High-Flow Nylon 6 by *In Situ* Polymerization: Synthesis and Characterization

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ABSTRACT: A new synthetic strategy for high-flow nylon 6 was developed in this article. Generation 1, 2, 3 (G1, G2, G3) polyamidoamine (PAMAM) dendrimers reacted with *p*-phthalic acid by equimolar terminal groups in water solution, respectively, and mother salt solution was then prepared. The high-flow nylon 6 was prepared with suitable quantity of mother salt solution, end-capping agent, and ε-caprolactam by *in situ* polymerization. Blue shifts are found for the peaks of NH (γN—H and 2δN—H) of the high-flow nylon 6 compared with pure nylon 6 in the IR spectra. Comparing with the pure nylon 6, the high-flow nylon 6 containing low content of PAMAM units, has high-flow property and almost the same mechanical property. The high-flow nylon 6 with low content of PAMAM units has greater melt-flow index (MFI) (the value of MFI increased by 70–90%). Hardly any decrease in the tensile strength is observed with the elongation at break decreasing by 20–35%. But the izod impact strength of the high-flow nylon 6 increases. The SEM images show that the high-flow nylon 6 presents brittle fracture with conglomeration-like structure, while pure nylon 6 exhibits plastic fracture with island-like structure. DSC thermograms of nonisothermal crystallization exhibit that the peak of high-flow nylon 6 broadens compared with pure nylon 6, and the broader peak means the wider processing temperature. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 2365–2372, 2008

Key words: nylon 6; processing; high flowability; PAMAM dendrimers

INTRODUCTION

Nylon with high flowability was often used in molded products of small parts with thin walls or precision parts, which has attracted a great deal of interest over several decades. Koning et al. improved the flow behavior of a high-molecular-weight polyamide composition by melt-mixing a high-molecular-weight polyamide and a polyamide oligomer having a melting point higher than that of the high-molecular-weight polyamide.[1] Miyabo prepared a polyamide resin composition with high-flow property, containing a polyamide resin, a metal oxide, and aliphatic dicarboxylic acid monomer.[2] Several works showed that high-flow polyamides were almost prepared by melting blend, and the flow behavior was improved by feeding low content of organic, inorganic, or oligomer components and so on; unfortunately, it might be hard to maintain their mechanical properties.[1–6]

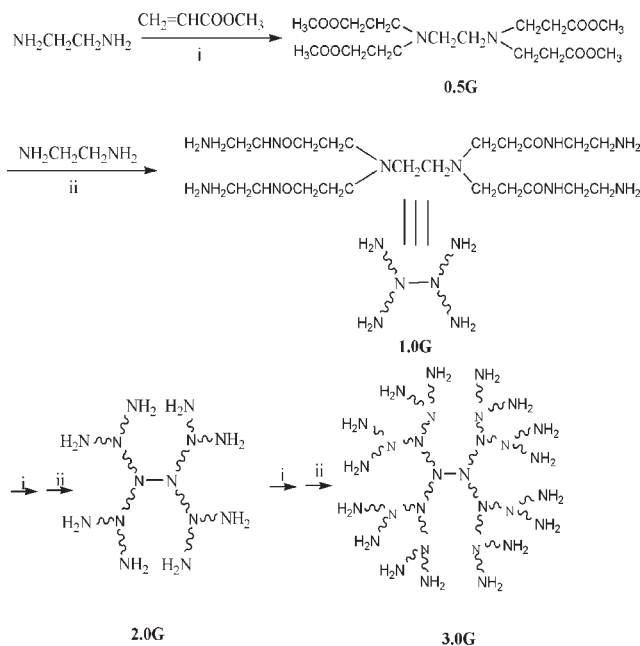Over the past two decades, polyamidoamine (PAMAM) dendrimers have been paid more and more attention due to their unique features such as three-dimensional architecture, low intrinsic viscosity, good solubility, and high reactivity because of the presence of large amount of terminal functional groups.[7–15] It is of no doubt that the research is among the fastest developing varieties, and the research efforts in this field have mushroomed in recent years.[16–25] PAMAM dendrimers, which are based on an ethylenediamine core and prepared from the reaction between methyl acrylate and ethylenediamine, have attracted much more attention for their many potential applications, including nanoscale catalysts,[26–28] reaction vessels,[29] drug or gene carriers,[30–37] chelating agent,[38] building blocks for assembly nanoconjugates,[39] and so forth. But few applications have been found in plastic engineering area.

