  $4.9 \times 10^6$  N belt-type high-pressure apparatus. A cross section of the high-pressure cell assemblage is shown in Figure 1. A capsule of hexagonal boron nitride (h-BN) was 6.0 mm in inner diameter and 8.0 mm in height for sample holding. The capsule was inserted into a pyrophyllite cylinder and was then subjected to high pressure. h-BN was used to prevent the migration of Si and Al from the pyrophyllite to the sample.

The magnitude of the pressure generated inside the cell was determined by a calibration curve, which was established by the determination of the applied loads corresponding to the phase-transformation pressures of bismuth, thallium, and barium. The temperature of the sample was controlled by the electric power supplied through the carbon heater and was calibrated by the insertion of a Pt30%Rh70%–Pt16%Rh84% thermocouple in the cell.

The samples were first pressurized to a high pressure and then heated to 250°C. After the desired pressure and temperature conditions were maintained for 30 min, the sample was quenched to room temperature before the release of the applied pressure. The final sample was designated according to the pressure at which it was treated; for example, Pa0.7g represents the sample treated under 0.7 GPa.

### Structural Characterization

X-ray diffraction measurements were carried out on a PW1700 Philips diffractometer (The Netherlands) with Cu K $\alpha$  Ni-filtered radiation over the diffraction-angle ( $2\theta$ ) range of 5–50°. The conditions of the experiments were as follows: the voltage was 40 kV, the current was 20 mA, and the scan speed was 4°/min.

IR spectra were recorded on a Nicolet Magna-IR 560 spectrometer (USA) equipped with thunderdom in the range of 675–4000 cm<sup>-1</sup>. The resolution was 4.0, the sample gain was 1.0, and a deuterated triglycine sulfate (DTGS) KBr detector was used.

### Thermal Analysis

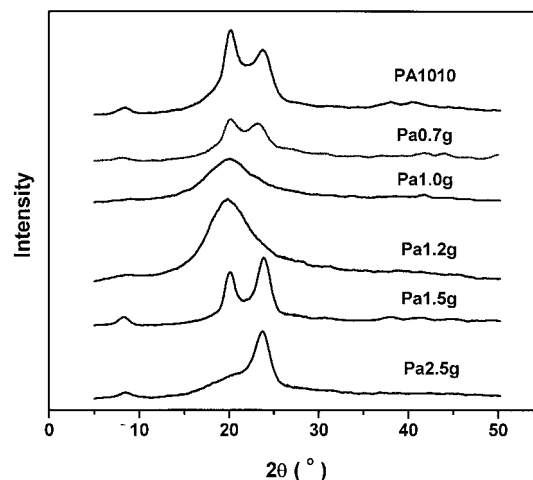
DSC measurements were performed on a PerkinElmer DSC-7 (USA) calibrated with indium and zinc standards under a nitrogen atmosphere. The scanning speed was 10°C/min.

TGA was carried out under a nitrogen flow (20 mL/min) with a PerkinElmer TGA-7 thermoanalyzer. Samples (ca. 2.0 mg) were heated from 20 to 600°C at a heating rate of 10°C/min.

## RESULTS AND DISCUSSION

### Effect of Pressure on the Structure

WAXD is commonly employed for comparative studies of the crystal form, unit cell, crystallinity, and crystallite dimensions of polymer samples crystallized under various conditions. The position, intensity, width, and number of diffraction peaks on WAXD patterns are the basic parameters for determining the crystal structure. The crystal structure of PA1010 annealed under atmospheric pressure was studied by Mo et al.<sup>12</sup> They found that the crystal structure of PA1010 belongs to the triclinic system. Three characteristic diffraction peaks of about  $2\theta = 8.5$ , 20, and 24° were observed on WAXD patterns, corresponding to the diffraction of the 002, 100, and

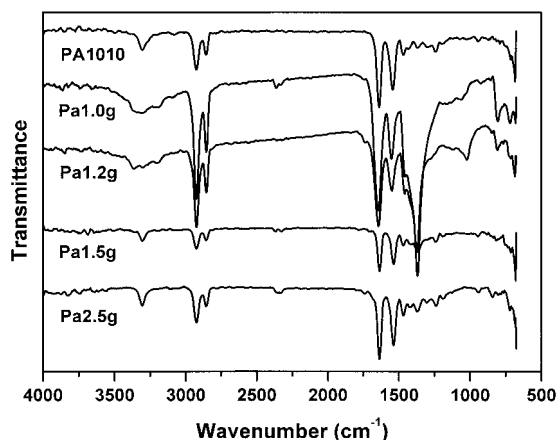


**Figure 2** WAXD patterns of PA1010 samples treated at 250°C for 30 min under various pressures.

010 planes, respectively. From a model of the structural arrangement of molecular chains in the PA1010 crystal, they concluded that the 010 plane contains hydrogen bonds and the 100 plane is absent from hydrogen bonding.

