

Review

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Progress in semicrystalline heat-resistant polyamides

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Abstract: For the past decade, market demands for semicrystalline heat-resistant polyamides (HPAs) with excellent performance and significantly improved heat-resistant temperature has grown rapidly, and they are widely used in the electronic and electrical industry, as light-emitting diodes and in the automobile field (as metal replacements). Industrialized HPAs to date, include PA46, PA6T copolyamides, PA9T and PA10T. Other HPAs being researched include full aliphatic HPA, PA5T, long carbon chain HPA, PXD10 and alicyclic HPA. This review addresses progress in HPAs, especially the properties of HPA, patents analysis and polymerization processes.

Keywords: heat-resistant polyamide; PA10T; PA46; PA6T; PA9T; semi-aromatic polyamide.

1 Introduction

A polyamide (PA) contains an amide group -CONH- as a recurring part of the polymer chain, it was the first synthetic, semicrystalline polymer with strength- and temperature-resistant properties that allowed its use as a thermoplastic capable of doing some things as well or better than metals. PA has excellent mechanical properties, high resistance to friction, scratching and solvents, is self-lubrication, has shock absorbing and noise absorption performances, so that it became the highest demand engineering plastic and has been widely used in the electronic, electrical and automobile industries, in household appliances, sporting goods, etc.

The melting point (T_m) of both PA6 and PA66 are lower than 260°C, and their short-term service temperature is

lower than 250°C and their long-term service temperature is lower than 220°C, which is scarcely capable of being used in those fields with high temperature resistance requirements. That is the target market of semicrystalline heat-resistant polyamides (HPAs), T_m of which is higher than 280°C, or at least 270°C as an industrial definition. For the past decade, the market demands for HPAs with excellent performance and significantly improved heat-resistant temperature has grown sharply, along with the increased requirements of plastics in the electronic and electrical, automobile, aerospace, military, chemical industries, etc.

HPAs are one of the most promising materials in the electronic and electrical industry. The continued trend of miniaturization and wide application of surface mount technology (SMT) of printed circuit board (PCB) has led to thinner surface mount devices, which needs to bear the high peak temperatures of modern reflow soldering processes. The material used must have advantages such as high long-term service temperatures, high hardness and low creep deformation at high temperatures. Due to their outstanding inherent properties of high heat deflection temperature (HDT, which is the temperature at which a polymer or plastic sample deforms under a specified load; ISO 75-2) (more than 260°C), including good toughness and fluidity, HPAs can meet all these requirements of SMT processes, especially heat-resistant requirements. Articles made with high-fluidity HPA can maintain dimension stability during reflow soldering processes with temperatures up to 270°C, in which liquid crystal polymers (LCPs) with high costs are usually used. HPAs can compete with polyphenylene sulfite (PPS), polyetherimide (PEI), polyether sulfone (PES) and LCPs in these fields, such as in circuit-breakers, power connectors, sockets, etc.

Heat-resistant plastics are replacing traditional engineering plastics and some metals, the driving forces of which derive from the demands of three growing trends in the automobile industry: 1) improving safety and comfort; 2) longer service life requirement; 3) increased temperature for engine parts. HPAs are an ideal metal-replacement material, on account of their creep resistance, good mechanical strength, rigidity and anti-fatigue at high

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temperature. Simultaneously, HPAs maintain the well-known advantages of plastics, such as being recyclable, being easily processable, having light weight, noise reduction and corrosion resistance, hence they are suitable use in engine, drivetrain systems, air systems and air inlet units, etc. HPAs perform well in these fields, for example, a chain tightener abrasion made with a HPA is far less than that made with PA66. Moreover, due to their rigidity at high temperature, HPAs can be used to produce all-plastics parts, which leads to low-cost and increase the service life 3 times more than PA66. HPAs can be used in corrosive and high temperature oil mediums, in which common polyamides are restricted. In vehicle control systems, HPAs can be used in a series of outlet parts due to its creep resistance, fatigue resistance and vibration resistance; HPAs can also be used in recyclable oil filter housing, which must bear high temperatures, for road bumps and in bad weather; they can be in vehicle generator systems, HPAs can be used in generators, starters and micromotors.

Light-emitting diodes (LED) are an emerging and rapidly developing business, and SMT must be used in the process of soldering LED illuminants on circuit boards, leading to the demands on LED stent material with high-temperature resistance and mechanical strength retention at high temperatures. Limited materials can meet these demands, such as HPA, LCP and polyether ether ketone (PEEK). Among them, PEEK is expensive, and LCP is darker and has low reflectivity, and HPAs are the most applicable heat-resistant material as LED stents.

Most HPAs are copolyamides which their modify properties, the structures of basic units were shown in Table 1.

The most important literature on PAs is the *Nylon Plastics Handbook* edited by Kohan (1), which summarized the

structures, synthesis, modification and application of various PAs including HPA. However, this book concentrated on the aliphatic PAs and offered less information on HPA, and has not been updated since its publication in 1995. The mushrooming development of HPAs dated from 2000, therefore, one finds it difficult to understand HPAs, especially the developments after 2000. Marchildon (2) also reviewed the variety of PAs, including a short introduction on HPAs.

Poly(phthalamide)s (PPA for short, viz., semi-aromatic polyamides) are specifically discussed in chapter 12 in *High Performance Polymers* edited by Fink (3), and it introduces various semi-aromatic PAs including HPAs and the transparent PAs with less references. Semi-aromatic PAs are discussed in chapter 3 in the *Practical Guide to High Performance Engineering Plastics* (4), and it introduces the mechanical performances, water absorption and other properties of commercialized HPAs, such as poly(hexamethylene teraphthalamide) (PA6T) and poly(decamethylene teraphthalamide) (PA10T), with 18 patents as references, which do not refer to polymerization.

There are more reviews in Chinese on the semi-aromatic PAs or HPAs. In 2002, Zhang and Wei (5) reviewed the principal characters, performances and applications of commercialized semi-aromatic Pas. In 2003, focusing on poly(nonamethylene teraphthalamide) (PA9T), Ma et al. (6) emphasized the performances of commercialized HPAs, such as water absorption, crystallization, heat resistance, toughness, abrasion, chemical resistance and dimensional stability. In 2006, Wang et al. (7) focused on the production processes of semi-aromatic PAs, and introduced solution polycondensation at high temperature and pressure, solution polycondensation at low temperature, polycondensation from polyester and direct melt-polycondensation, with no detailed description on commonly used processes in industry. In 2009, Li and Zhong (8) from DSM and Yi et al. (9) from Kingfa briefly introduced the properties of several commercialized HPAs. In 2012, Zhang et al. (10) from Kingfa introduced the new HPAs emerging after 2000, such as PA10T, PA4T, PA5T, PA12T, PAPXD10, PA6C, etc. Since 2015, Zhang et al. (11), Wang et al. (12) and Ma (13) have reviewed commercialized semi-aromatic PAs and special PAs (long-carbon-chain PAs, HPAs, bio-based PAs and transparent PAs).

These reviews are from each authors' point of view with few references, and one cannot acquire a full view of HPAs from them, viz., an in-depth review on the variety, performances and polymerization processes of the latest HPAs is absent, which is the objective of this review. In consideration of the fact that the technical challenges of HPAs are mainly on the production of resins, this review focuses on HPAs' resin-related contents.

Table 1: Basic HPA copolyamide units and their structures.

Basic copolyamide unit	Structure
46	$-\text{NH}(\text{CH}_2)_4\text{NH}-\text{OC}(\text{CH}_2)_4\text{CO}-$
nT	$-\text{NH}(\text{CH}_2)_n\text{NH}-\text{OC}-\text{C}_6\text{H}_4-\text{CO}-$
PXD10	$-\text{NHCH}_2-\text{C}_6\text{H}_4-\text{CH}_2\text{NH}-\text{OC}(\text{CH}_2)_8\text{CO}-$
nC	$-\text{NH}(\text{CH}_2)_n\text{NH}-\text{OC}-\text{C}_6\text{H}_4-\text{CO}-$
6I	$-\text{NH}(\text{CH}_2)_6\text{NH}-\text{OC}-\text{C}_6\text{H}_4-\text{CO}-$
66	$-\text{NH}(\text{CH}_2)_6\text{NH}-\text{OC}(\text{CH}_2)_4\text{CO}-$
6	$-\text{NH}(\text{CH}_2)_6\text{CO}-$
M5T	$-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}-\text{C}_6\text{H}_4-\text{CO}-$

Table 2: Milestones during HPAs' development history.

Year	Milestone	Representative Organization
1938	Carothers synthesized PA46 with $T_m = 278^\circ\text{C}$ and dark color	Dupont
1975	Gaymans synthesized white color PA46 with high molecular weight	Twente University
1990	Industrialization of PA46	DSM
1990s	Industrialization of PA6T	Dupont/Solvay/Mitsui/EMS
2003	Industrialization of PA9T	Kuraray
2007	Industrialization of PA4T	DSM
2009	Industrialization of PA10T	Kingfa/EMS/Evonik/Arkema
2012	Pilot production of PA11T and PA12T	Zhengzhou University/Junheng Industrial
	Pilot production of PXD10	Mitsubishi
2013	Industrialization of pentamethylenediamine	Cathay/Toray
2014	Pilot production of alicyclic HPAs	Asahi Kasei/Kuraray

In fact, as early as 1930s when Dr. Carothers produced Nylon for the first time, he noticed PA46 has a melting point (T_m) of 278°C (14, 15). Due to the intra-molecular deamination of butanediamine to produce pyrrole during heating, the molecular weight growth becomes difficult because pyrrole acts as a terminator in polycondensation. Hence, without precise control over polymerization processes, one can only get a dark color low molecular weight oligomer without any commercial value, which was the problem Dr. Carothers met then. Naturally, when he discovered the more valuable PA66, the development of PA46 was shelved.

PAs developed in large scale in 1960–1980s, and various PAs were produced during this period, including HPAs. Ordinary HPAs, such as PA6T and PA9T, were patented at this time, however, PAs were mainly used as fibers rather than as engineering plastics during this period. The high melting point of HPAs was considered to be a disadvantage in the spinning process.

HPAs developed remarkably quickly after 2000, benefiting from the Restriction of Hazardous Substances (RoHS) Directives of lead-free alloys ($>260^\circ\text{C}$) used in surface mount technology (SMT) in Europe and even in the worldwide market (16). The European Union has comprehensively prohibited the application of lead-containing alloys in soldering processes in the electronic and electrical industry. The operating temperature of new lead-free alloys exceeds 250°C , and the traditional materials PA66 and poly(butylene terephthalate) (PBT) find it impossible to work normally under such circumstances, and development of materials with higher heat resistance becomes inevitable. With considerable high temperature stability, good toughness and excellent fluidity, HPAs can fulfil the aforementioned requirements satisfactorily on the premise of reasonable economic efficiency.

Commercialized HPAs include the PA46 series, PA6T series, PA9T series and PA10T series, and others are in

research or being used on a pilot scale. Table 2 lists the milestones during HPAs' development history.

In China, HPAs began to develop after 2000 and now both the HPA industry and the market are in full swing. Kingfa Sci & Tech Co., Ltd. (Guangzhou City, Guangdong Province, China) launched bio-based HPA PA10T (brand Vicnyl) in 2009, and it has become the largest HPA manufacturer in China with annual sales of more than 5000 tons; Zhejiang NHU Special Materials Co., Ltd (Shaoxing City, Zhejiang Province, China) has built a 1000 t/a HPA product line (brand NHU PPA, presumably the PA6T series), and a 10,000 t/a HPA product line has been constructed since 2015, which is believed to have been put into production recently (17); Shanghai GENIUS Advanced Material (Group) Co., Ltd. (Shanghai City, China) began its production of HPA in a 1000 t/a product line as early as 2006 (18); DZT Engineering Plastics, Ltd. (Jiangmen City, Guangdong Province, China) has also launched its semi-aromatic PAs (brand: DZT PANT) (19). There are two series: I series with T_m of 270°C , and D series with T_m of 290°C , which are used in the metal-replacement field, such as in the automobile and sanitary industries; Henan Junheng Industrial Group Biotechnology Co., Ltd. (Puyang City, Henan Province, China) cooperated with Zhengzhou University (Zhengzhou City, Henan Province, China) to launch long carbon chain HPAs, with the capacity of 500–1000 t/a (20).

2 Industrialized semicrystalline heat-resistant PAs

2.1 PA46

As mentioned already, the most difficult part in PA46 polymerization is polymer chain termination caused by pyrrole from the cyclization of 1,4-butanediamine as shown in Figure 1.

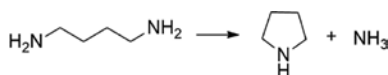


Figure 1: Cyclization of 1,4-butanediamine.

Pyrrole can act as a terminator in PA46 polycondensation, leading to a low molecular weight product (14, 21–23). Interfacial polymerization processes can be used to avoid cyclization by mixing adipoyl chloride in chloroform and 1,4-butanediamine in water, in which high-activity monomers and organic solvent must be used (24–26). Interfacial polymerization is a good laboratory-scale process for polymer production and demonstration, but not for industry.

In 1977, pale to white high-molecular-weight PA46 ($M_w = 45,000$, inherent viscosity 2.09 in 98% formic acid at 30°C) was produced through a solid-state polymerization (SSP) technique by Gaymans et al. (23), which gave hope to industrialization of PA46. Thereafter, PA4T (27) and PA46/4T (28) were synthesized through the same process by Gaymans. Then, DSM cooperated with Twente University of Technology to accomplish the commercialization of PA46 in May 1984, and DSM announced that it had mastered the industrialized process of PA46 (brand: Stanyl); in late 1985, a 150 t/a pilot-plant was built; in 1990, a PA46 plant with capacity of 20,000 t/a was run in Geleen, The Netherlands (29–35).

According to patents and the literature, one can conclude that the color of the product is key to the industrialization of PA46. The two-step process of prepolymerization + SSP technique is usually used to produce PA46, and a white product can only be obtained using nitrogen/steam mixtures as the protection gas, or a yellow or even a black product is obtained. Other than the traditional knowledge of SSP, that a protection gas with less water should be used to avoid a reverse reaction, the introduction of steam seems to protect reactants and inhibit side reactions in PA46 SSP (36–39). Kim et al. (40) studied the SSP of PA46/4T and found that the resin was yellow when using pure nitrogen as the SSP protection gas and was white when using $\text{N}_2/\text{steam} = 2/1$ as shown in Figure 2. Until now, there has been no clear explanation for this phenomenon, and two patents gave some hints: Karl Fischer Industrieanlagen GmbH (41) mentioned that “A high dewpoint of the inert gas at the same time has the advantage that the product in the case of PA66 shows less yellowing”; and DSM (42) further pointed out that “Such a gas atmosphere (mixed gas with a high dewpoint of at least 70°C) has a high heat capacity, thereby enabling a very efficient heating of the polyamide via the gas stream”. Hence, steam enables an efficient heating transfer to the

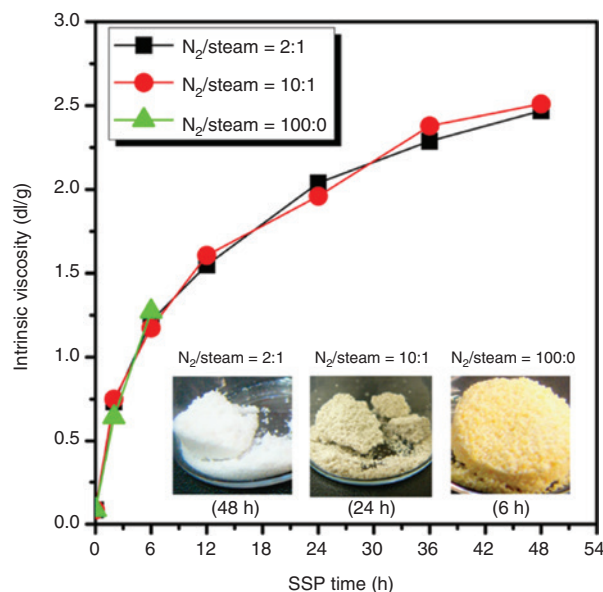


Figure 2: The effect of N_2/steam ratio on PA46/4T color in solid state polymerization.