Warakomski prepared star-branched nylon 6 via cationic polymerization, using amine end groups as initiator. This star-shaped polyamide exhibited characteristic low viscosity in the melt and in solution and provided advantages in processing such as injection and blending.[40] Traditionally, cationic polymerization should proceed free of water, as a result, its industrial production on a large scale may not easily come true. However, his research gives us quite a considerable guide to improve the processing of nylon 6.

A new strategy was developed for preparation of high-flow nylon 6 on a large scale. It was done by

Scheme 1 Synthesis route for PAMAM dendrimers.

two steps: (i) Generation 1, 2, 3 (G1, G2, G3) PAMAM dendrimers reacted with *p*-phthalic acid by equimolar terminal groups in water solution at 50–80°C, respectively, and mother salt solution was then prepared, (ii) ε-caprolactam, end-capping agent (acetic acid) and suitable content of the salt solution of PAMAM dendrimers were charged in an autoclave; the high-flow nylon 6 was then synthesized according to the same process as pure nylon 6.

To our knowledge, high-flow nylon 6 containing low content of PAMAM units via *in situ* polymerization was first prepared with mother salt solution, end-capping agent and ε-caprolactam. A new question might be asked: why mother salt not PAMAM dendrimers were used as material? To answer this question, thermo gravimetric analysis (TGA) was carried out. Another kind of nylon 6 was also prepared with G2 PAMAM dendrimers, end-capping agent, and ε-

caprolactam by *in situ* polymerization for comparison. Melt flow index (MFI), FTIR spectra, mechanical properties, scanning electron microscopy (SEM), and differential scanning calorimetry (DSC) were reported.

EXPERIMENTAL

Materials

Ethylenediamine (EDA), methanol, acetic acid, and methyl acrylate (MA) were purchased from Shanghai Reagents Company. *p*-Phthalic acid and ε-caprolactam were supplied by Shijiazhuang Chemical Fiber Co. Methyl acrylate (MA) was purified under reduced pressure before use.

Preparation of mother salt solution

Generation 1, 2, 3 (G1, G2, G3) PAMAM dendrimers can be easily prepared according to the procedures described in the literature.[16,18,41,42] Scheme 1 is the depiction of the typical synthesis process.

A typical example of the preparation of mother salt solution is given as follows (the preparations of all mother salt solution were carried out in a similar manner): PAMAM G1 (3.5 g, 0.0062 mol) dissolved in 10 mL distilled water was added into the solution of *p*-phthalic acid (2.1 g, 0.0124 mol) and distilled water(10–20 mL); the mixture was stirred at 50–80°C for 45 min, thus the mother salt solution was prepared and directly used for next preparation of high-flow nylon 6. The feed compositions of all mother salt solutions are detailed in Table I.

Preparation of high-flow nylon 6, LAP6, and BPAG2/0.5 by *in situ* polymerization

Typically (a sample of BPAG1*0.5 preparation in Table I), mother salt solution (25.6–35.6), acetic acid (2.1 g), and ε-caprolactam (694.4 g) were added into a 2-L autoclave. The autoclave was then placed under vacuum and crushed with high-purity nitrogen thrice to remove any air. Then, the temperature was elevated

TABLE I
Detailed Feed Composition of Different Nylon 6 Samples

| Sample[a,b] | ε-caprolactam (g) | Mother salt solution | | |
		PAMAM (g)	*p*-phthalic acid (g)	Distilled water (g)
LPA6	700.0	0.0	0.0	21
BPAG1*0.5	694.4	3.5 (G1)	2.1	20–30
BPAG2*0.5	694.9	3.5 (G2)	1.6	20–30
BPAG3*0.5	695.6	3.5 (G3)	1.1	20–30
BPAG2*0.3	696.9	2.1 (G2)	1.0	20–30
BPAG2*1.2	687.6	8.4 (G2)	4.0	30–40
BPAG2/0.5	696.5	3.5 (G2)	0.0	20–30

[a] All kinds of nylon 6 were made by *in situ* polymerization.
[b] Acetic acid (2.1 g) was used as end-capping agent for every sample.

from room temperature to 220°C over a period of about 45 min with stirring. The inner pressure reached 0.4–0.8 MPa due to spontaneous pressure generated by water vapor from reaction system in the autoclave, and heating was continued with removal of water from the system so that the inner pressure did not exceed 0.8 MPa. After heating for additional 2 h, the temperature was elevated to 260°C over 30 min. The reaction was allowed to proceed for further 45 min at an inner temperature of 260°C. Thereafter, the inner pressure was gradually reduced to atmospheric pressure over a period of about 15 min, rapidly the autoclave was filled with N_2, and the inner pressure reached to about 0.6 MPa. After 20 min, the inner atmosphere was replaced with fresh N_2 again. This kind of operation was repeated three times. Then, the inner temperature was cooled to about 230°C, and the autoclave was opened from a bottom valve. The production was drawn into long strands in a water bath and then pelletized with scissors. Subsequently, these particles were extracted in boiled water for 24 h, and dried under vacuum at 100°C for 4 h. Sample BPAG1*0.5 containing 0.5 wt % of 1.0 G PAMAM units was then obtained.