Figure 2 gives the WAXD patterns of PA1010 treated under different pressures at 250°C. Characteristic diffraction peaks of PA1010 can be observed for high-pressure-treated samples, except for samples Pa1.0g and Pa1.2g. With increasing pressure, the intensity of the peak at 23.5° is enhanced and that of the peak at 20.5° is decreased. Similar results were also reported for polyamide-6,<sup>7</sup> polyamide-11,<sup>9</sup> and polyamide-12.<sup>10</sup> For Pa2.5g sample, the diffraction of the 100 plane is depressed nearly thoroughly. At the same time, a shifting of the three peaks in the direction of higher angles, as for virgin PA1010, was noticed, indicating smaller spacing between crystal planes and dense packing of PA1010 chains in the crystal lattice. These experimental facts indicate that the annealing of PA1010 under high pressure improved the crystal structure but that the crystal form of the triclinic system was unchanged.

For PA1010 samples treated under 1.0 and 1.2 GPa, only broad peaks are observed in Figure 2, indicating that no crystal grew during annealing under these pressures. The two samples were insoluble in any solvent such as formic acid, which is suitable for PA1010. The facts indicate that crosslinking occurred when PA1010 was treated in the pressure range of 1.0–1.2 GPa at 250°C for 30 min. This phenomenon of crosslinking was also reported for polyamide-11<sup>9</sup> and polyamide-12<sup>10</sup>



**Figure 3** IR spectra of PA1010 samples treated at 250°C for 30 min under various pressures. The spectrum of Pa0.7g was similar to that of PA1010 and was omitted for clarity.

treated at 320°C and 1.0 GPa by Gogolewski and Pennings, and it seemed that crosslinking occurred at the highest value of the pressures achieved in their experiments. In our work, one may infer that crosslinking occurred in a certain pressure range and crystallization grew again when the pressure was beyond that range.

Additional information on the structural changes of PA1010 can be obtained from the IR analysis. Figure 3 shows the IR spectra of PA1010 samples treated under different pressures at 250°C. All the samples exhibited the characteristic absorption bands of polyamides. These are the asymmetric and symmetric vibrations of  $\text{CH}_2$  groups at 2924 and 2855  $\text{cm}^{-1}$ , respectively; the stretching vibration of  $\text{C}=\text{O}$  (amide I) at 1642  $\text{cm}^{-1}$ ; the combination of  $\text{N}-\text{H}$  bending and  $\text{C}-\text{N}$  stretching vibrations (amide II) at 1550  $\text{cm}^{-1}$ ; and the combination of  $\text{C}-\text{N}$  stretching and  $\text{N}-\text{H}$  bending vibrations (amide III) at 1240  $\text{cm}^{-1}$ . Except for samples Pa1.0g and Pa1.2g, the  $\text{N}-\text{H}$  stretching vibration at 3305  $\text{cm}^{-1}$  can be observed clearly in Figure 3. This peak can focus the information about hydrogen bonding. The formation of hydrogen bonding facilitates the crystallization of polyamides. This means that crystal has grown in these samples of PA1010 treated at pressures less than 1.0 GPa or greater than 1.2 GPa; this agrees with the WAXD results. In the IR spectra of Pa1.0g and Pa1.2g, the intensity of this peak is weakened and broadened, indicating that most of the hydrogen bonds have been destroyed.

Another absorption band was noticed at 1370  $\text{cm}^{-1}$ . For Pa1.0g and Pa1.2g samples, the absorp-

tion band was enhanced significantly; however, it is negligible for the crystallization samples. The peak is usually assigned to the  $\text{CH}_3$  bending vibration in standard IR spectra of polyamides.<sup>16</sup> Both polylactams and diacid-diamine-type nylons tend to decompose when subjected to a thermal treatment. Polylactams tend to re-equilibrate to monomeric or oligomeric cyclic products. Diacid-diamine-type nylons produce mostly linear or cyclic oligomeric fragments and monomeric units.<sup>17,18</sup> Therefore, it has been postulated that numerous molecules of low molecular weight were created in the amorphous PA1010 formed under these pressures with a crosslinking structure, and abundant methyl groups accompanied them.