[Source: Ind Eng Chem Res. 2012;51(49):15801–10, printed with permission].

prepolymers, which may be the reason for the good color of the steam-containing system.

In 2002, DSM (43) disclosed a patent on PA4T/6T, the T_m of which is lower than both PA4T (430°C) and PA6T (370°C) and can be as low as 330°C. Different from the reduction of both T_m and degree of crystallization in PA6T copolymerization, low T_m of PA4T/6T was not accompanied by a degree of crystallization reduction. And water absorption of PA4T/46 is much lower than expected. But relative viscosity of the products was lower than 2.0, which was too low to be applied in practice. The low-molecular-weight problem was then solved by the introduction of other monomers such as adipic acid and decanediamine (44, 45). Based on the aforementioned work, DSM launched PA4T (brand Stanyl ForTii) in September 2007. The high degree of crystallization and good mechanical properties of PA46 are maintained in PA4T, and the HDT of PA4T is as high as 305°C (1.8 MPa) and water absorption is as low as 0.3% (23°C, 24 h), which can compare favorably with PA9T (46). Considering its high amide concentration, the low water absorption of butanediamine-based PAs is extraordinary, which can solve the blistering problem of PA46 in reflow soldering processes used in high humidity circumstances.

PA46 has significant characteristics of a high amide group concentration and a high rigidity of molecular chain, leading to a high degree of crystallization, good rigidity at high temperature and high water-absorption.

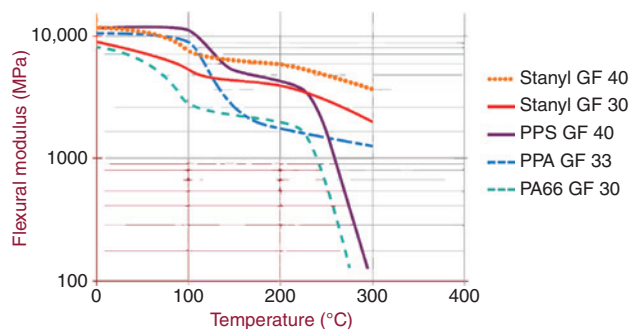


Figure 3: Flexural modulus of PA46 and other materials.
[Source: http://www.dsm.com/products/stanyl/en_US/product-info/properties/thermal.html, printed with permission].

Figures 3 and 4 show the properties of PA46 (Stanyl), PPS, PA6T (PPA) and PA66, and PA46 has better rigidity at high temperature.

For the water absorption problem of PA46, two solutions were given by DSM:

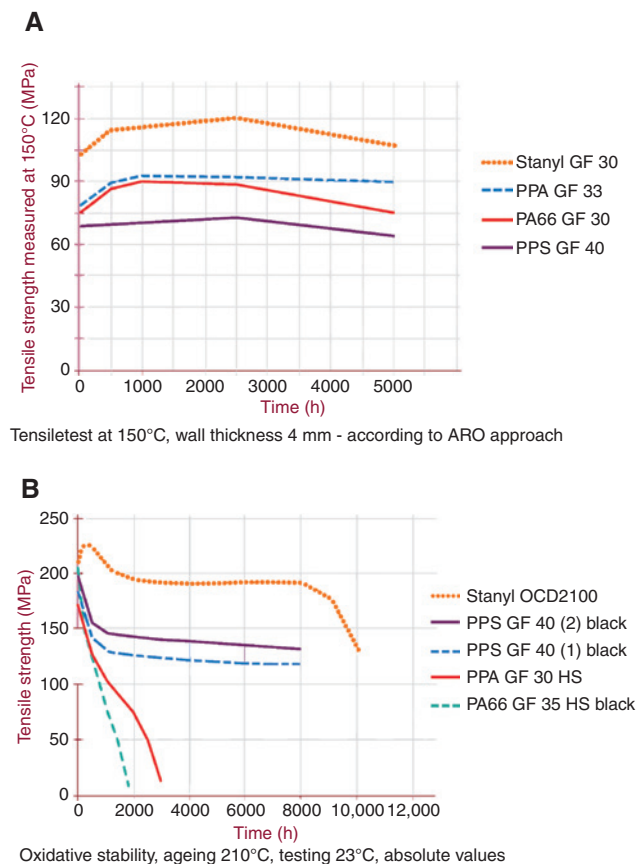


Figure 4: Tensile strength of PA46 and other material after long term thermal-oxidative aging at: (A) 150°C (test temperature 150°C) and (B) 210°C (test temperature 23°C).
[Source: http://www.dsm.com/products/stanyl/en_US/product-info/properties/thermal.html, printed with permission].

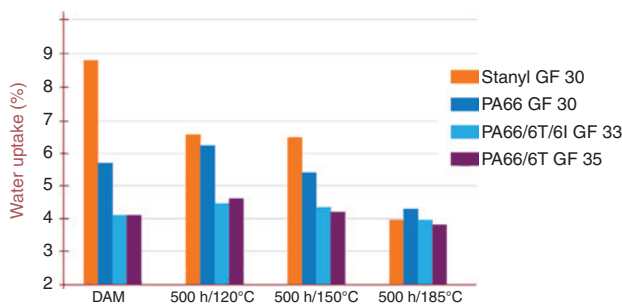


Figure 5: Water absorption of PA46 and other materials at different annealing conditions.
[Source: http://www.dsm.com/products/stanyl/en_US/product-info/properties/moisture.html, printed with permission].

Annealing. Water absorption of PA46 can be decreased to be lower than 30% of normal after annealing at higher than 100°C. The reason is obvious: the amorphous part of PA46 crystallizes after annealing and the water molecule finds it difficult to insert into crystal lattice, and water absorption decreases naturally. DSM declared that this reduction of water is continuous and maintainable, which did not occur in other heat-resistant materials, as shown in Figure 5.

To launch a new material PA4T by copolymerization modification of PA46. DSM declared that PA4T maintained most excellent properties of PA46, simultaneously, water absorption decreased notably and dimensional stability increased, as shown in Figure 6.

In 2010, DSM launched a bio-based PA, PA410 (brand: EcoPaXX) with a T_m of 259°C (47, 48). DSM attached great importance to its promotion, aiming to cultivate a competitor for PA66 in view of their similar structures. Based on its good performance and bio-based concept, PA410 has been widely used in faucet system components (49, 50), components for automotive cooling systems (51), abrasive monofilament (52, 53), snowboard binding (54), engine coverings (55), etc.

Recently, cooperating with National Technical University of Athens, DSM began to study the process of direct SSP of 4T salts, which can get rid of the stringent requirements for reactor of traditional prepolymerization process under high pressure (56–59). Salts can be obtained under low temperature (<100°C) and atmospheric pressure. Direct SSP of nylon salts also encountered problems, such as transition from the solid to the melt state, diamine loss, etc. The phase transition brought about wall sticking of reactant particles, and the diamine loss resulted in end group imbalance and low molecular weight polymers. The industrialized process of direct SSP of nylon salt are hindered by both problems.

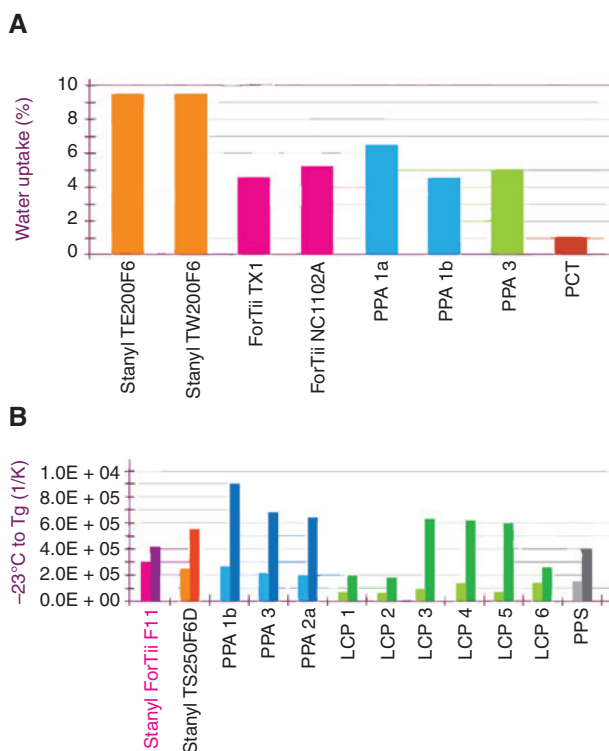


Figure 6: Water absorption (A) and linear coefficient of thermal expansion (B) of PA6T and other materials.

[Source: http://www.dsm.com/products/stanylfortii/en_US/product-info/properties/dimensional-stability.html, printed with permission].

Considering its great value in commerce, there is successive literature on water absorption (60–62), crystallization properties (63–65), transamidation (66–69) and applications (70–72) of PA46.

2.2 PA6T

In the narrow sense, PA6T refers to a PA derived from hexanediamine and terephthalic acid only. However, the T_m of neat PA6T (370°C) is higher than decomposition temperature (350°C), leading to its impractical value. Most declared PA6Ts in business are copolyamides derived from hexanediamine, terephthalic acid and other monomers, with a T_m lower than 330°C. Common comonomers include 2-methylpentanediamine, adipic acid, caprolactam, isophthalic acid, etc. PA6T series PAs are the most widely used HPAs due to their low cost.

In consideration of confidentiality, the PA6T comonomers compositions of most companies are ambiguous, and it is difficult to get precise information on them. A list of PA6T and their structures is shown in Table 3.

Table 3: Structures and thermal properties of various PA6T copolyamides.

Supplier	Brand	Structure	T_m (°C)	T_g (°C)
Dupont	ZYTEL® HTN	51 6T/M5T	300	141
		52 6T/66	310	90
		53 6T/66/6I	260	80
		54 6T/66/6I	300	
		55 6T/66/6I	296	
Solvay	Amodel® PPA	A-1000 6T/6I/66	311	126
		A-4000 6T/66	325	100
		A-5000 6T/X	294	89
		A-6000 6T/66	312	88
EMS	Grivory	HT 1 6T/6I	325	
		HT 2 6T/66	310	
		GVX 66+6I/X	260	
		G4V 66/6I/X	235	
Evonik	Vestamid®	M1000 6T/X	315	125
		HT plus		
Radici	Radilon®	XTreme 6T/X	280	90
BASF	Ultramid®	T 6T/6	298	125
Mitsui	ARLEN™	– 6T/6I	320	125
Kingfa	Vicnyl®	400 6T/66	308	90
		500 6T/6I	323	135
Zhejiang NHU	NHU PPA	N600 6T/X	308	92
		N602	325	95
		N201	323	100
		N100	315	132
GENIUS	HPN	E 6T/X	310	
DZT Engineering Plastics	PANT	I 66/6T/X	270	
		D 6T/X	290	

The performance of PA6T can be deduced from the analysis of other HPAs (PA46, PA9T and PA10T) in this review. In general, because of their high amide group concentration, the water absorption of PA6T copolyamides is high, which is troublesome in the electronic and electrical field, especially when drying processes are not operated properly, blistering of moulding articles is inevitable during reflow soldering processes at high temperature and humidity conditions.

Isomorphous replacement copolyamides and nonisomorphous random copolyamides are two key concepts for copolyamides, especially for PA6T copolyamides.

Edgar and Hill (73) studied the melting behavior of isomorphous replacement copolyamide PA6T/66 and nonisomorphous random copolyamide PA6T/610, as shown in Figure 7.

The T_m of all isomorphous copolyamides derived from PA6T and PA66 are higher than PA66, which can be attributed to the similar chain length of adipic acid and terephthalic acid. Neither the symmetry nor conformation of the chain changes when replacement happens between adipic acid and terephthalic acid. Hence, the T_m

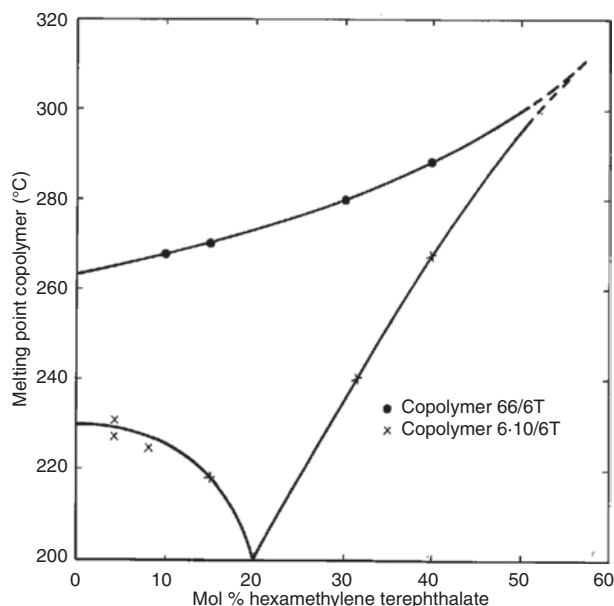


Figure 7: Relationship between T_m and constitutions of PA6T copolymers.

[Source: J Polym Sci Part A-1: Polym Chem. 1952;8(1):1–22, printed with permission].

alters linearly with the concentration of comonomers; for nonisomorphous random copolyamide PA6T/610, due to the obvious chain length difference of sebacic acid and terephthalic acid, both symmetry and conformation of the chain are damaged after replacement of the terephthalic acid with sebacic acid. One can find that melting point of PA6T copolyamides can be lower than that of PA610, which is similar to the eutectic melting phenomenon of small molecules.

Yu and Evans (74) demonstrated the isomorphous replacement behavior of PA6T/66 further as shown in Figure 8. In the case of the isomorphous replacement of adipic acid with terephthalic acid, the length of four methylene groups of adipic acid is 0.508 nm and the length of the benzene ring is 0.417 nm. The benzene ring is at an angle of 35° to the direction of the chain, and the length

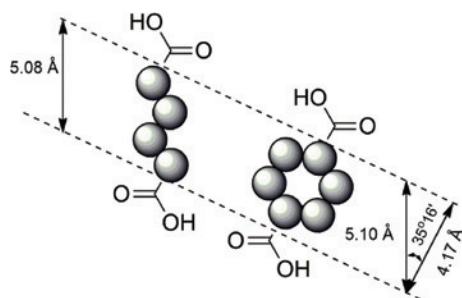


Figure 8: Isomorphous replacement module of PA6T/66.

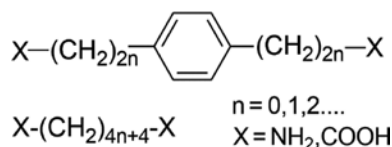


Figure 9: Structures of monomers of isomorphous replacement PAs.

in the direction perpendicular to the planes of the amide bonds is 0.510 nm, which is very similar to the length of the four methylene groups of adipic acid (0.510 nm). Therefore, by inclusion of terephthalic acid instead of adipic acid, the planes of the amide bonds remain equivalent and the chain deviates slightly within the planes. Although such a lattice, containing both acids, might be defective, the continuous association of hydrogen bonds across the chains can be retained. Generalizing this concept to other monomers containing a benzene ring, the monomers shown in Figure 9 can produce isomorphous replacement copolyamides.

Asahi Kasei (75) disclosed a patent where the T_m and HDT of common PA6T/66 ($T_m=279^\circ\text{C}$, HDT= 220°C) can be raised to 306°C and 260°C , respectively, after melting for a while in nitrogen. Both the T_m and HDT of PA66 and PA6 increased a little after the same thermal process. Of course, the T_m of PA6T/66 can be altered conveniently by the formula adjustment of monomers, making the aforementioned process meaningless.

Due to their low cost and moderate performances, PA6T copolyamides were recognized as the most commercial valuable HPAs, and many scientific research institutions have studied PA6T since 2006 in China.