FTIR measurement

FTIR spectra were recorded on a WQF-410 FT-IR spectrometer by using potassium bromide (KBr) discs prepared from powdered samples mixed with dry KBr.

Thermal gravimetric analysis

Thermal gravimetric analysis was carried out on a Netzsch STA 449C TGA, at a rate of 10°C/min under nitrogen atmosphere. The mother salt of G2 PAMAM dendrimers and *p*-phthalic acid was prepared from its mother salt solution by removing the water under vacuum at 80°C. The solvent methanol of PAMAM dendrimers was removed under the same condition.

Testing for intrinsic viscosity

The intrinsic viscosity of LPA6, BPAG2/0.5 and all kinds of novel nylon 6 were measured at 0.1 g/100 mL of solution in 98% sulfuric acid in a 25°C bath using Ubbelohde viscometer.

Testing for melt flow index

Melt flow index (MFI) in g/10 min of high-flow nylon 6 containing different generation or content of PAMAM units were measured by a melt flow indexer made from Shanghai S.R.D Scientific Instrument Co. at specified temperature and load of 235°C and 235 g, respectively.[43] Also MFI of LPA6 and BPAG2/0.5 was measured for comparison.

Mechanical property testing

All specimens for mechanical tests were injection-molded in an injection-molding machine. The izod impact strength was measured according to GB 1043. Tensile strength and elongation at break were measured according to GB16825. All tests were done at room temperature, and the measurements were conducted over five specimens for tests and the average was reported, respectively.

Microscopy characterization

A field emission scanning electron microscope (SEM) (Jeol JSM6700F) was used to observe the fractured morphology of the novel high-flow nylon 6 and pure nylon after izod impact testing. Fractured surfaces were coated with gold in an SPI sputter coater. The morphology was determined using an accelerating voltage of 5.0 kV.

Differential scanning calorimetry

Nonisothermal crystallization behaviors of high-flow nylon 6 containing PAMAM units with different content or generation and pure nylon 6 were determined using Netzsch STA 449C differential scanning calorimetry, under nitrogen atmosphere.

RESULTS AND DISCUSSIONS

The synthetic mechanism of high-flow PA6 and FTIR analysis

The high-flow nylon 6 was prepared with suitable quantity of mother salt solution, end-capping agent (acetic acid), and ε-caprolactam by *in situ* polymerization. Scheme 2 illustrates several ideal chemical structures existing in the nylon 6 matrix. Samples of BPAG1*0.5, BPAG2*0.5, and BPAG3*0.5 contained 0.5% by weight of G1, G2, and G3 PAMAM dendrimers units, respectively. Samples of BPAG2*0.3 and BPAG2*1.2 contained 0.3 and 1.2%, respectively, by weight of G2 PAMAM dendrimers units for comparative experiments to sample BPAG2*0.5. Sample LPA6 (pure nylon 6) is for contrast with all kinds of high-flow nylon 6 discussed earlier.

All experiments were conducted in the same reaction condition. Interestingly, a new phenomenon was found: the synthetic reaction of high-flow nylon has quicker exothermic speed than that of pure nylon 6, and exothermic speed increased more quickly with increase in the content of mother salt. Why? The preparation of pure nylon 6 is only a ring-opening reaction and water was used as ring-opening agent, but the synthesis of high-flow nylon 6 was a complicated reaction containing not only a ring-opening reaction just like that of pure nylon 6 but
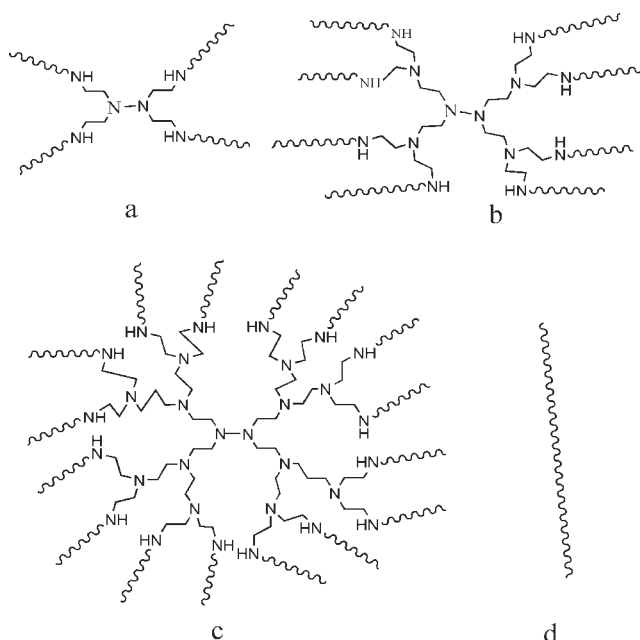
Scheme 2 Schematic illustration of G1.0-PA6 (a), G2.0-PA6 (b), G3.0-PA6 (c), and LPA6 (d).