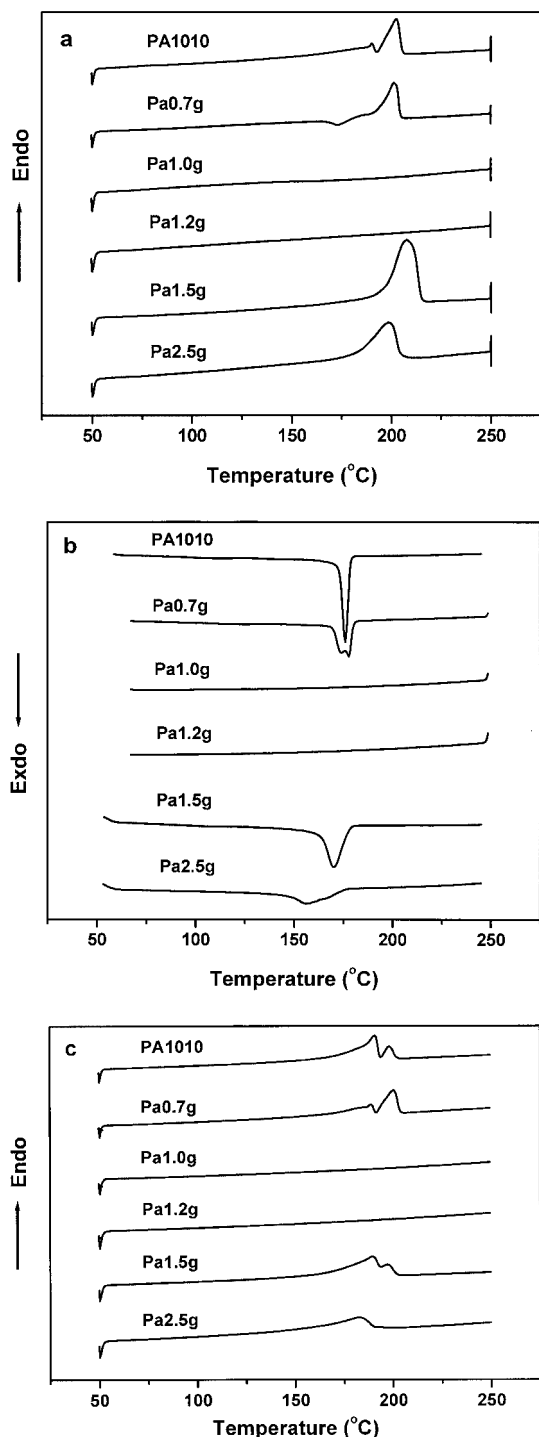
### Analysis of the Thermal Properties

Figure 4 shows the melting and crystallization curves of PA1010 samples treated under different pressures. The curves were obtained by the heating of samples from 50 to 250°C to record the first melting curves [Fig. 4(a)]. The samples were held at 250°C for 10 min and then were cooled to room temperature at 10°C/min to record the crystallization curves [Fig. 4(b)]. Finally, they were heated to 250°C again to record the second melting curves [Fig. 4(c)] at the same scanning speed. All the experiments were performed under the protection of a nitrogen atmosphere.

The crystallization and melting behaviors of PA1010 crystallized under atmospheric pressure have been studied.<sup>19,20</sup> For PA1010 crystallized isothermally from the melt, a single crystallization peak was observed. The crystallization peak shifted to a lower temperature, and the original sharp peak broadened with an increasing cooling rate. PA1010 exhibited multiple melting behavior. Experimental results indicated that the sample underwent a process of continuous melting and recrystallization during DSC scanning. PA1010 contained a distribution of crystallites of different degrees of perfection that was strongly dependent on its previous thermal history.

As shown in Figure 4(a), PA1010 exhibits double melting peaks. The peak located at 190°C is the melting of unstable crystals, and that of 203°C is the melting of more stable crystals. Between the two melting peaks, a recrystallization peak can be observed.  $T_m$  of Pa0.7g was lowered to 201°C, and a cold-crystallization peak was observed at 173°C. When the pressure increased to 1.5 GPa,  $T_m$  increased to 208°C. That is the high-





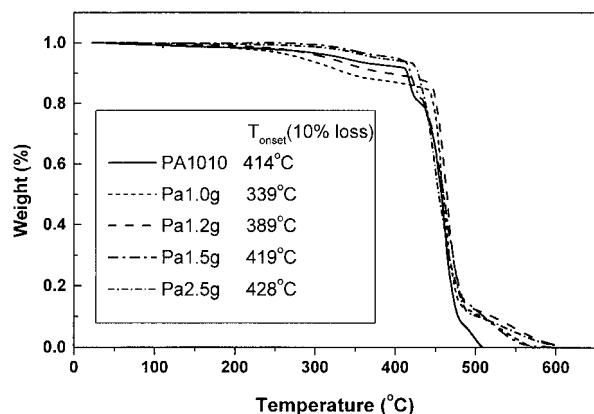
**Figure 4** DSC curves of PA1010 samples treated at 250°C for 30 min under various pressures at a scanning speed of 10°C/min: (a) the first heating runs, (b) the cooling runs, and (c) the second heating runs.

est value of  $T_m$  obtained in this work. However, one cannot infer from the 5°C increase in  $T_m$  that extended-chain crystals grew in PA1010. This means that at this pressure and temperature, the

folded chains of PA1010 were extended and the thickness of lamellae was increased. When the pressure approached 2.5 GPa, the motion of PA1010 chains was restricted and less thick lamellae were formed, leading to a lower  $T_m$  value of 199°C. Only one broad melting peak is shown for Pa1.5g and Pa2.5g, which means that pressure leads to a higher perfection of crystallization. For samples Pa1.0g and Pa1.2g, no melting peaks were found.