Feng's group (76–80) in Zhejiang University synthesized aliphatic PA, semi-aromatic PA and whole-aromatic PA using water, N-methylene-2-pyrrolidinone (NMP) and ionic liquids as solvents; acetylation and alkylation techniques were used to sparingly dissolve soluble polyamides in tetrahydrofuran (THF), so that common gel permeation chromatography (GPC) can be used to characterize the molecular weight and molecular weight distribution; a new method to characterize mass distribution of insoluble PA6T was developed, viz., matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS); synthesis of high molecular weight semi-aromatic polyamides were studied using the SSP process, during which effects of time, nitrogen flow, temperature and aromatic ring concentration on SSP were investigated (81); prepolymerization of PA6T/66 under water was studied (82) and it was found that prepolymerization occurs only when the temperature is higher than 200°C .

Liu and Zhao group at Zhengzhou University studied the synthesis and properties of PA6T/66 (83) and

PA6T/1010 (84). As a typical nonisomorphous random copolyamide system, the T_m of copolyamides of PA6T/1010 present themselves a typical V curve along with 6T concentration increasing, and the T_m can be as low as 165°C when the concentration of 6T is 40 mol%.

Other groups in China have also studied HPAs such as PA6T/6 (85), PA6T/11 (86), PA6T/6I/66 (87), PA6T/66/1010, PA6T/6I/1010 (88) and PA6T/2T (89).

Galy et al. (90) investigated properties of PA6T/6I through the use of molecular modeling techniques and compared them with experimental data, and the method can be used to predict the thermal properties of new PAs; PA6T/6I and PAMXD6 (91, 92) were melted together by a twin-extruder, after which the mixture was heated at 300°C for 30 min (DSC). Then ^1H nuclear magnetic resonance (NMR) was used to investigate transamidation at a constant temperature (DSC), and it was found that PA6T/6I and PAMXD6 did not distribute randomly; Frauenrath et al. (93) studied melt blending of PA6T/6I with PA66, PA610 and PA12 using a twin-extruder with a retention time of 20 min, a transamidation during extruding process was studied. It was found that high efficient transamidation occurred when PA6T/6I mixed with PA66 and PA610 to produce PAs with only one glass transition temperature and high degree of crystallization. In comparison, transamidation efficiency tended to be low for PA12 and phase separation was also found.

2.3 PA9T

PA9T is derived from nonamethylenediamine/2-methyleneoctanediamine and terephthalic acid and was first produced by Kuraray. The industrialization technology of nonamethylenediamine is a unique technique of Kuraray's, and it begins with butadiene as raw material through hydration, carbonylation and ammoniation. BASF launched HPAs named Ultramid® Advanced and they declared that this material was a semi-aromatic PA with $T_m = 300^\circ\text{C}$ and $T_g = 125^\circ\text{C}$, which was also considered to be PA9T.

T_m of pure PA9T is about 308°C, and some PA9T HPA introduce a third monomer (usually less than 20 mol% of 2-methyleneoctanediamine) to decrease the T_m in favor of processing. In comparison to PA6T copolyamide, PA9T has a lower amide concentration and a higher methylene concentration. Low amide concentration leads to low water absorption and high methylene concentration means a good flexibility of the molecular chain, resulting in a faster crystallization rate. The relative crystallization rate of PA9T and other polyamides is shown in Figure 10 (94).

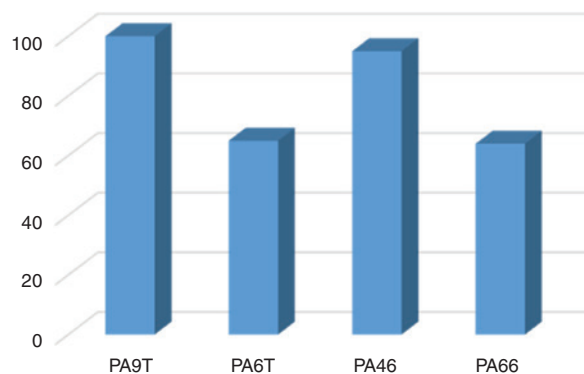


Figure 10: Relative crystallization rate of PA9T and other PAs. [Source: Eng Plast Appl. 2002;30(2):58–60, printed with permission].

Integrating processability and heat resistance, PA9T is an ideal material with advantages of both aliphatic and aromatic PAs, such as a high crystallization rate, good dimensional stability and high temperature rigidity. Articles of PA9T can also be recycled, and it can be used as functional components in the automobile and mechanical industry, especially as a bearing support and in transmission gears. The low water absorption of PA9T is incomparable to PA6T, which is significant to applications at high temperature and high humidity.

According to information on Kuraray's website (95), PA9T (Genestar™) can be widely used in the electronic, electrical and automobile industries and as LED stents.

Both blistering and dimensional stability properties are a concern in the electronic and electrical field. The blistering properties of three HPAs: PA46, PA6T and PA9T under different soldering conditions (Figure 11) are compared as shown in Table 4.

Thanks to the low water absorption derived from inherent structural advantages, the blistering property of PA9T

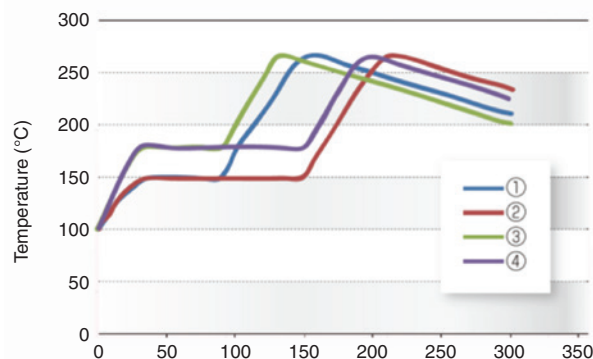


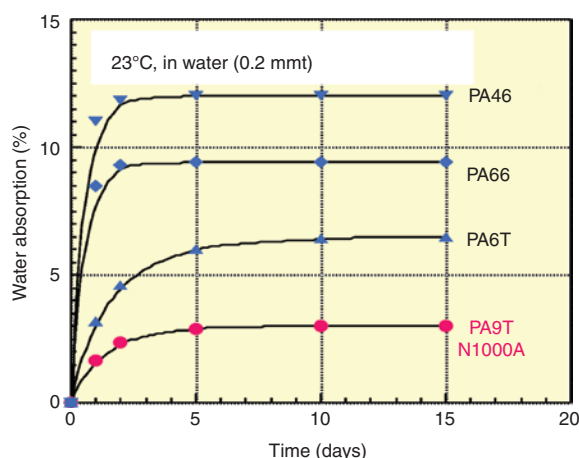
Figure 11: Reflow soldering conditions. [Source: https://www.kuraray.eu/fileadmin/Downloads/k_2016/EVAL/GENESTAR_-_E_E_LED.pdf, printed with permission].

Table 4: Blistering properties of different HPAs under reflow soldering.

Pattern	Preheat conditions		Peak temperature: 260°C			Peak temperature: 265°C		
	Temperature (°C)	Time (s)	PA9T	PA6T	PA46	PA9T	PA6T	PA46
	150	60	○	x	x	○	x	x
	150	120	○	○	x	○	x	x
	180	60	○	○	x	○	x	x
	180	120	○	○	x	○	○	x

○, Good; x, blistering.

[Source: https://www.kuraray.eu/fileadmin/Downloads/k_2016/EVAL/GENESTAR_-_E_E_LED.pdf, printed with permission].

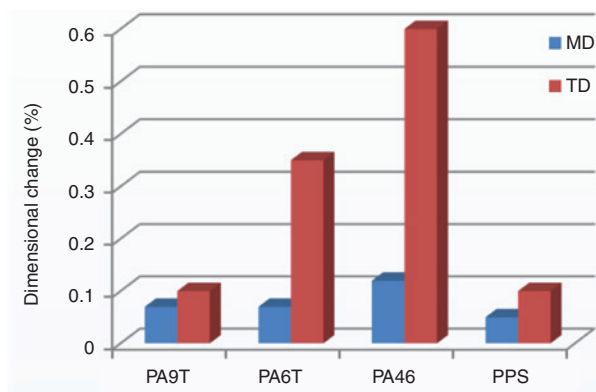
**Figure 12:** Water absorption of four PAs.

[Source: https://www.kuraray.eu/fileadmin/presse/publikationen/downloads_k_fair_2013/genestar/GENESTAR_Auto.pdf, printed with permission].

is the best as is shown in Figure 12, and the dimensional stability after water absorption is also good (Figure 13). Therefore, PA9T can be used as gear components of air conditioners in vehicles, which require low water absorption, abrasive resistance and high temperature rigidity. In contrast, the commonly used polyoxymethylene (POM) and PA66 usually crack when used in subsize components.

PA9T has good resistance to solvent as shown in Table 5. Protecting pipes for vehicle wire harnesses requires good calcium chloride resistance and heat resistance. The commonly used PA46 is prone to degrade in contact with calcium chloride solution, leading to a decrease in performance. PA9T can also be used as a thermostat cover, which requires that the material has resistance to hydrolysis, low density and toughness. The commonly used PPS is heavy, and the impact resistance is poor.

PA9T has favorable high temperature rigidity and thermal aging resistance as shown in Figures 14 and 15. It can be used in vehicle intercoolers, which requires materials with good calcium chloride resistance, thermal aging resistance and high temperature fatigue resistance performance.

**Figure 13:** Dimensional stability of four materials (MD, machine direction; TD, transverse direction).

[Source: https://www.kuraray.eu/fileadmin/Downloads/k_2016/EVAL/GENESTAR_-_E_E_LED.pdf, printed with permission].

Table 5: Solvent resistance of different materials.

	Retention of tensile strength (%) ^a				
	PA9T	PA6T	PA46	PA66	PPS
Gasoline	86	86	71	86	98
Engine oil	89	88	67	81	97
Methanol	72	35	54	39	98
Toluene	82	77	74	68	95
Chloroform	87	85	71	68	87
Hot water (80°C)	90	63	40	44	96
Sulfuric acid (10% aq.)	81	52	42	39	98
NaOH (50% aq.)	85	62	59	71	92
CaCl ₂	92	64	52	73	97

^aRetention (%) of tensile strength after dipping in solvent at 23°C for 7 days.

Thickness of specimen: 0.2 mm.

[Source: https://www.kuraray.eu/fileadmin/presse/publikationen/downloads_k_fair_2013/genestar/GENESTAR_Auto.pdf, printed with permission].

The commonly used materials include aluminium die casting, PA46 and PA66: either too heavy or poor calcium chloride resistance and bad thermal aging resistance.

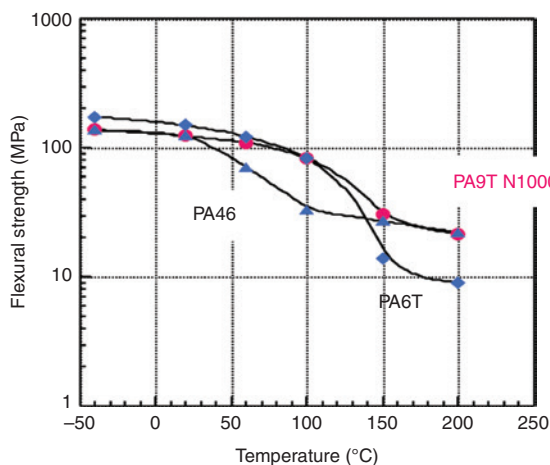


Figure 14: Flexural strength of unreinforced grade HPAs.

[Source: https://www.kuraray.eu/fileadmin/presse/publikationen/downloads_k_fair_2013/genestar/GENESTAR_Auto.pdf, printed with permission].

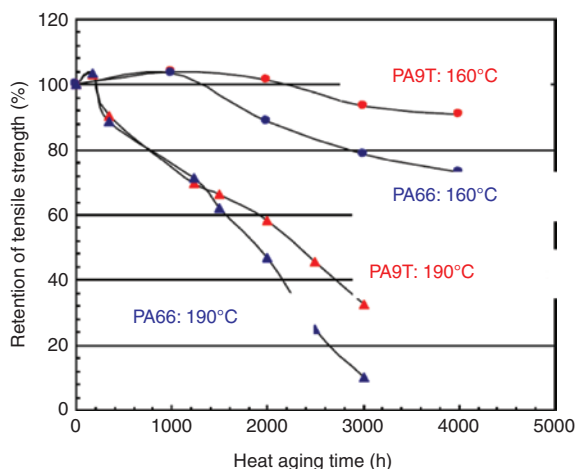


Figure 15: Flexural modulus of unreinforced grade HPAs.

[Source: https://www.kuraray.eu/fileadmin/presse/publikationen/downloads_k_fair_2013/genestar/GENESTAR_Auto.pdf, printed with permission].

PA9T also has good fuel barrier property as shown in Figure 16.

Fluidity, reflectivity and long-term stability properties are critical in the LED stent field, and Kuraray launched two products: TA112 and TA104. Lately, they launched a new product R270D, which was considered to be a cyclohexanedicarboxylic acid-based HPA (PA9C) with extraordinary ultraviolet resistance.

Figure 17 shows the comparison of reflectivity after short-term thermal aging and ultraviolet aging of three products of Kuraray's (TA112, TA104 and R270D), PCT and PA6T. Initial reflectivity and the reflectivity after short-term thermal aging of TA104 is excellent, and the ultraviolet

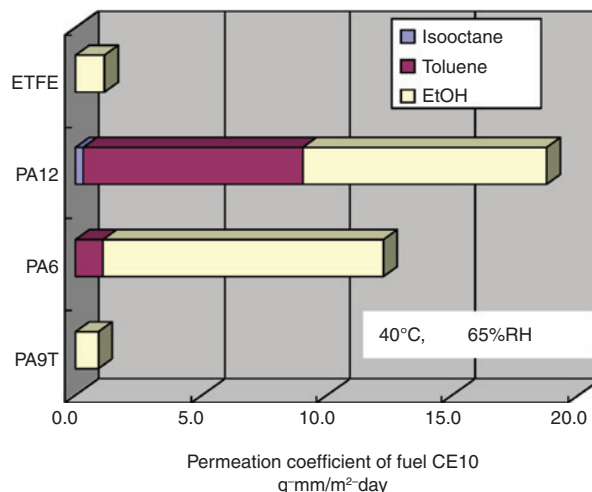


Figure 16: Fuel barrier property of different materials (Specimen configuration: film, thickness: 100 μ m); Analytical instrument: gas chromatography; Fuel CE10: isooctane/toluene/ethanol = 45/45/10 vol.%).

[Source: https://www.kuraray.eu/fileadmin/presse/publikationen/downloads_k_fair_2013/genestar/GENESTAR_Auto.pdf, printed with permission].

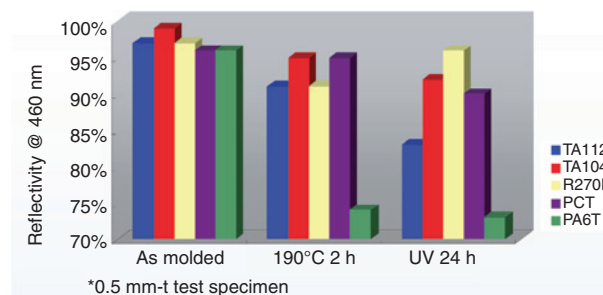


Figure 17: Short-term thermal aging and light resistance properties of different materials.

[Source: https://www.kuraray.eu/fileadmin/presse/publikationen/downloads_k_fair_2013/genestar/GENESTAR_LED.pdf, printed with permission].

aging property of R270D (PA9C) is good. Figure 18 shows the long-term thermal aging properties of different materials, and PCT performs best, followed by TA104.

In cooperation with Kuraray, Shinshu University studied the crystallization behavior (96, 97) and applications in the fiber of PA9T (98, 99), and Chisholm et al. (100) produced a series of PA9T/96 and studied their thermal properties, crystal structures and water absorption.