Figure 1 FTIR spectra of linear and high-flow nylon 6 (LPA6 and BPAG2*0.3).

also a cationic polymerization and the mother salt is used as the initiator.[40,44,45] The first step is the formation of the initiator [Eq. (1)], Eq. (2) shows the initiation and propagation steps. The mechanism of initiation with GNH_3^+ ions and propagation must involve the transfer of two protons from the active species. Two possible mechanisms for this step might be not close association or complete protonation.[45] The mother salt as the initiator certainly accelerates the reaction.

$$G\text{-}NH_2 + HOOCC_6H_4COOH \rightleftharpoons G\text{-}NH_3^+ \ COO^-C_6H_4COO^-GNH_3^- \quad (1)$$

$$G\text{-}NH_3^+ COO^-C_6H_4COO^-GNH_3^- \ + \ 2n\underset{\|}{\overset{O}{C}}(CH_2)_5NH \longrightarrow$$

$$COO^-C_6H_4COO^-\{G[NH\overset{O}{\overset{\|}{C}}(CH_2)_5]_{n-1}\overset{O}{\overset{\|}{C}}(CH_2)_5NH_3^-\}_2 \quad (2)$$
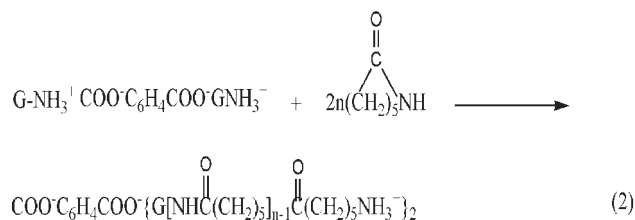
Figure 1 shows the detailed FTIR spectra of sample BPAG2*0.3 and pure nylon 6. The high-flow nylon 6 has almost the same structure as pure nylon 6, the carbonyl bonds(C=O) likewise occur at 1643 cm^{-1}, the same features also occur at 1542 cm^{-1} (δN—H + γC—N) and 689 cm^{-1} (γN—H). The different features occur at 3310 and 3299 cm^{-1} (γN—H), 3089 and 3067 cm^{-1} ($2\delta N$—H). Blue shifts are found for the peaks of NH (γN—H and $2\delta N$—H) of the high-flow nylon 6 compared with the pure nylon 6 in the IR spectra, which might be due to the fact that the low content of PAMAM units
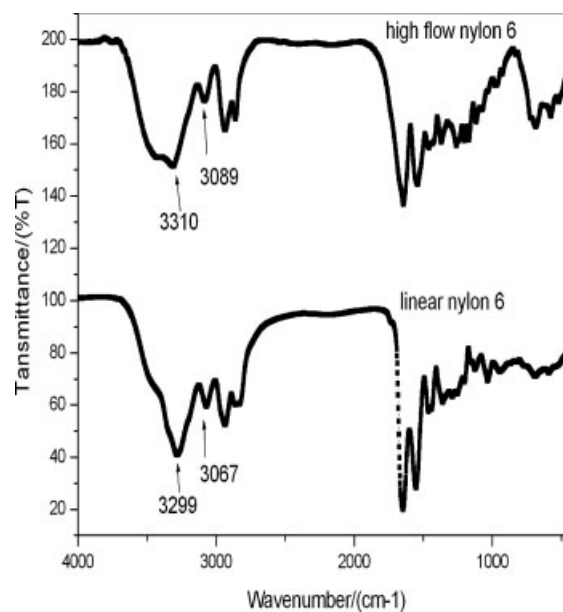
in nylon 6 matrix disturbs the hydrogen bonds between the neighboring molecular chains.[46]