As shown in Figure 4(b), PA1010 exhibits one sharp crystallization peak at 176°C, whereas Pa 0.7 g shows two overlapping peaks at 174 and 178°C, respectively. When the pressure is greater than 1.2 GPa, the crystallization peaks were broadened and shifted to lower temperatures, indicating that the supercooling of high-pressure-treated PA1010 was increased. For Pa1.0g and Pa1.2g, crystallization peaks were not found. The aforementioned results led to the conclusion that crosslinking occurred in PA1010 during annealing under pressures of 1.0 and 1.2 GPa. For polyamide-11<sup>9</sup> and polyamide-12,<sup>10</sup> Gogolewski and Penning also noticed this phenomenon of crosslinking. However, in their studies, crosslinking occurred at upper limitation values of temperature and pressure, that is, at 320°C and 10 kbar. In this work, for PA1010 crosslinking occurred at a relatively lower temperature (250°C) and lower pressures.

The melting behaviors in the second heating scan of the samples in DSC pans were quite different from those in the first heating scan [Fig. 4(c)]. Significant evidence of this is that the melting peak was split into double peaks for PA1010 crystallized under pressures of 0.7, 1.5, and 2.5 GPa on the DSC melting curves. Their values of  $T_m$  and main features are similar to those of PA1010 crystallized under atmospheric pressure, indicating that the effect of the pressure disappeared when these samples of PA1010 were molten. However, the thermal behaviors of Pa1.0g and Pa1.2g did not change at all during the heating of the samples because the crosslinking structure in PA1010 was not recovered. An identical procedure of DSC measurement was performed also for the PA1010 sample quenched under atmospheric pressure. Both melting peaks and crystallization peaks were observed. This indicates that temperature cannot lead to the crosslinking of PA1010 under the experimental conditions. The pressure factor should be taken into account. Although the results of the crosslinking of PA1010 have good reproducibility, the exact



**Figure 5** TGA curves in  $N_2$  for PA1010 samples treated at 250°C for 30 min under various pressures at a heating rate of 10°C/min. The curve of Pa0.7g was omitted for clarity.

structure and mechanism of crosslinking are unknown.

The thermal stability of both virgin and high-pressure-treated samples was characterized by TGA. The thermal stability in terms of the onset temperature of degradation is usually measured as the temperature at which 10% degradation occurs. Figure 5 shows the TGA curves of various samples at a heating rate of 10°C/min under a nitrogen atmosphere. The shape of the curves of high-pressure-treated samples is little changed from that of virgin polymer. As shown in Figure 5, the onset of degradation occurs earlier in crosslinked PA1010 than in the virgin polymer, probably because of the formation of some low molecular weight fragments in the crosslinking process. The high-pressure-crystallized PA1010 has a higher onset temperature of degradation. Crystallized samples seem to have a higher thermal stability than crosslinked samples. However, the degradation of crosslinked PA1010 is retarded to a slightly higher temperature as the temperature increases. This indicates that after the loss of low molecular weight fragments, the thermal stability of crosslinked PA1010 is enhanced.

## CONCLUSIONS

Obviously, structural changes in PA1010 were found when the polymer was treated at 250°C for 30 min under pressures of 0.7–2.5 GPa. Crystals grew when the pressures were less than 1.0 GPa or greater than 1.2 GPa, and crosslinking occurred in the pressure range of 1.0–1.2 GPa. WAXD patterns

of crystallized PA1010 samples in this work are similar to those of high-pressure-crystallized polyamides reported in the literature. The  $T_m$  value of crystallized PA1010 was slightly increased in comparison with the  $T_m$  value of virgin PA1010. However, no chain-extended crystal was detected. Crosslinked PA1010 showed no endothermic and exothermic peaks on DSC curves and no WAXD diffraction peaks, unlike virgin PA1010. The facts indicate that PA1010 lost its crystallization ability after treatment in the pressure range of 1.0–1.2 GPa. Crystallized PA1010 exhibited a higher thermal stability than crosslinked PA1010 when used at 400°C. However, the mechanism of the crosslinking of PA1010 under high pressure requires further investigation, which will be reported in a future article.

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