2.4 PA10T

Figure 19 shows melting points data of copolyamides derived from terephthalic acid and linear aliphatic

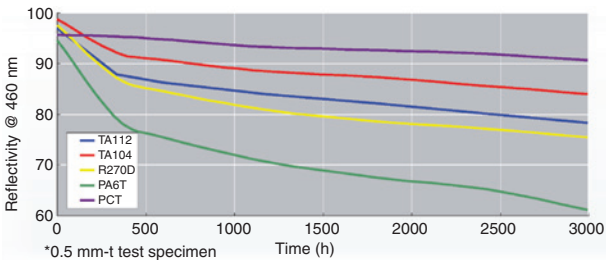


Figure 18: Long-term thermal aging properties of different materials.
[Source: https://www.kuraray.eu/fileadmin/presse/publikationen/downloads_k_fair_2013/genestar/GENESTAR_LED.pdf, printed with permission].

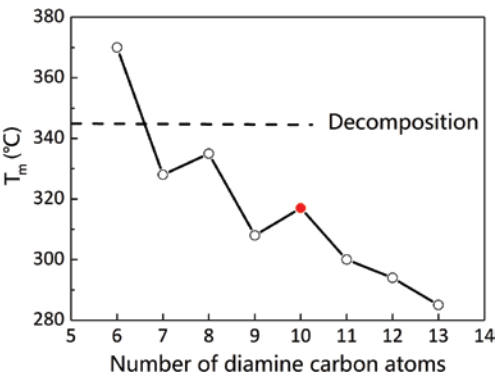


Figure 19: Melting point of copolyamides derived from terephthalic acid and linear aliphatic diamines with different carbon atoms.

diamines with different carbon atoms (101, 102). PAs decompose little by little from 340°C, so process temperature is generally lower. The T_m of PA10T is higher than PA9T.

Table 6 shows PA10T's properties of the main companies.

Rilsan® HT resin of Arkema is declared to be a HPA, but the T_m of it is only 260°C as shown on the website, which cannot be considered as a HPA, strictly speaking. On the other hand, the resin was declared to contain bio-based components, and we speculate that its structure may be PA10T/11 in accordance with their patents.

Table 6: PA10T properties of main companies.

Company	Brand	Structure	T_m (°C)	T_g (°C)
EMS	Grivory	HT 3	10T/X	295
		XE	10T/X	295
Evonik	Vestamid®	M3000	10T/X	285
		HT plus	F2001	10T/X
			C2505	10T/X
Kingfa	Vicnyl®	700	10T	316
		6100	10T/X	295
				105
Arkema	Rilsan®	HT	10T/X?	260

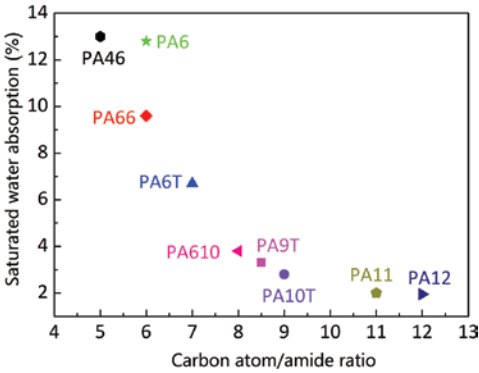


Figure 20: Water absorption of polyamides with different amide concentration.

Figure 20 shows water absorption of PAs with different amide concentrations, from which it can be concluded that the water absorption of PA10T is the lowest among the industrialized HPAs and it is only a little higher than long chain PAs.

The performances of various PAs (these data were finished by Asahi Kasei and Kingfa) are shown in Figures 21–24 (103), and the comprehensive performances of PA10T are excellent.

In comparison with other HPAs, PA10T has another advantage in that its monomer decanediamine is derived from castor oil and it is a bio-based material.

Kingfa, EMS, Evonik and Arkema can produce PA10T, and Unitika (104) launched a HPA (XecoT) in 2012 and declared that more than 50% of XecoT was bio-based, with lower water absorption than the common semi-aromatic PA6T. It can be speculated from the plant-derived declaration that XecoT should be PA10T, however, Unitika declared that its T_g was higher than 160°C, which deviated from that of PA10T greatly. Definite structure information on XecoT is not clear to-date.

Based on the abundant bio-based decanediamine monomer resources of China, Kingfa has made

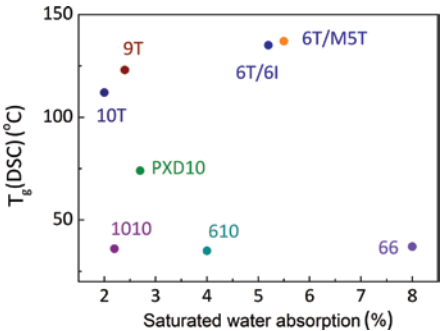


Figure 21: Glass transition temperature and saturated water absorption of various PAs.

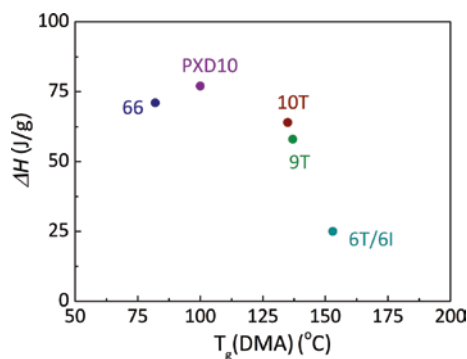


Figure 22: Melting enthalpy and glass transition temperature of various PAs.

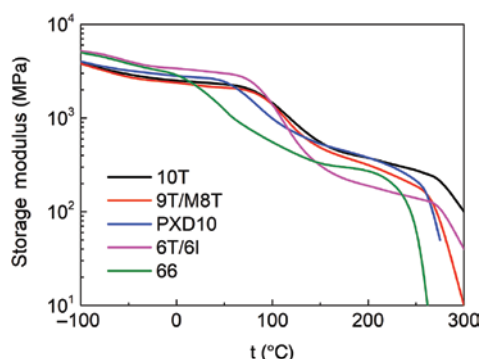


Figure 23: Storage modulus changing with temperature of various PAs after water absorption.

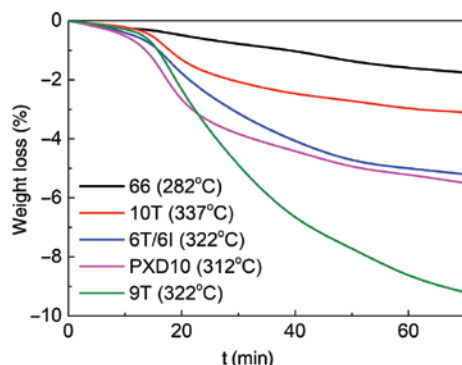


Figure 24: Thermal stability of various PAs.

breakthrough in polymerization process and equipments of PA10T HPA resin:

i. Solid suspension polymerization technology

With water as reaction medium, decanediamine and terephthalic acid react at 220–250°C to produce PAs, in which the temperature, pressure and water discharge are controlled carefully. In this system, monomers or prepolymers remain in the solid phase throughout, so it is defined as “solid” suspension polymerization to

distinguish it from traditional suspension polymerization, which is carried out by suspending the monomer (discontinuous phase) as droplets (50–500 mm in diameter) in water (continuous phase). Both discontinuous the phase and continuous phase remain liquid in the beginning, but in this system water concentration is a critical parameter: the high concentration of water leads to low polymerization rate and low concentration of water results in agitator blocking.

ii. Gel inhibition technique

The generation of triamine can be depressed by using CO₂ as a protecting gas, and the formation of gel can be avoided naturally. CO₂ combines with decanediamine to produce carbamates, which can decompose to decanediamine during the heating process. This reaction can compete with the deamination of decanediamine to reduce the triamine concentration. (Note: i–v are techniques of Kingfa PA10T, and they are not parallel to other HPAs).

iii. Controlled branched polymerization technique

The effect of multi-functional compounds on the properties of PA10T branched PAs was studied, and branched PA10T PAs can be produced by using 0.4 mol% benzenetricarboxylic acid (BTCA) as a comonomer, with considerable improved fluidity and increased toughness. Branched PA10T can be used in LED stents, and in electronic and electrical components, which require high fluidity materials to get rid of hollow in thin-wall articles.

iv. Diamine-water mixture recycling technique

The diamine-water mixture recycling system was developed to introduce discharged water into the next pot as a reactant. The diamine in the mixture can compensate for diamine loss during the water discharge process to guarantee a mole balance of diacid and diamine and raw material utilization was increased.

v. Key equipment

An automatic control system for solid suspension polymerization was developed to achieve precise control on key parameters such as water discharge weight, water discharge time, temperature and pressure; the wall on top of the reactor can be washed by an atomization spray system to wash off sublimated decanediamine to reduce diamine loss and improve dark spot concentrations of the resin; a diamine-water mixture recycling system can increase yield and reduce waste water discharge.

Kingfa's PA10T has gained OK bio-based certification from Vincotte, as shown in Figure 25. Now, the Zhuhai Vanteque



Figure 25: Bio-based certification from Vincotte of Kingfa PA10T.

Specialty Engineering Plastics Co., Ltd. has been founded by Kingfa since 2015 to work on research and development of specialty engineering plastics. Up to 2017, Zhuhai Vantec's capacity for HPAs is about 10,000 t/a, and a 20,000 t/a HPA construction project began recently. In addition, Zhuhai Vantec has built 5000 t/a thermal liquid crystal polymer (TLCP) product line and 800 t/a polyphenylene sulfone (PPSU) pilot-scale product line.

As the biggest PA10T HPA provider worldwide, Kingfa has done much research and development work on PA10T-related HPAs.

Cao et al. (105) synthesized PA10T, PA10T/66, PA10T/10I and PA10T/10I through a prepolymerization+SSP process, and found that some polyamides had two melting points, which was attributed to faulty crystals under annealing conditions; Zhang et al. (106) synthesized PA10T with different molecular weights, and the terminal structures of them were determined by ^{13}C -NMR. Then a low molecular weight PA10T oligomer was used as a fluidity modifier to increase the fluidity of HPA and while maintaining the mechanical properties; Zhang et al. (107) synthesized PA10T/10F using a bio-based material, 2,5-furandicarboxylic acid, through a prepolymerization+SSP process. It was found that the molecular weight of PA10T/10F increased with difficulty due to the blocking effect of 2-furancarboxylic acid generated by the decomposition of 2,5-furandicarboxylic acid at high temperature, but the final product PA10T/10F had good thermal stability. This work provided a new way to produce bio-based HPAs beyond castor oil; Sun et al. (108) studied nonisothermal crystallization kinetics of PA10T, PA10T/10I and PA10T/10F and found that PA10T/10F had lower crystallization activation energy and a high crystallization rate, which was attributed to good flexibility of the furandicarboxylic acid unit in comparison to terephthalic acid unit; Yi studied the modification of PA10T resin: the effect of graphite and graphene (109), boron nitride and magnesium oxide on the mechanical properties and heat-conducting properties of

PA10T composites (110); phosphinate was used as flame retardant to modify reinforced PA10T (111–113); the effect of combinations of screw and feeding style on the dispersion of spherical alumina filled in PA10T were studied (114); as were the crystallization kinetics of PA10T (113) and PA10T&PA6T/66 alloy (115).

The main producing area of monomer decanediamine is China, hence PA10T research was also carried out in other institutions in China: Yang et al. (116) from the Institute of Chemistry Chinese Academy of Sciences studied isothermal and nonisothermal crystallization kinetics of PA10T/10I/6; Wang et al. (101, 117–120) from the South China University of Technology synthesized decanediamine-based HPAs including PA10T through the prepolymerization+SSP process, and studied their crystallization, thermal stability and mechanical properties; Zhao (121) from the South China University of Technology found that the fluidity of PA10T (Vicnyl 700 from Kingfa) can be improved by adding a thermotropic liquid crystalline polymer (TLCP, Vectra A950 from polyplastics), and simultaneously, the mechanical properties were maintained; Hu et al. (122–125) from the North University of China studied the synthesis and properties of PA10T and PA10T/11.

Takenaka et al. (126) studied the tribological properties of PTFE/PA10T composite and found that tribological properties of PA10T such as the frictional coefficient, specific wear rate and limiting pv value improved with the addition of PTFE; Li and Dingemans (127) developed a mild temperature solution polymerization method to synthesize melt-processable PA10T precursors with cross-linkable functionalities, which were thermally cured into polyamide thermosets. Finally, semi-crystalline PA10T thermoset films were evaluated as single-component high-temperature shape memory materials.

3 Semicrystalline heat-resistant PAs in research

3.1 Whole-aliphatic heat-resistant PAs

PA46 is the only commercialized whole-aliphatic HPA, and others are in research, which is not accidental. Whole-aliphatic HPAs require a short methylene length and a high amide concentration, which results in poor thermal stability and high water-absorption of polymers. This contradiction makes it difficult to find a structure with both good heat resistance and low water absorption.

Table 7: Melting points of whole-aliphatic polyamides.

		Number of carbon atoms in a diamine						
		2	3	4	5	6	7	8
Number of carbon atoms in diacid								
2				391 (128)	305 (129)	331 (130) 320 (131)		276 (131)
3					191 (14)			
4	Decomposition (132)			Decomposition (132)		275 (132)	220 (133)	254 (132)
5					198 (14)			
6	308 (134) 315 (132)			290 (132)	254 (135)	265 (132)	226 (136)	250 (132)
7				233 (136)	183 (136)	202 (136)	196 (136)	
8	294 (132)			253 (132)	202 (136)	234 (132)		227 (132)
Number of carbon atoms in amino acid or lactam								
1	2	3	4	5	6	7	8	
		340 (137)	265 (138)	280 (63)	227 (137)	233 (137)	200 (137)	

[Source: Chem Rev. 2016;116(7):4597, printed with permission].

Table 7 shows the melting points of PAs derived from diamines or diacids with two to eight carbon atoms (139). T_m differences of different studies can be attributed to three reasons: 1. The heat history effects were not considered by some studies, in which the endothermal peak of the first-heating process was recorded as T_m ; 2. the molecular weight and structures of resins from different polymerization processes can be different, which may affect T_m ; 3. the T_m was usually measured by a melting point apparatus in early studies and DSC became an option only recently.

UBE has disclosed a considerable number of patents about oxalic acid-based polyamides production and modification since 2008 (140–146). The T_m of pure PA62 is 320°C, which is higher than its decomposition temperature at 310°C, and the copolymerization of PA62 has become inevitable for commercial use. PA92/62 with a T_m of 276°C has been synthesized by UBE, and its relative viscosity is higher than 3.0, which is suitable for use as an engineering plastic. Moreover, UBE declared that PA92/62 performed well for water absorption and chemical resistance: its water absorption is lower than PA6 and PA66, and both its acid and water resistance performances exceed PA6 and PA66, and is even better than PA12, which is very extraordinary considering its high amide concentration.

Mitsubishi disclosed a patent in 1994 (147) showing that the T_m and degree of crystallization of common PA6 and PA66 increased greatly by heating them under nitrogen for 24 h at 15 MPa, 235°C and 265°C, respectively: the T_m and degree of crystallization of PA6 can be increased from the original 225°C and 30% to 270°C and 90%; the T_m and degree of crystallization of PA66 can be increased

from the original 255°C and 30% to 300°C and 95%, which can certainly be defined as a HPA. However, due to the extreme conditions it was not practical for use.

PA4 should be paid more attention as regards the AB type PAs derived from lactam or amino acid. PA4 can be produced by the ring opening polymerization of 2-pyrrolidone or direct polymerization of γ -aminobutyric acid (GABA), which can be synthesized by glutamic acid catalyzation, as shown in Figure 26 (148). Hence, PA4 is a 100% bio-based material and it can be hydrolyzed to GABA in the presence of activated sludge, which implies that it is a potential as a biodegradable plastic (138–150). However, due to its poor thermal stability and the source issue of GABA and 2-pyrrolidone (151), PA4 has not been commercialized until now.