Thermogravimetric analysis

TGA results may give full evidence about the thermal stability of G2 PAMAM dendrimers and mother salt of G2 PAMAM dendrimers and p-phthalic acid. As shown in Figure 2, the weight loss curve of G2 PAMAM dendrimers is obviously below that of the
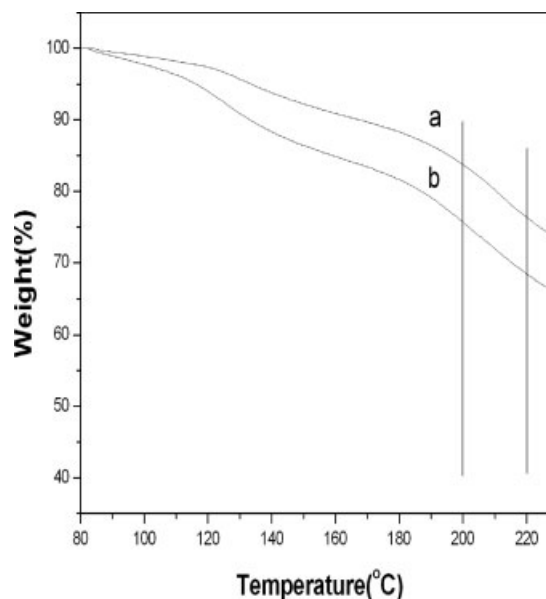

Figure 2 TGA curves of the mother salt of G2 PAMAM dendrimers and p-phthalic acid (a) and G2 PAMAM dendrimers (b).
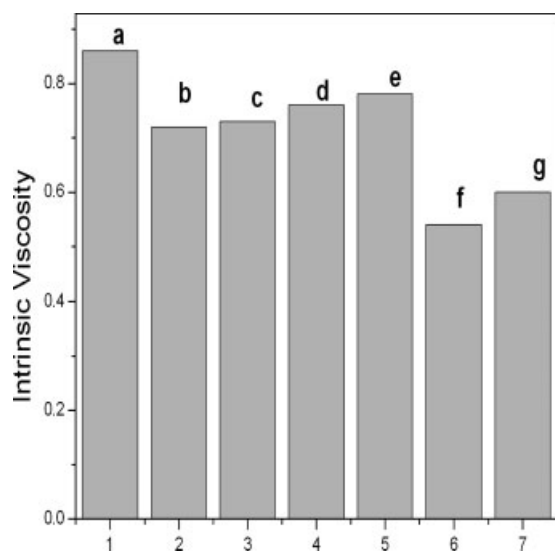
Figure 3 The intrinsic viscosity of LPA6 (a), BPAG1*0.5 (b), BPAG2*0.5 (c), BPAG3*0.5 (d), BPAG2*0.3 (e), BPAG2*1.2 (f), and BPAG2/0.5 (g).

mother salt of G2 PAMAM dendrimers. Especially, the remaining weight percents of the residues at 200–220°C (prepolymerization temperature) in nitrogen are 83.2%–75.6% and 74.6%–68.3% for mother salt and G2 PAMAM dendrimers, respectively. Generally, the PAMAM dendrimers lost their mass less than 5% till 200°C.[43] The greater weight loss might be attributed to the residual small molecules such as water and solvent. The results of the thermogravimetric analysis indicate that the mother salt has better thermal stability than that of G2 PAMAM dendrimers at 200–220°C.

Flow property analysis

Test results for intrinsic viscosity

Figure 3 shows the intrinsic viscosity of BPAG1*0.5(b), BPAG2*0.5(c), BPAG3*0.5(d), BPAG2*0.3(e), BPAG2*1.2(f), and BPAG2/0.5(g) was lower than that of pure nylon 6(a). The intrinsic viscosity decreased markedly with increasing content of PAMAM units (f), which agreed with the research by Warakomski.[40] By comparing b, c, and d, it was also found that the intrinsic viscosity increased slightly with increase in the generation of PAMAM units. The intrinsic viscosity of BPAG2/0.5 was lower than that of BPAG2*0.5, which indicated that BPAG2/0.5 had better flow property than BPAG2*0.5.

Melt flow index

Melt flow index (MFI), as a measure of fluidity of a thermoplastic, is usually reported as grams of polymer extruded through a die in 10 min at specified

load and temperature.[43] It was seen from Figure 4 that each of the samples of high-flow nylon 6 (samples BPAG1*0.5, BPAG2*0.5, BPAG3*0.5, and BPAG2*0.3) with low content of PAMAM units had greater MFI than that of pure nylon 6 (LPA6), the value of MFI was improved by about 70–90%. It was also found that there was a drastic increment in MFI when the content of PAMAM units in PA6 matrix increased more (e.g., BPAG2*1.2). The difference in MFI may be attributed to the existence of PAMAM units, which decreased the intermolecular forces in nylon 6 matrix. In other words, dendritic structures in nylon 6 matrix disturb the intensive interaction of hydrogen bonds between neighboring molecules, and thus improve the fluidity of a thermoplastic. Interestingly, there is also a drastic increment in MFI by comparing BPAG2*0.5(c) with BPAG2/0.5(g), the proper reason might come from the thermal stability difference between PAMAM dendrimers and the mother salt. The worse thermal stability made the PAMAM dendrimers to decompose faster than the mother salt at about 220°C and had an influence on the molecular weight of nylon 6, and the value of MFI certainly increased.

Mechanical property testing

The data of tensile strength, elongation at break, and impact strength of LPA6, high-flow nylon 6, and BPAG2/0.5 were given in Table II. The tensile strength of high-flow nylon 6 containing low content of PAMAM units (sample BPAG1*0.5, BPAG2*0.5, BPAG3*0.5, and BPAG2*0.3) did not decrease compared with the pure nylon 6 (LAP6). However, the
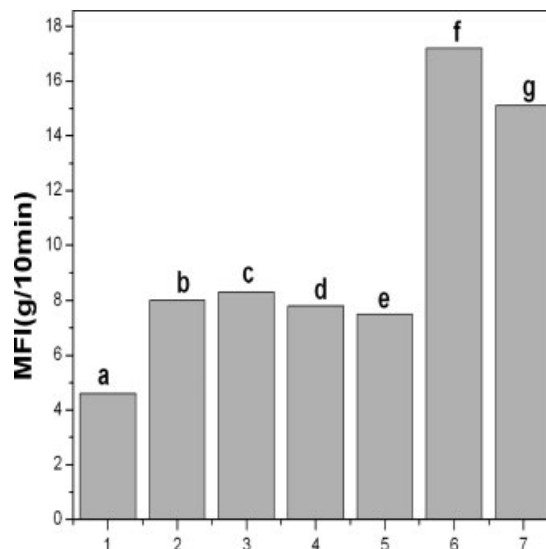

Figure 4 MFI test results of LPA6 (a), BPAG1*0.5 (b), BPAG2*0.5 (c), BPAG3*0.5 (d), BPAG2*0.3 (e), BPAG2*1.2 (f), and BPAG2/0.5 (g).

TABLE II
Test Results for Mechanical Properties of LPA6, High-Flow Nylon 6, and BPAG2/0.5

Sample	PAMAM content (wt %)	Tensile strength (MPa)	Elongation at break (%)	Izod impact strength (KJ/m^2)
LPA6	0	74	183	2.22
BPAG1*0.5	0.5 (1.0G)	74	150	2.58
BPAG2*0.5	0.5 (2.0G)	75	152	2.60
BPAG3*0.5	0.5 (3.0G)	74	115	2.75
BPAG2*0.3	0.3 (2.0G)	75	148	2.62
BPAG2*1.2	1.2 (2.0G)	65	180	2.45
BPAG2/0.5	0.5 (2.0G)	70	150	2.10