3.2 PA5T

Pentamethylene diamine-derived polyamides were not developed before 2010 due to the difficulties to produce pentamethylene diamine on a large scale. In 2013, Cathay Industrial Biotech (152–154) improved the efficiency of amino acid decarboxylase by 100 times during the biological fermentation processes through a gene engineering technique, and now pentamethylene diamine can be produced from biomass or sugar using microorganism after solving the cyclization of pentamethylenediamine during the purification process, laying the foundation for the industrialization of PA56 and even PA5T.

Table 8 shows the basic properties of PA56 and PA66. Saturated water absorption of PA56 is much higher than

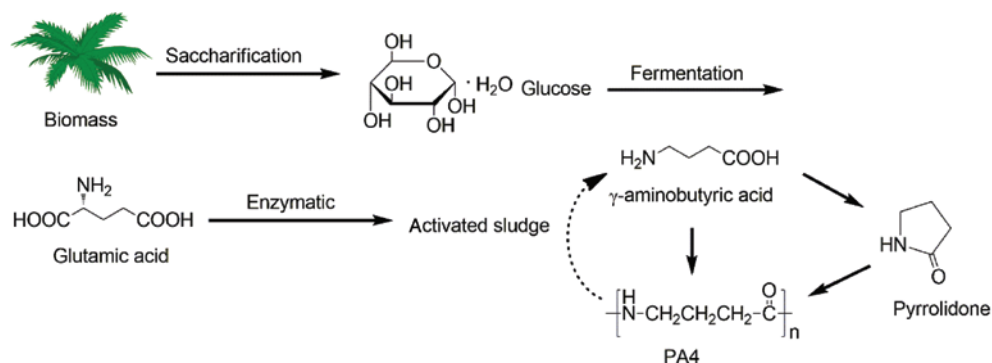


Figure 26: Polymerization and degradation of PA4.

Table 8: Basic properties of PA56 and PA66.

	Density (g/cm ³)	T _m (°C)	T _g (°C)	Saturated water absorption (%)
PA56	1.14	254	54	14
PA66	1.14	255	50	8.5

PA66, and it is a great disadvantage for applications such as engineering plastic when considering the obvious dimensional change after water absorption of injection moulding articles, hence the application of PA56 in engineering can be difficult.

Insiders have obviously recognized this problem, which can be deduced from their interests in the applications of PA56 as a fiber. In 2013, the Quartermaster Research Institute of the General Logistics Department of People's Liberation Army of China (PLA), Cathay Industrial Biotech, Suni Chem Co., Ltd. and Youxian Technology (Dandong) Co., Ltd. cooperated to achieve tons of PA56 fiber and verified the spinning properties of PA56. Eleven garment fabric samples were produced, and the strength, abrasive resistance, heat resistance, dyeability, water absorption and flame retardance were tested (135, 155). The moisture regain and dry moisture content of PA56 is 1.5% higher than PA6 and PA66, which is critical for fiber applications. The drying rate of PA56 is also faster than PA6 and PA66, which can meet the requirements of being dry, comfortable and breathable for use in the textile industry. A series of research on production and characterization of PA56 fiber has also been done by Donghua University in China (156–161).

Two lakhs tons per year of a green polyamide 56 project laid the foundation in Jining, Shandong Province, China in December 2015 (162). One can also find the news in Cathay's website (163) that an expansion project of monomers and polyamide using Cathay's biological method began to be built in Xinjiang on May 22nd, 2016. Cathay is promoting PA56 with the brand name Terry!® (164).

In February 2012, Ajinomoto Co., Inc. and Toray Industries, Inc. signed an agreement to collaborate together, including the production of pentamethylenediamine derived from plant through Ajinomoto's fermentation technology and commercialization of bio-based polyamides from pentamethylenediamine (165).

Cathay (166) and Toray (167) have applied PA5T-related patents. The T_m of PA5T is lower than that of PA6T, and the T_g of it is higher, and the acid resistance and thermal stability of it is also improved. However, the water absorption of PA5T is high due to its high amide group concentration. In general, there is no obvious advantage of PA5T in comparison to PA6T, and it the same for PA56: with high cost and mediocre performances. It is the cost of pentamethylenediamine that limits the development of PA5X, and the large-scale production and selling of PA5X will only come to fruition when the cost of pentamethylenediamine is close to that of hexanediamine.

3.3 Long carbon chain heat-resistant PAs

Early in 1970, Kanegafuchi Boseki Kabushiki Kaisha (168) developed PA11T with a T_m of 279°C, which was produced by melt polymerization of under canediamine and terephthalic acid under CO₂.

The source of long carbon chain diamines has been a problem for the industrialization of long carbon chain HPA. Long carbon chain HPA can be produced from long carbon chain diacid, however, the large-scale production of long carbon chain diacid relied on chemical synthesis process over a long period of time, which was complicated, expensive and had a serious pollution problem.

In 2000, Cathay (169, 170) produced long carbon chain diacid through a biological fermentation process using liquid paraffin as the raw material, which was a by-product of the refinery of oil. The crucial purification process was solved during diacid production, and finally,

Table 9: Basic properties of PA11T, PA12T and PA13T.

	T_m (°C)	T_g (°C)	Water absorption (ASTM D570) (%)
PA11T	300	123.4	0.13
PA12T	294	118.5	0.12
PA13T	285	111.4	0.10

industrialization of long carbon chain diacid was achieved, marked by the low-cost production of polymerization grade long carbon chain diacid. The aforementioned achievement offered hope for the development of long carbon chain HPA.

Zhengzhou University cooperated with the Henan Junheng Industrial Group Biotechnology Co., Ltd. to develop a series of long carbon chain HPAs, including PA11T, PA12T, PA13T and PA14T, which are now in the pilot stage (20, 171–182). The properties of PA11T, PA12T and PA13T are shown in Table 9. Overall, long carbon chain HPA has low water absorption, a good melting point and good processability (101, 183).

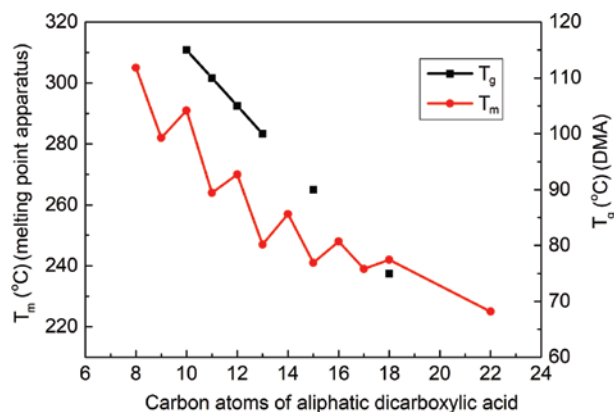
The North University of China and Taiyuan Zhonglian Zenong Chemical Ltd. Co. developed semi-aromatic polyamide PA11'T' with a T_m 312°C, derived from *p*-amino benzoic acid and a castor oil derivative 11-aminoundecanoic acid (184). However, *p*-amino benzoic acid is expensive, leading to the high cost of this process.

A series of PA12T and its copolymers were synthesized and characterized by Mathias, including terminal structures of PA12T blocked by benzoic acid (185), thermo-properties of PA12T/6T copolymers (186), and block composition of PA12T/6 (187, 188).

3.4 PAPXD10

Para-xylene diamine (PXD) related polyamides can be traced back to the well-known patent of Dr. Carothers, in which PA66 was discovered in May 1936 (15). The synthesis process of PXD10 was discussed in detail: using *o*-cresol as a solvent, and the white solid can be obtained by precipitating the reaction solution into mixtures of ethyl acetate and ethanol, with T_m 267–269°C and inherent viscosity 0.63 dl/g.

Frunze (189) synthesized a series of PAs based on PXD and aliphatic acids and aromatic acids, and using the same synthesis method, Vogelsong (190) from Dupont studied the crystallization behavior of PAs produced from PXD and linear aliphatic acids with six to 10 carbon atoms; Saitome and Komoto (191) and Ridgways (192) studied the structure-property relationship of PAs containing cyclohexane and a

**Figure 27:** Melting point and glass transition temperature of PAs derived from PXD and a series of linear aliphatic acids.

benzene group, and synthesized PAs derived from PXD and a series of linear aliphatic acids, the T_m (tested by a melting point meter) and T_g (tested by dynamic mechanical analysis, DMA) of which are shown in Figure 27.

Patents on meta-xylenediamine (MXD) and PXD were concentrated on fibers (193–200) before 1980s, after which the gas barrier properties of them were given more prominence and industry players began to use them in films (201, 202) and PAs moulding composition (203–205) fields.

Mitsubishi has been developing a particular normal-pressure melt polymerization process (206, 207) based on MXD since 1984, and an industrial chain has been formed revolving around MXD (208–229); Toyobo is also an important supplier of MXD-PAs using a high-pressure melt polymerization process, which concentrates on improving fiber-grade products and concentrates on gel and colour problems (201, 209, 230–248).

PXD has played a role of modifier in MXD production for a long time, T_m can be increased after adding PXD to improve heat resistance of MXD copolyamide. In most cases, the PXD content is lower than 30 mol% based on the whole diamines. Mitsubishi had not realized the importance of PXD in the HPA field until this century along with blooming HPA industry. Then PXD began to act as the main diamine in PA synthesis in Mitsubishi's patents, and the T_m of PXD10 is higher than 280°C and that of PXD6 is higher than 330°C (249, 250). The T_m of PXD6 is too high to act as a promising material, however, PXD10 can be a good candidate due to its medium T_m and low water absorption.

3.5 PANc

The cyclohexyl group is widely used in polyesters, especially in poly(1,4-cyclohexylene dimethylene

terephthalate) (PCT), which has found wide application in LED stents due to its excellent heat resistance, low water absorption and good UV aging resistance, and it even threatened the status of HPAs in this area (251). The configuration transformation of 1,4-cyclohexanediacid (CHDA) has been intensively studied in polyester (252–254), cis-trans ratio and configuration transformation rate of CHDA are determined by the physical state of PCT: crystal or liquid crystal favors the formation of trans configuration (packing effect), and the thermostable cis-trans configuration ratio is 34/66 in the isotropic case.

The configuration of CHDA in polyamide was studied by Koning using PA126/12CHDA as model polymer. CHDA cis-trans ratio of the final product was inconsistent with feeding ratio through traditional prepolymerization+SSP process in water: feeding ratio 80/20→prepolymer 32/68→final product 15/85; in contrast, the CHDA cis-trans ratio of the final product is consistent with the feeding ratio through low temperature (75°C) solution polymerization (255). CHDA with different cis-trans configuration ratios reacted through low temperature (75°C) solution polymerization (256), and the T_m of products were shown in Figure 28. The T_m of cis-derived products in the first heating process decreased with increased the CHDA feeding ratio, and instead, the T_m of trans-derived product increased. However, whatever the cis-trans feeding ratio, the cis-trans ratio of the final product remained 25/75 (257, 258), leading to the same melting point. Figure 29 shows the mechanism.

The configuration of CHDA was determined by DSC, WAXD, solution NMR and solid NMR techniques (256): solid NMR showed that cis-CHDA is distributed in the amorphous region and the trans-CHDA is located in both the crystal and amorphous regions; the existence of CHDA in crystals was confirmed by WAXD, in which cyclohexyl tended to be perpendicular to main chain.

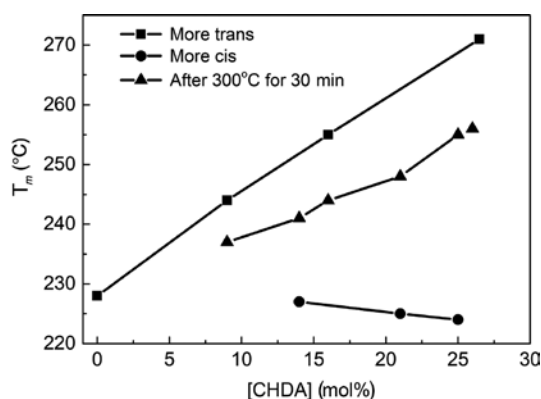


Figure 28: The effect of CHDA content and thermal treatment on T_m of 12.6/12CHDA.

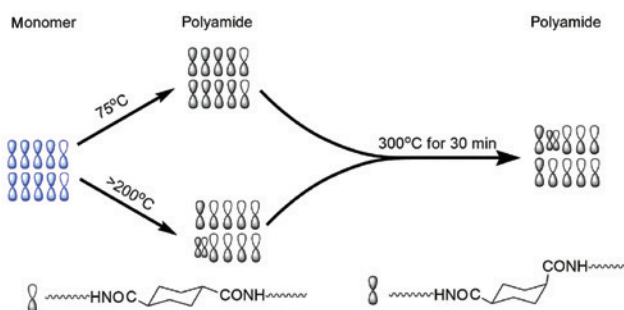


Figure 29: Cis-trans configuration transformation in polymerization and thermal treatment.

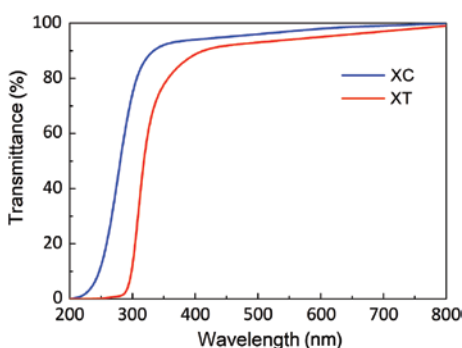


Figure 30: Absorption of polyamides based on terephthalic acid (XT) and CHDA (XC).

[Source: Advertising brochure of Asahi Kasei, printed with permission].

DSM (259, 260) attempted to replace adipic acid with less than 40 mol% of CHDA to estimate its effect on PA46 and PA66. PA66/6C with 30 mol% CHDA replacement melted on 298°C, and its water absorption was 5.5%, which was considered to be a promising HPA material.

Asahi Kasei studied the effect of replacing terephthalic acid with CHDA on polymer properties and launched alicyclic HPA (261–269). The light absorption properties of HPAs based on terephthalic acid and CHDA are shown in Figure 30. The absorption of alicyclic HPA on a short wavelength light was low, in favor of light permanency. The T_m and T_g of HPA are shown in Figure 31, and it can be found that alicyclic HPA have high T_m and high T_g . The most outstanding properties of alicyclic HPAs are their excellent color and light aging permanency, which has advantages in LED and other fields.

3.6 Semicrystalline heat-resistant PAs containing sulfur

The most typical representative of sulfur-containing polymer is polyphenylene sulfide (PPS). The main chain of

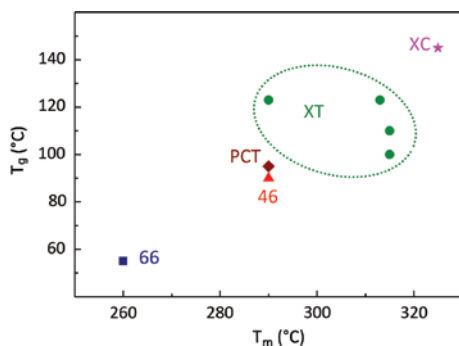


Figure 31: Melting point and glass transition temperature of various materials.

PPS alternates phenyl and sulfur units with well-defined structures, in which massive phenyl in the main chain provides rigidity and the thioether bond provides facility. The crystallinity of PPS can be up to 75% with melting points of 280–290°C. Yang (270) of the Sichuan University in China devoted himself to researching and developing PPS and its derivatives (271–275), and a series of HPAs containing sulfur were produced.

Poly(meta-aryl sulfide amide amide) (m-PASAA) with an intrinsic viscosity of 0.45 dl/g was prepared by an aromatic nucleophilic substitution reaction: by the step polycondensation of sodium sulfide ($\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$) with 3,3'-bis(4-difluorobenzoyl) aryl diamine between 180 and 202°C at atmospheric pressure. The polymers were found to have excellent thermal performance with glass transition temperature (T_g) of 233.5–277.8°C, initial degradation temperature (T_d) of 447–456.7°C (276). However, due to the poor processability of wholly-aromatic PAs, the performances of m-PASAA can only be determined by film through the solution method.