tensile strength decreased markedly while the high-flow nylon contained higher content of PAMAM units (sample BPAG2*1.2). The elongation at break of all kinds of high-flow nylon 6 decreased by about 20–35%. These results agreed with the published literature.[40] It also was found that sample BPAG2*0.5 had a better mechanical property than BPAG2/0.5, which indicated that the preparation process of BPAG2*0.5 was better than that of BPAG2/0.5. All kinds of high-flow nylon 6 have a higher impact strength compared with pure nylon 6. The cause of the higher impact strength in the present research is
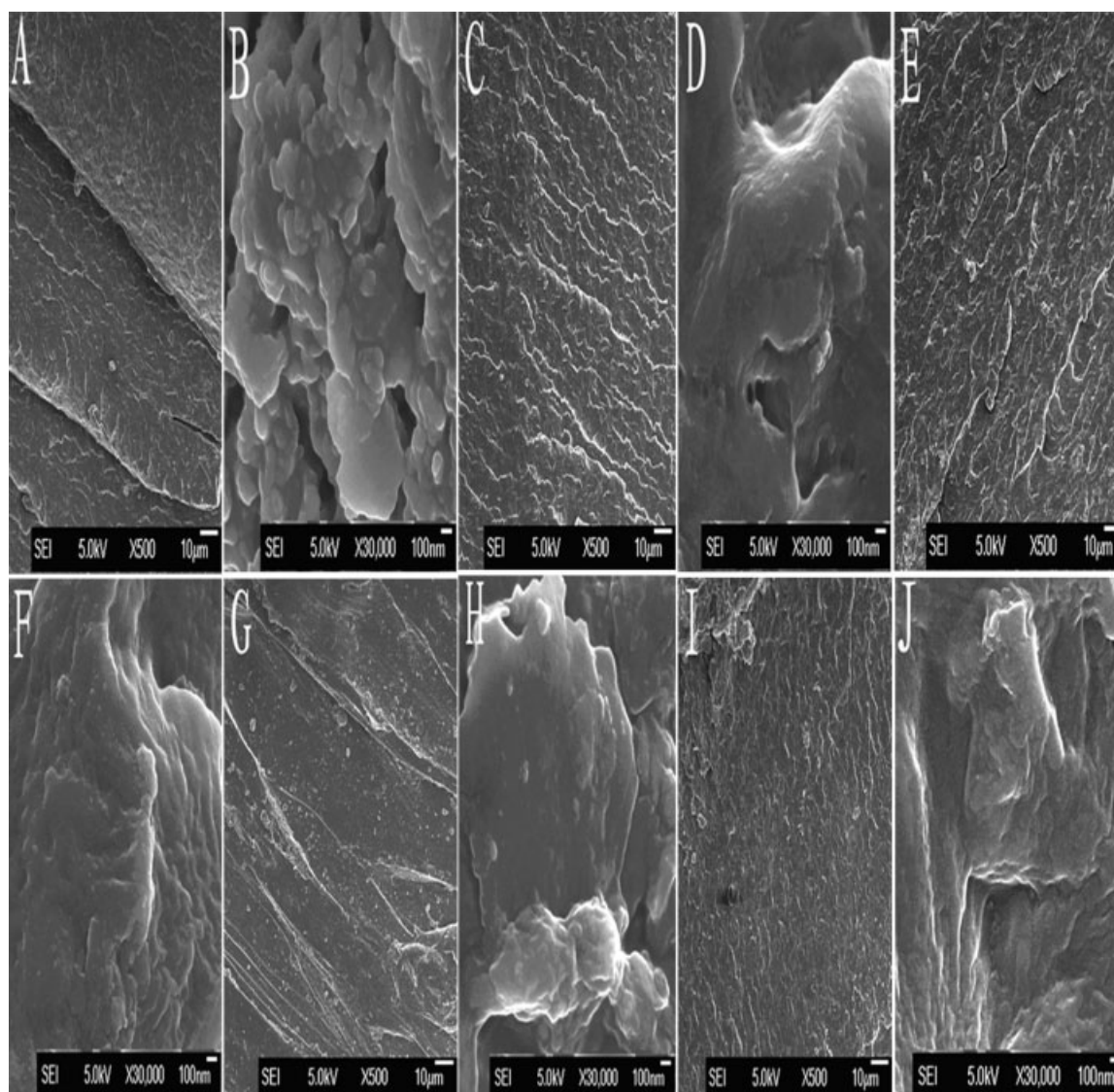

Figure 5 Typical SEM images of LPA6 (A, B), BPAG1*0.5 (C, D), BPAG2*0.5 (E, F), BPAG3*0.5 (G, H), and BPAG2*1.2 (I, J).
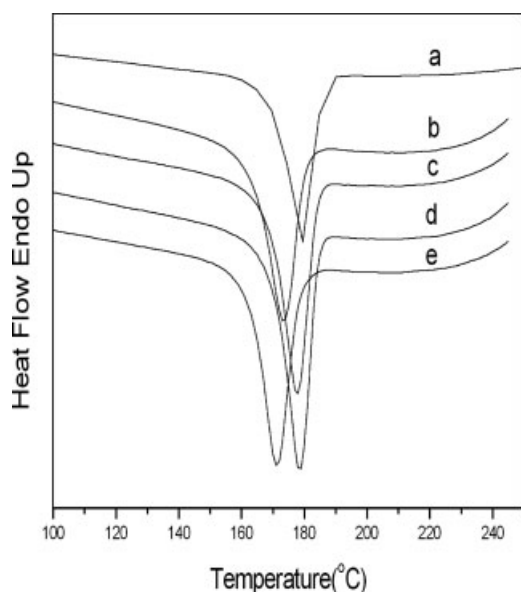
Figure 6 Cooling scans of samples taken from LPA6 (a) and high-flow nylon 6: BPAG1*0.5 (b), BPAG2*0.5 (c), BPAG3*0.5 (d), and BPAG2*1.2 (e).

certainly due to the presence of PAMAM units in nylon 6 matrix.

To understand why the impact strength of high-flow nylon 6 increased compared with pure nylon 6, the impacted surfaces of LPA6 and high-flow nylon 6 after impact testing were observed by SEM. Figure 5 shows SEM images of the fracture surfaces of LPA6 (A, B) and high-flow nylon 6: BPAG1*0.5(C, D), BPAG2*0.5(E, F), BPAG3*0.5(G, H), and BPAG2*1.2(I, J). There is a clear difference between pure nylon 6 and high-flow nylon 6. It could be seen that images C, E, G, and I exhibited a relatively smooth fracture surface with large amount of small crackle. This indicated a typical brittle fracture behavior, thus accounting for the low fracture toughness of high-flow nylon 6, while image A presented a typical ductile fracture behavior that exhibited a more smooth fracture but with some long and big strip-like crack.[43,47,48] Interestingly, some silk-like thing was found from image G, which meant that high-flow nylon 6 containing 3.0G PAMAM units presented different performance from that containing 1.0G or 2.0G PAMAM units; at the meantime, image I exhibited smaller crackle. More detailed information was given from images B, D, F, H and J. Image B exhibited clear island-like structure or cavitation, which indicated a typical plastic fracture behavior, while images D, F, H, and J were all big conglomeration-like, certainly the same conclusion was drawn as above. The increase of impact strength might be due to the crosslinking between neighboring molecules, the conclusion could be clearly confirmed by image G.

Differential scanning calorimetry

To get more information about the difference between pure nylon 6 and high-flow nylon 6, noni-sothermal crystallization behaviors for LPA6 and high-flow nylon 6 at a cooling rate of 10°C/min were investigated by DSC. The samples were heated from RT to about 250°C at 30°C/min, maintained at this temperature for 5 min, and then cooled from about 250°C to RT at 10°C/min. Figure 6 shows the DSC thermogram curves for LPA6 (a) and high-flow nylon 6: BPAG1*0.5 (b), BPAG2*0.5 (c), BPAG3*0.5 (d), and BPAG2*1.2 (e). The corresponding peak temperature (T_p), initial temperature (T_i), end temperature (T_e), and the peak width of crystallization ($\Delta T = T_e - T_i$) were listed in Table III. Some useful information was given: the ΔT values of high-flow nylon 6 were all higher than that of pure nylon 6 at the same crystallization condition, which increased with increase in the generation or the content of PAMAM units. Broader peak means wider processing temperature, which benefits molding of small parts with thin walls or precision parts. This may be due to the fact that PAMAM units in nylon 6 matrix decrease the intensive interaction of hydrogen bonds between neighboring molecules, which agree with the discussions about IR characterization and the test results of MFI. In the course of injection molding, it was found that the processing temperature and pressure of novel nylon 6 lowered about 15°C and 5 bar, respectively, compared with linear nylon 6.

CONCLUSIONS

The high-flow nylon 6 was first prepared with ε-caprolactam, end-capping agent, low content of mother salt solution of PAMAM dendrimers, *p*-phthalic acid, and distilled water by *in situ* polymerization, which presents excellent flow property. Blue shifts are found for the peaks of NH (γN—H and 2δN—H) of the high-flow nylon 6 compared with pure nylon 6 in the IR spectra. Compared with pure nylon 6, the MFI of high-flow nylon 6 containing low content of PAMAM units increases by about 70–90%, the tensile strength almost does not decrease

TABLE III
Values of T_i, T_p, T_e, and ΔT measured by DSC at a cooling rate of 10°C/min for LPA6 and high-flow nylon 6 containing PAMAM units (BPAG1*0.5, BPAG2*0.5, BPAG3*0.5, and BPAG2*1.2)

Sample	T_i (°C)	T_p (°C)	T_e (°C)	ΔT (°C)
LPA6	162.9	177.3	188.7	25.8
BPAG1*0.5	156.7	173.6	184.5	27.8
BPAG2*0.5	159.1	177.6	187.2	28.1
BPAG3*0.5	158.2	178.4	188.1	29.9
BPAG2*1.2	150.6	171.2	186.8	36.2

while the elongation at break decreases by about 20–35%, but the izod impact strength of different kinds of high-flow nylon 6 increase. Another kind of nylon 6 was prepared with PAMAM dendrimers, ε-caprolactam, end-capping agent, *p*-phthalic acid, and distilled water under the same condition, which presents good flow property, but bad mechanical property compared with pure nylon 6 or corresponding high-flow nylon 6. SEM analysis shows that the high-flow nylon 6 presents a typical brittle fracture behavior, and the crosslinking between neighboring molecules may be the main cause. DSC shows that the high-flow nylon 6 had a wider peak than pure nylon 6, which indicates that the processing condition of the high-flow nylon 6 was improved.

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