A series of acyl chloride containing thioether units (277–279) were synthesized to condensate with linear aliphatic diamines to produce high-molecular-weight semi-aromatic PAs as shown in Figure 32. All of the PAs exhibited good thermal stability, corrosion resistance, low-temperature mechanical properties, and low dielectric constants, almost the same as the properties of PA9T.

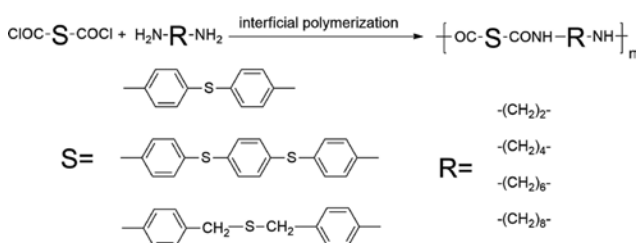


Figure 32: Synthesis of semi-aromatic PAs containing thioether units.

Although semi-aromatic PAs containing thioether units have good performances, monomers have not been commercialized until now and complicated organic synthesis procedures must be taken to produce them, and furthermore, interfacial the polymerization technique is a rare procedure in industry.

4 Patents analyses

HPAs are currently a hot spot for industry development, most companies have a strong sense of confidentiality and little information can be found in published literature. Research on patents are also limited to enterprise internally as confidential research findings and are rigidly controlled. In addition, in view of its own characteristics that the consistency and the repeatability of a patent were rarely validated, only novelty and inventiveness are considered in patent examination, and the data of some patents seemed doubtful objectively. Especially in recent years, HPAs have entered a comparatively smooth development period, and even some companies have begun to manipulate the experiment results to cut costs and accelerate authorization, which has even stunted technological progress. One should bear in mind the Mencius's byword "If you believe everything you read, better not read".

Although there are the mentioned problems, the most convenient and efficient way to study progress in HPAs is from patents. Feng et al. (280) of Zhejiang University has analyzed patents on semi-aromatic polyamides in China and discussed polymerization processes, such as low-temperature solution polycondensation, interfacial polycondensation, melt polycondensation and aqueous phase polycondensation, but the global situation was absent. Global patents on HPA synthesis were analyzed in this paper using data retrieved from Thomson Innovation (281).

4.1 Search strategy

Patents on HPA synthesis (1935–2016) were retrieved and analyzed working with the database *Thomson Innovation*. The International patent classification (IPC) provides a facility for retrieving, and C08G69 can locate POLYAMIDE resin related patents. Then a series of keywords can be used to screen out common PAs, such as terephthalic acid, high melting points, etc. Furthermore, patents from the same family were integrated and duplicates were removed to get 1186 patents, which are the basis of our analysis.

4.2 Basic analysis

4.2.1 Time trend

It can be seen from Figure 33 that HPA patents gradually appeared in 1950s in 20th century, and as mentioned before, in this period people focused on the fiber application of PAs and HPA did find its position in this field. After 1980s, along with the progress of PAs used as engineering plastic, the heat-resistant properties of HPA were highlighted and the patents began to obviously increase. Benefiting from the RoHS directives of lead-free alloys ($>260^{\circ}\text{C}$) using in SMT after 2006, HPA became a favorite material and patents began to boom. In China, patents began to appear from 2000, and exploded after 2006 in accordance with global trends.

4.2.2 Distribution by country

Generally, a patent can be applied in many countries including the applicant's own country, leading to family patents with similar contents. This may puzzle us when we decide to determine if a patent is from an applicant's own country or a family patent from another country, and when the latter happens, the real technological level of a country cannot be determined. The strategy of priority country statistics can solve the problem, such that in most circumstances, applicants tend to apply for a patent in their own country first when scientific achievements are made. And then the applicants achieve a priority to apply for international patents, meaning that priority country statistics can reflect a country's real technological level.

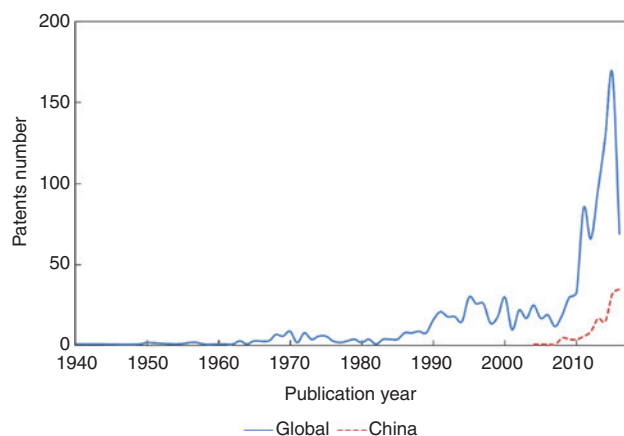


Figure 33: Time trend of HPA patents.

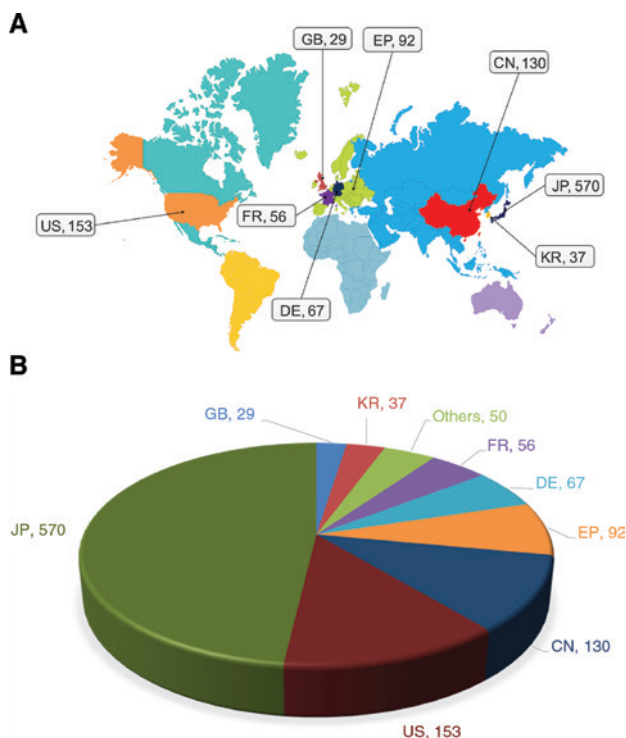


Figure 34: Countries distribution of HPA patents: (A) map; (B) pie chart.

The distribution as regards country was obtained according to the aforementioned method as shown in Figure 34. Japanese patents made up nearly 50%, implying that Japanese government and enterprises attached much significance to intellectual property rights. Most Japanese patents were applied in the domestic market, and only some key patents were exported to other countries.

As expected that US occupied the second position. China occupied the third position, meaning that development of HPA in China is rapid.

4.2.3 Analyses of the main applicants

Figure 35 shows companies with more than 10 patents. There are 19 companies and 17 of them are still active in the HPA field, and most of them have mature products.

As like the impact factor (IF) of academic journals, the patent impact factor (PIF) of a company can be defined as total citations divided by the total number of its patents. Similar to the IF, the PIF can also be used to reveal a company's contribution to this field. Patent family is defined as combination of a same patent applied in different countries. The total number of family patents (N) reflects internationalization of a

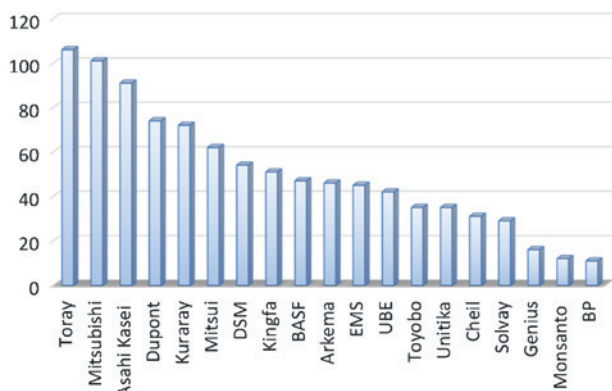


Figure 35: Main applicants of HPA patents.

company, but not the real technological prowess. Only the number of family patents without duplicates (viz., a series of patents of different countries are defined as one patent) (M) can reflect the real technological prowess of a company.

A bubble chart (Figure 36) shows the PIF as Y-axis, N as X-axis, and M as bubble area.

Both Mitsubishi and Solvay are distinctive: the N and M of Mitsubishi are high, but the PIF is comparatively low, N and M of Solvay are average, but the PIF is high. As old PA suppliers, the N, M and PIF of Dupont and EMS are balanced, which matches their position in this field. The outstanding characteristics of Asahi and Toray are a high M, a moderate N, and a low PIF. As the first commercialized HPA supplier, the PIF of DSM is low, which is derived from butanediamide, the exclusive monomer DMS used, and other companies do not have the monomer and have no incentive to do the related research. Both Genius and Kingfa in China are uncompetitive: the PIF of Genius is a little high, but their N and M are low; the M of Kingfa is ok, but the PIF and N are low.

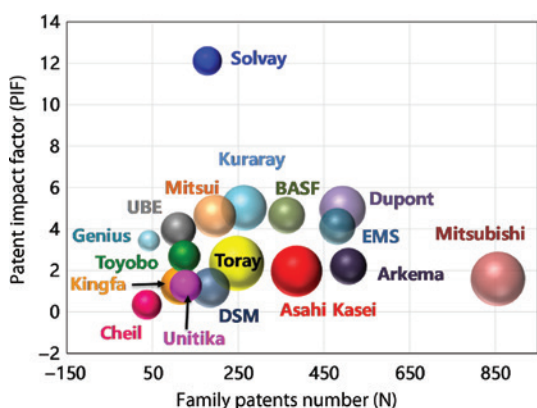


Figure 36: HPA Patents bubble chart of main companies.

4.3 Technical analysis

With regard to HPA resin patents, there are two key points: the structure of the resins and the polymerization procedure, which are generally demonstrated in examples of a patent. Now cluster analysis is used extensively as a common patent analysis tool to get some keywords to create an image map, which is called the cartographic visualization. However, only rough information can be achieved due to the absence of information from examples in this analysis.

Although the claims made for patent are wide, the real technology is generally shown in examples, which demonstrate the specific technology of the applicant. Based on the aforementioned knowledge, examples of HPA resins patents were summarized and analyzed to get a series of image maps to conveniently understand technique trends in HPA resins synthesis field.

4.3.1 Structures of resins

Both a three-dimensional (3D) topography map and a contour map can be obtained to statistically analyze monomers in examples of patents, as shown in Figure 37. With no surprise, the main monomers include terephthalic acid, hexanediamine, adipic acid and isophthalic acid, considering their low costs. In addition, due to the technical barrier of monomer production, DSM and Kuraray dominate butanediamine and nonamethylene diamine related HPAs, respectively. Toray has many caprolactam- and pentamethylenediamine-related patents, and Kingfa occupy a predominant position for decanediamine-related HPA, which matches its lead in this field.

Figure 38 shows the development trends of monomers after 2000. It can be seen that the number of HPA patents has soared since 2010, and other new trends should be paid attention besides the typical four monomers such as terephthalic acid, hexanediamine, adipic acid and isophthalic acid. Remarkable peaks appear in the 3D relief map in the area of sebacic acid, alicyclic acid, decanediamine, long-carbon-chain amino acid/lactam and dodecanediamine, which were rare before 2010. All these monomers should be focused on by those who intend to devote themselves to the HPA field.

4.3.2 Polymerization processes

Figure 39 shows the polymerization processes of 17 main companies, and explanations of polymerization processes are shown in Table 10.

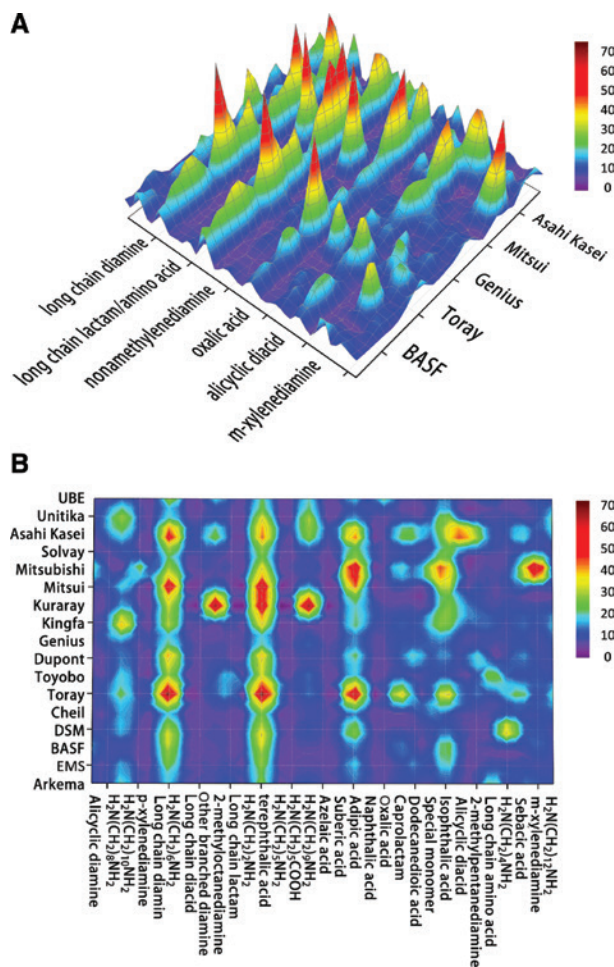


Figure 37: 3D topography map (A) and contour map (B) by monomers analysis of HPA patents.

It can be seen from Figure 39 that Pre+SSP is the main polymerization process, which is closely related to the properties of HPA resin: high melting point close to the decomposition temperature and yellowing and performance deteriorating of the polymer when melting. OHPMP and Pre+TSE processes are evenly matched. The advantage of OHPMP is that both prepolymerization and tackification are conducted in the same autoclave conveniently, however, yellowing and performance deteriorating are inevitably due to the long reaction time; the advantage of Pre+TSE is that decomposition of the resin can be avoided due to the short residence time in the twin screw extruder, however, prepolymerization should be carried out first. In addition, tackification must be conducted in a specially designed twin screw extruder, which has special demands on screw combination and exhaust system.

Figure 40 shows patents number of various polymerization processes.

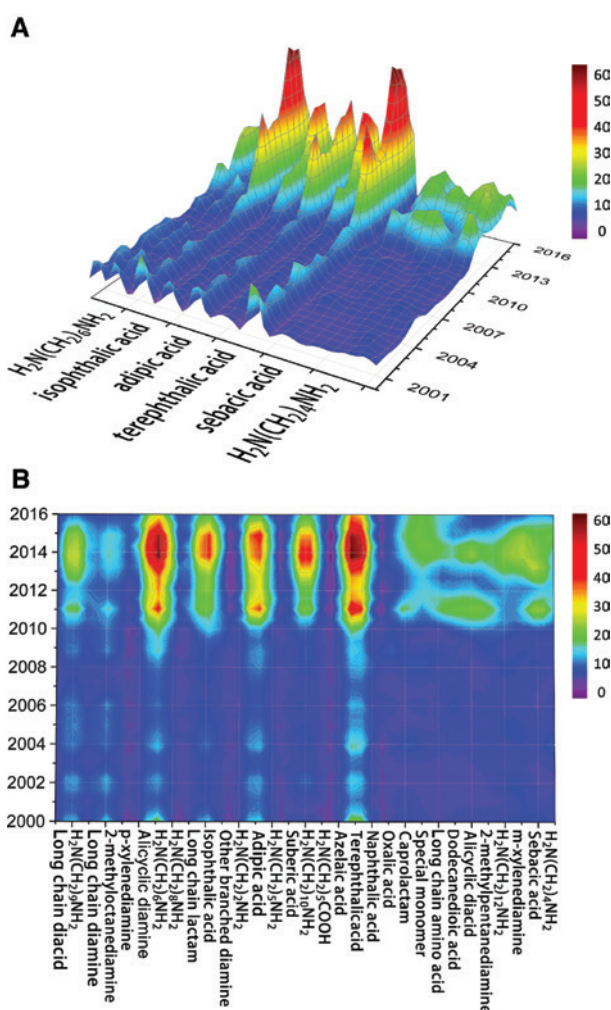


Figure 38: 3D topography map (A) and contour map (B) by monomers analysis of HPA patents after 2000.

4.3.2.1 Pre+SSP

Most Pre+SSP processes are conducted in a non-melting state system, in which the reaction temperature is lower than the melting point of prepolymer or polymer to avoid their decomposition or performance deterioration at high temperature.

4.3.2.1.1 Prepolymerization

A typical prepolymerization procedure is shown below: a 20 l autoclave was filled with terephthalic acid (2960 g), 1,10-diaminodecane (3200 g), benzoic acid (82.8 g), sodium hypophosphite (6.2 g) and deionized water (2550 g). The autoclave agitator was set to 0 rpm and the contents were purged with nitrogen at 10 psi for 10 min. Then the autoclave was heated to 225°C and during the heating process the agitator was set to 50 rpm and rotated at about 180°C. The temperature reached 250°C after about 3 h and was held there for about 40 min, after

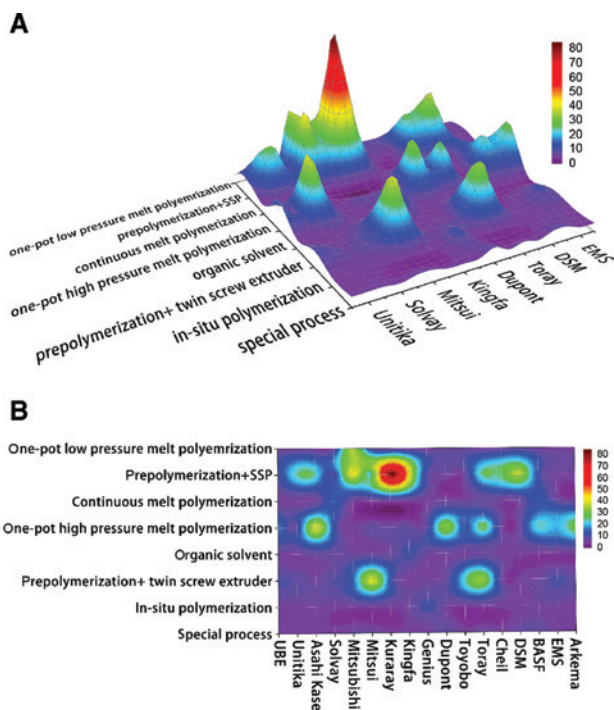


Figure 39: 3D topography map (A) and contour map (B) by polymerization processes of HPAs.

which water discharge was carried out to release 1650 g of water condensated by a reflux condenser over 1 h. Then the reaction product formed in the reaction vessel was flushed into the open air through a nozzle to take it out in a solid form which was then dried to obtain a solid low-degree condensation product [in most cases, additional drying is not necessary because flashing is the only choice for those liquid water more than 100°C in autoclave (282)].

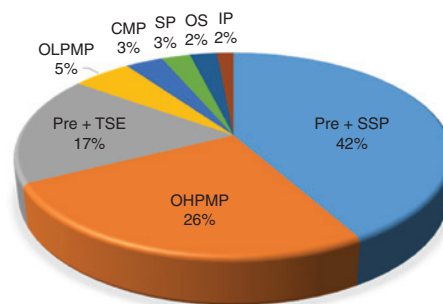


Figure 40: Pie chart of HPAs polymerization processes.

The low-degree condensation product can be easily taken out without being adhered to the wall surfaces or to the discharge port.

The materials' status in the reactor is critical in the prepolymerization process, and a lack of control on temperature, pressure and residence time leads to powder caking and stir jam when the solid content, after water discharge, is as high as or more than 80 wt%. Asahi Kasei and EMS studied prepolymers' status in 1990s and found that a homogeneous prepolymer system can be obtained through precise control on temperature, pressure, water discharge and residence time (283, 284). In 2001, Dupont studied the issue further and a phase diagram of PA6T copolymer was found as shown in Figure 41 (285).

If prepolymerization was conducted at a temperature and pressure below the critical line in seen in Figure 41, solid deposits occur after 60 min, 120 min and 180 min, respectively. Hence, the prepolymerization must be finished in the aforementioned time to avoid blowing

Table 10: Polymerization processes of HPAs.

Process	Description
Prepolymerization + solid State Polymerization (Pre + SSP)	A prepolymer was obtained by prepolymerization process, and then SSP was conducted at a temperature lower than T_m
One-pot high pressure melt polymerization (OHPMP)	High pressure polymerization (>2.0 MPa) was conducted at self-generated pressure of water, and then temperature was raised to higher than T_m and pressure was reduced to atmosphere to get a polymer
Prepolymerization + twin screw extruder (Pre + TSE)	A prepolymer was obtained by prepolymerization process, and then the prepolymer was fed into a twin-screw extruder to get a polymer
One-pot low pressure melt polymerization (OLPMP)	Generally, water was not added and low pressure polymerization (<1.0 MPa) was conducted by regulate phase properties of diamine and diacid carefully. Then temperature was raised to higher than T_m and pressure was reduced to atmosphere to get a polymer
Continuous melt polymerization (CMP)	The polymerization was conducted in a tubular reactor at a temperature higher than T_m
Special process (SP)	Less common processes, such as supercritical CO_2 polymerization, dinitrile + diamine polymerization
Organic solvent (OS)	Polymerization using organic solvent
In-situ polymerization (IP)	Additives, such as fillers and flame retardants, were added with monomers into the reactor simultaneously

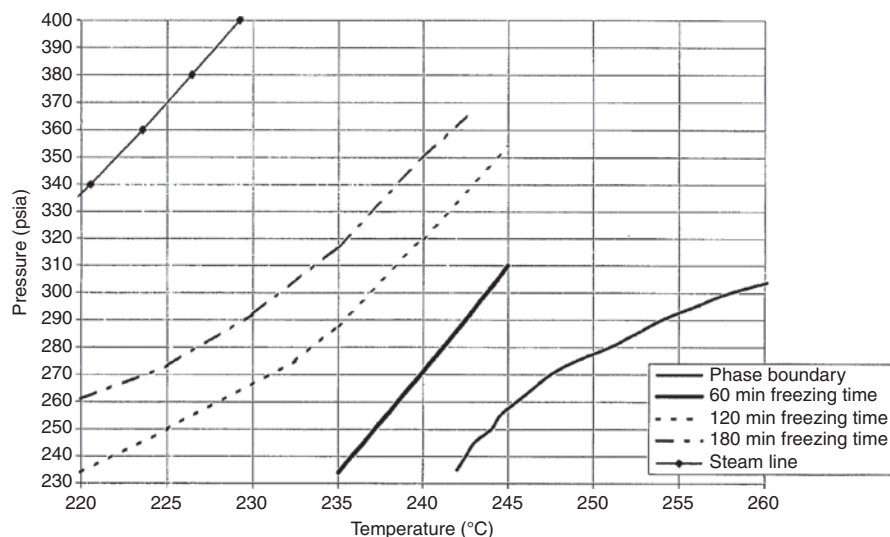


Figure 41: Phase diagram of PA6T copolyamide in prepolymerization stage.
[Source: US6759505B2, printed with permission].

difficulty, which is an impossible situation for large-scale production. Dupont pointed out that a continuous polymerization production line ceased due to powder caking, and it took 8 days to clean it up.

4.3.2.1.2 Solid state polymerization

Tackifying is conducted after prepolymerization, and prepolymerization and the tackifying process are conducted step by step. The particle size of prepolymers is critical: too big a particle leads to volatile escape trouble, and the degree of polymerization distributes gradiently, leading to a polymer with a wide molecular weight distribution; too

small a particle is easy to be removed during tackifying process, causing pipe blocking.

The solid state polymerization process has been discussed in detail in a book (286) and a review (287), which concentrated on experimental data or theoretical calculation, and there are few references on industrial situations.

There are two main SSP pieces of equipment: a tackifying tower and a vacuum drum, as shown in Figure 42 (41).

A tackifying tower is suitable for a 10,000-tonnage scale production, and the product properties are constant. However, there are blind corners in the tower, and some

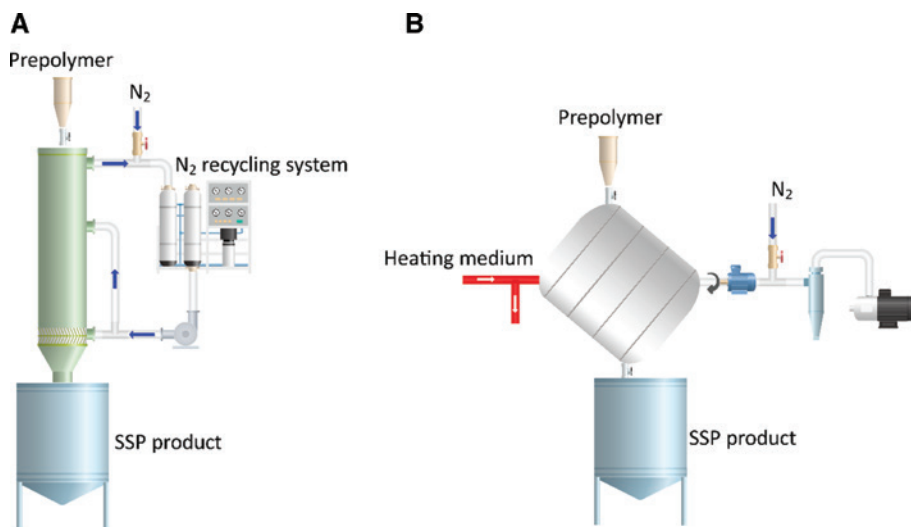


Figure 42: Industrialized equipment for SSP: (A) tackifying tower; (B) vacuum drum.

polymers may be detained in the tower to produce gel or char; a vacuum drum is a good match for 1000-tonnage scale production, which is flexible but inefficient.

New equipment was invented to solve the aforementioned problem.

PA6T/66/12 continuous tackifying process was conducted in a fluidized bed by UBE as shown in Figure 43 (288). The novelty of the equipment is the vibration motor to mix uniform prepolymers. The particle size of the prepolymer is about 0.2 mm, and the standard deviation of the resin after tackifying is only 0.016. In contrast, the standard deviation of the resin with tackifying tower is 0.058.

Kuraray used an equipment similar to a blade paddle dryer for SSP processing (Figure 44) (289), which was also used by UBE (290). PA9T resin with relative viscosity less than 0.04 can be obtained on the premise of a particle size 2 μm to 1 cm: if the particle size is smaller than 2 μm , the recycling of protective gas becomes difficult due to the filtration problem; if the particle size is bigger than 1 cm, the surface and internal degree of polymerization deviate greatly, and the molecular weight distribution becomes broad. With the same prepolymer, the standard deviation

of relative viscosity of polymers from tackifying tower can be as high as 0.3, and the particle wears seriously, leading to a high powder content.

4.3.2.2 One-pot high pressure melt polymerization

Most procedures of one-pot high pressure melt polymerization were conveniently conducted in one reactor, which is very suitable for small factories.

A typical OHPMP procedure is shown below (291):

A 10 l autoclave was charged with terephthalic acid (1040.48 g), dodecanedioic acid (160.27 g), 1,10-diaminododecane (1236.33 g), an aqueous solution containing 0.5 wt% sodium hypophosphite and 2.5 wt% sodium bicarbonate (42.99 g), an aqueous solution containing 28 wt% acetic acid (29.34 g), an aqueous solution containing 1 wt% Carbowax® 8000 (4.30 g) and water (3562.91 g). The autoclave agitator was set to 5 rpm and the contents were purged with nitrogen at 10 psi for 10 min. The agitator was set to 50 rpm, the pressure relief valve was set to 250 psig, and the autoclave was heated to 225°C. The pressure reached 250 psig after about 60 min and was held there for another about 40 min until the temperature of the

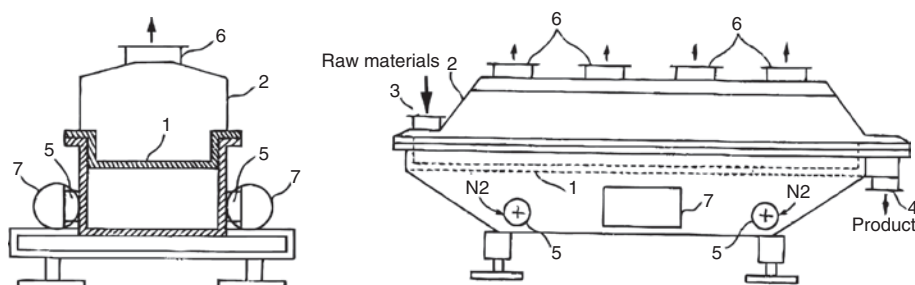


Figure 43: Fluidized bed by UBE for SSP (1 bed; 2 shell; 3 inlet; 4 outlet; 5 nitrogen inlet; 6 nitrogen outlet; 7 vibration motor). [Source: JP10087824A, printed with permission].

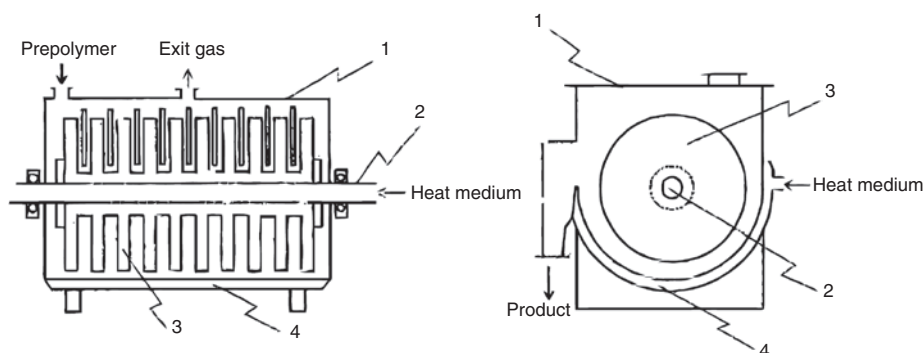


Figure 44: SSP equipment of Kuraray (1 body; 2 rotation axis; 3 stir axis; 4 heating medium jacket). [Source: JP2000044677A, printed with permission].

autoclave contents had reached 225°C. The temperature relief value was then set at 350 psig. The pressure rose to 350 psig over about 15 min, where it was held for about 85 min. During this time, the temperature of the autoclave contents rose to about 295°C. The pressure was then reduced to 0 psig over about 45 min. During this time, the temperature of the autoclave contents rose to 320°C. The autoclave was pressurized with about 50 psig nitrogen and the molten polymer was cast from the autoclave. The collected polymer was cooled with steam and water and cut. The melting point of the polymer PA10T/1012 is 300°C.

The key point of OHPMP is the water discharge stage, during which pressure is constant (350 psig) and temperature increases constantly. If water content decreases continuously and the temperature cannot increase to higher than the melting point of the prepolymer of the polymer, the solid content will be high, leading to agitation and heat transfer difficulties.

4.3.2.3 Prepolymerization + twin screw extruder

The prepolymerization procedure of both the Pre + TSE process and the Pre + SSP process are similar, but the residence time of the resin in the twin screw extruder process is short, requiring a higher degree of prepolymerization. The low degree of the prepolymer may find it difficult to polymerize completely, and plenty of steam from the amidation requires a special design of the exhaust system.

Mitsui and Toray realized this problem: in early patents of Mitsui (292), the molecular weight of prepolymers was no more than 1000 g/mol, and after 2000 (293), Mitsui usually adopted the procedure that prepolymers were conducted on the SSP process to increase the molecular weight before they were added into a twin screw extruder; Toray (294–298) pointed out that the degree of the prepolymer should be increased to favor of the following polymerization. For example, the relative viscosity of PA6T/66 should be higher than 1.3.

4.3.2.4 One-pot low pressure melt polymerization (OLPMP)

MXD6 derived from m-xylene diamine and adipic acid has been produced nearly exclusively by Mitsubishi through the OLPMP process for decades. The melting point of MXD6 is less than 250°C, hence strictly speaking, MXD6 is beyond the HPA field and Mitsubishi conceptualized it as gas barrier material in the early days. But if m-xylene diamine is replaced by p-xylene diamine, the melting point of the PA increases sharply. Mitsubishi launched its HPA PXD10 with a melting point of 290°C to compete with traditional HPAs.

A typical OLPMP procedure for PXD10 is shown below (299–302):

Into a jacketed 10-l reaction vessel (pressure resistance: 2.5 MPa) equipped with a stirring device, a partial condenser, a cooler, a dropping vessel, and a nitrogen gas inlet tube, 2.140 kg (10.58 mol) of sebacic acid was charged. After sufficiently purging the reaction vessel with nitrogen, the pressure was raised to 0.3 MPa by nitrogen and the temperature was raised to 160°C to uniformly melt sebacic acid. Into the reaction vessel, 1.443 kg (10.60 mol) of p-xylylenediamine (boiling point = 274°C, under atmospheric pressure) was added dropwise over 170 min while stirring the contents. During the addition, the inner temperature was continuously raised from 160°C to 283°C. In the dropping step, the pressure was maintained at 0.5 MPa and the water released by condensation was removed from the reaction system through the partial condenser and the cooler. The temperature of the partial condenser was regulated within 148–152°C. After the dropwise addition of p-xylylenediamine, the pressure was reduced to atmospheric pressure at a rate of 0.2 MPa/h over 120 min. During the pressure fall, the inner temperature rose to 303°C. Thereafter, the reaction was further continued for 30 min under 0.082 MPa. The total reaction time from the start of dropping p-xylylenediamine was 320 min. The solidification and precipitation of oligomer or PA were not noticed at all throughout the whole reaction process, and the reaction system was maintained in a uniform molten state from the beginning to end of the reaction. The obtained polymer had: a terminal amino concentration of 42 (μeq/g); a terminal carboxyl concentration of 81 (μeq/g), a number average molecular weight (Mn) of 14,900 by GPC analysis, a weight average molecular weight (Mw) of 40,900 by GPC analysis, a degree of dispersion (Mw/Mn) of 2.7, and a melting point of 289°C.

It can be seen from the aforementioned process that the solidification risk in the OLPMP process still exists, and precise control on formula, feeding ratio, temperature and residence time is necessary.

4.3.2.5 Other processes

There are also other processes for HPA polymerization, especially the laboratory scale technique, such as interfacial polymerization, aminolysis of polyester, polymerization with ionic liquid as solvent, diol + diamine polymerization and supercritical CO₂ polymerization. However, organic solvent or high-pressure conditions must be used in those processes, and purification and solvent recycling can be difficult, leading to unsuccessful industrialization.

4.3.2.5.1 Interfacial polymerization

In 1959, Dupont published a series of articles to expound interfacial polymerization in detail (24–26, 303–310). When a water-immiscible acyl chloride solution is brought into contact with an aqueous solution of an aliphatic diamine, a film of high molecular weight polymer forms at once where the two solutions meet. The film is very thin but strongly coherent. The film can be pulled out of the interface and is immediately and continuously replaced to form a long, endless cord of PA. In retrospect, interfacial polycondensation provided a much-needed alternative route to polymers that could not be prepared by the melt polycondensation process. In addition, it was a simpler and faster procedure that was especially useful in a laboratory with an objective to search for new polymers and fibers with new property combinations. Dupont even published a popular science piece in the *Journal of Chemical Education* to introduce this technique (311). In recent years, interfacial polymerization has found its application in membrane and microcapsule synthesis (312–318). But there is little research on HPA interfacial polymerization (177).

4.3.2.5.2 Aminolysis of polyester

A polyamide similar to PA6T was produced by Nakano et al. through aminolysis of PET with hexanediamine, melting point (300°C) which was much lower than that of pure PA6T (>370°C) (319, 320). The polymerization process was very complicated, and at least two steps have to be carried out to get high molecular weight HPAs: oligomer with inherent viscosity 0.4 dl/g was produced by the reaction of a polyester with a diamine in an organic solvent (o-dichloro benzene, toluene, etc.), and the oligomer produced in water was of much lower molecular weight ($[\eta] = 0.08$ dl/g). The oligomer was poured into ethanol to precipitate a white solid for drying; then the dried oligomer was tackified by SSP or a twin-screw extruder. In addition, the oligomer with an inherent viscosity of 0.5 dl/g can be obtained by SSP only, and a polymer with $[\eta] > 0.8$ dl/g can only be obtained by melt polymerization.

Fan et al. (321) produced a semi-aromatic PA PA6T through the macromolecular amidation in sulfolane using PET and hexanediamine as raw materials. They found that the temperature was a key parameter and the product had a satisfactory yield, ester-amide conversion and inherent viscosity can be obtained at 200–210°C for 10 h. Trace amount of catalyst (10^{-4} mol/0.1 mol PET) resulted in good yields. Kim et al. also studied the reaction of PET with aromatic diamine in dodecylbenzene (322, 323).

To ensure aminolysis of the polyester, it can be usually be dissolved in a high boiling point polar solvent, leading

to difficulties in solvent removing and recycling. In addition, due to the inherent defect of the macromolecular reaction, the complete reaction is impossible as the ester and amide group coexist in the product with complicated structures and poor performances. The commercialization of this technique is very uncertain although the polyester waste can be recycled by this process.

4.3.2.5.3 Polymerization with ionic liquid as solvent

There was a review on the application of ionic liquid in polyamide synthesis (324). Vygodskii et al. produced PXD6 with an inherent viscosity of 0.91 dl/g (in H_2SO_4) with PXD and adipic acid in an ionic liquid, in which a 2.25 times equivalent of triphenylphosphine must be adopted as the activating agent (325). However, the removal of triphenylphosphine was so complicated (78) that BASF used a nitrogen purge to remove water thus avoiding triphenylphosphine, and PA6T can be obtained using monomers and ionic liquid only (326). PA46, PA6T/M5T and PA6T/6 were produced by Invista in the similar process (327). In view of its good microwave absorption properties, ionic liquid was usually used together with microwaves to produce PAs (328–332).

4.3.2.5.4 Diol + diamine polymerization

Guan et al. (333) proposed a completely new PA synthesis process: PA can be synthesized by the direct reaction of diol and diamine in the presence of Milstein catalyst to release by-product (H_2) as shown in Figure 45 (334). A series of PAs including semi-aromatic PAs with $M_n > 22,000$ g/mol were produced at 120°C for 48 h in anisole or anisole/DMSO mixtures, but most PAs contained an ether bond. Further, a series of common PAs, such as PA66, PA6I, PA6T and whole-aromatic PAs, were produced in 1,4-dioxane using Milstein catalyst by Milstein et al. (335). A high molecular weight PA66 could be obtained even without solvent using a new bis-pyridine catalyst. A series of PAs including PA10T and PXD10 were also produced by Dupont without solvent using the Milstein catalyst at 180°C for 9–20 h (336).

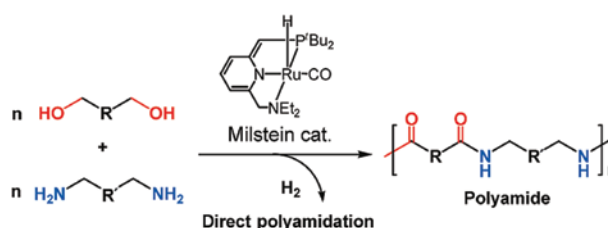


Figure 45: Scheme of diol + diamine polymerization. [Source: J Am Chem Soc. 2011;133(5):1159–61, printed with permission].

The diol + diamine polyamidation reaction could proceed under solvent-free conditions, and only 0.2 mol% of catalyst was required, representing a “green” reaction. This polyamidation reaction is general, environmentally benign and atom economical. Citations of the aforementioned literature are considerable, however, most of them were reviews or organic chemistry-related papers and there is only rare literature on the study of PA synthesis. The reasons are as follows: 1) a considerable amount of Milstein catalyst must be used, which is a catalyst with a complicated structure, complex synthesis procedure, large adding amount and a high cost. In contrast, low cost sodium hypophosphite is used as a catalyst in traditional diamine and diacid polycondensation; 2) the Milstein catalyst is sensitive to water and oxygen, and the rigorous Schlenk technique must be adopted throughout the procedure. In contrast, only anaerobic circumstances can be promised in traditional diamine and diacid polycondensation, and rough control on oxygen concentration is tolerable; 3) the by-product of diol + diamine polymerization is hydrogen, and that of traditional diamine and diacid polycondensation is water. Although the atom economy of the latter is lower, it does not require a complicated factory building design in consideration of organic solvents and absence of hazardous chemicals. In contrast, the diol + diamine process involves highly dangerous hydrogen, which requires a highly reliable factory building design and equipment, leading to high investment in fixed assets and operating costs. Therefore, diol + diamine process is still in the study stage.

4.3.2.5.5 Supercritical CO₂ polymerization

Zhang studied the polymerization of nylon 46 salt in supercritical CO₂ at 30 MPa (337). The viscosity-average molecular weight of the product was as high as 4.8×10^4 g/mol, and the melting point was 310°C, which may be derived from its high crystallinity (63.9%). A series of PAs including HPA (PA6T, PXD10) were produced with monomers, water and CO₂ at 15 MPa, with relative viscosity as high as 2.5 (338). High pressure (>10 MPa) must be used in supercritical CO₂ polymerization, which is an obstacle for industrialization.

5 Conclusions

PA46 is mainly produced by DSM, and it has high crystallinity, good mechanical performance and high water-absorption. Hence, blistering usually happens when the

article is exposed to a significant amount of atmospheric moisture before soldering. For this reason, DSM launched an upgraded version (PA4T), and it maintained high crystallinity and good mechanical performance of PA46 and had water absorption as low as 0.3% (23°C, 24 h), which was comparable to that of PA9T. Benefiting from low cost of hexanediamine, PA6T copolyamides have become the largest HPAs until recently. PA6T/66 is an isomorphous replacement copolyamide, in which the crystallization of PA6T cannot be affected by the introduction of adipic acid. Most HPA suppliers have their own PA6T products. PA9T is mainly produced by Kuraray, and its major characteristics are low water absorption (low amide concentration), high crystallization rate (high methylene content leads to high flexibility of molecular chain), in contrast to PA6T copolyamides. PA10T is mainly produced by Kingfa, Evonik, EMS and Arkema, which is a bio-based material and has comparable or even better performances than that of PA9T.

HPA's based on full aliphatic monomers demand a short molecular chain and a high amide concentration to ensure heat resistance, which leads to high water absorption and low thermal stability. It is a fine balance, and therefore, PA46 is the only commercialized full aliphatic HPA to date. Cathay industrialized pentanediamine through a biological fermentation process, and brought hope to industrialization of pentanediamine-based HPAs. But Cathay concentrated on the market for PA56 fiber till now. The Henan Junheng Industrial Group Biotechnology Co., Ltd. cooperated with Zhengzhou University to produce a series of pilot-scale long carbon chain HPAs, such as PA11T, PA12T, PA13T and PA14T, using long carbon chain diacids as raw materials, which were synthesized through the biological fermentation of light liquid paraffin, a by-product from oil refining. Mitsubishi has begun to apply for patents on PXD10, which is a good new HPA category. Alicyclic HPA has a higher melting point and a higher glass-transition temperature than that of semi-aromatic HPAs, and both its color and light aging performance are outstanding. Kuraray and Asahi Kasei have launched a small-scale alicyclic HPA. Polyaryl sulfide amides have excellent heat resistance and processability comparable to that of PA9T, however, monomers from a series of complicated procedures have not been industrialized until now and interfacial polymerization has been adopted in the synthesis process.

After the 1980s, along with the progress of PAs as an engineering plastic, the heat-resistant properties of HPAs were highlighted and patents began to increase noticeably. Benefiting from the RoHS Directives of lead-free alloys (>260°C) using in SMT after 2006, HPAs became the

favorite materials and patents were booming. The number of Japanese patents is the highest of all, and they encompass nearly 50% of all HPA synthesis patents. But they are limited to Japan only, concentrating on the domestic market. American comes second, and plenty of American patents are PCT patents. China ranks third, it tends to develop late but progresses quickly.

The Pre+SSP is the main polymerization process in this field, which is closely related to properties of HPA resins: high melting point close to the decomposition temperature, and yellowing and performance deteriorating of the polymer when melting. Temperature, pressure and residence time must be adjusted carefully in the prepolymerization procedure to avoid solidification of the prepolymer. A vacuum drum or tackifying tower are usually used in the SSP process, and Japanese companies offer a modified fluidized bed and a blade paddle dryer-like equipment for improvement. Most procedures of OHPMP are conducted in one reactor conveniently, which is very suitable for small factories. The residence time of the resin in the Pre+TSE process is short, avoiding polymer decomposition. However, a low degree of prepolymer may find it difficult to polymerize completely, and plenty of steam from amidation requires a specially designed exhaust system. MXD6 derived from *m*-xylene diamine and adipic acid has been produced nearly exclusively by Mitsubishi through the OLPMP process for decades, and precise control on formula, feeding ratio, temperature and residence time is necessary. There are also other processes for HPA polymerization, especially laboratory-scale techniques, such as interfacial polymerization, aminolysis of polyesters, polymerization with ionic liquid as the solvent, diol+diamine polymerization and supercritical CO₂ polymerization. However, organic solvent or high-pressure conditions must be used in those processes, and purification and solvent recycling can be difficult, leading to unsuccessful industrialization.

Benefitting from low cost of raw materials, PA6T has the largest market share in the HPA field. The decreasing cost of other HPA may be difficult in the near future, and PA6T will be the predominant product. Although PA46 has high water-absorption and poor dimensional stability, its crystallinity is high and its mechanical performance are good. Coupled with the launching of PA4T, which is declared to be solution to the high water-absorption of PA46, PA4X will be assured of a place in the HPA market. The properties of PA9T and PA10T are comparable, which have many advantages in comparison to PA46 and PA6T, especially as regards water absorption. The synthesis technique of nonamethylene diamine is owned exclusively by Kuraray, by contrast, there are many decamethylene

diamine suppliers all over the world (most of them are in China). Together with the concept of bio-based materials, one can anticipate a more promising development of PA10T. Alicyclic HPA has a higher melting point and a higher glass transition temperature than semi-aromatic HPAs, and it has excellent color performance and light aging resistance, thus we can foresee a bright future of it in the LED field. HPAs based on pentamethylene diamine and long carbon chain diamines depend on a breakthrough in the synthesis technique of monomers, and if their price decreases, their development can be anticipated.

6 Future perspectives

The polymerization processes of HPAs have been developing well since 2000, and the main problem is the source and cost of monomers for large-scale HPA production. Benefitting from the successful industrialization of long carbon chain diacid through biological fermentation process, long carbon chain diamine-based HPA are expected to be the next industrialized product, in consideration of their low water absorption. Cathay is now popularizing the fibre application of PA56 due to its high water absorption and fast drying rate, and PA5T may be another potential candidate if Cathay succeed in PA56 industrialization, when the cost of pentanediamine will be acceptable. Large-scale production of other HPAs will be difficult due to the high cost of the corresponding diamines within the next decade.

The batch polymerization process currently dominates HPA production, and it will dominate for a very long time in the future. The reason is obvious: the global market capacity of HPAs is less than 200,000 ton/a, which is too small for continuous polymerization processes. And generally, clients usually customize some products to accommodate their special needs in this field, and batch polymerization plays to its strengths in this respect. There are advantages and disadvantages to both solid polymerization and melt polymerization processes: the polymerization temperature of solid polymerization is lower and polymer color is excellent, but removal of carbide and other impurities can be difficult; and with melt polymerization the opposite is the case. A process combining the advantages and avoiding the disadvantages of both processes is anticipated in this field to get HPAs with excellent color and little impurities.

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