

Thermal properties of α,ω -aminoalkylterephthalamides prepared from waste poly(ethyleneterephthalate) bottle and aliphatic diamines

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ABSTRACT

Trimers and pentamers of α,ω -aminoalkylterephthalamides were prepared from aminolysis of waste poly(ethyleneterephthalate) (PET) bottle with tetramethylene diamine (TMDA) and hexamethylene diamine (HMDA). The thermal properties of these products determined by DSC and TG showed that the melting points were the temperatures at which physical melting process and chemical transamidation polymerization occurred

concurrently. This chemical reaction had converted trimers and pentamers into polymers, then at the higher temperature ranges, the observed decomposition temperatures were just specific for newly formed polyamides, not for initial trimers or pentamers. The application of thermogravimetric chamber as mini reactor is quite useful to investigate the heating conditions for solid-state polymerization of α,ω -aminoalkylterephthalamides.

Keywords: α,ω -Aminoalkylterephthalamides, differential scanning calorimetry, solid-state polymerization, thermogravimetry analysis, thermal properties, transamidation

INTRODUCTION

Polyalkyleneterephthalamide is categorized as a semi-aromatic amide that formed from an aromatic dicarboxylic acid or diester and an aliphatic diamine. The presence of an aromatic moiety in the chain normally increases the thermal and mechanical properties of polymers. The synthesis and characterization of this polyamide and its copolymers have long been reported. Poly(hexamethyleneterephthalamide) (PA6T) is known for their low density, high abrasion resistance, easy dyeing, high alkali resistance, thermal stability and high modulus as fibers [1]. Copolymer of nylon 6 and PA6T is used in high-temperature applications, automobile parts (e.g., radiator, ventilation, and fuel supply systems), electronics housings, plug

and socket connectors, printed circuit boards, tennis rackets, golf clubs [2]. A series of terephthalamides and isophthalamides of aliphatic amines were synthesized and then used as montmorillonite clay modifiers [3]. Thermal properties of all products were determined by thermogravimetric analysis (TGA).

Solid-state polymerization of semiaromatic poly(tetramethyleneterephthalamide) (nylon-4,T) and nylon-4,6 copolyamides was studied using prepolymers with different nylon-4,T contents [4]. The copolyamides with higher nylon-4,T contents had higher glass transition, melting, and decomposition temperature. A series of semi-aromatic polyamide salts were prepared in solution by neutralizing aliphatic diamines of

different aliphatic length with terephthalic acid. The obtained semiaromatic salts were further subjected to direct solid state polycondensation that performed in a TGA chamber [5, 6].

α,ω -Aminoalkyl terephthalamides are oligomers that are prepared by reaction of terephthalic acid or its derivatives with excess of diamines.

N,N' -Bis(4-aminobutyl) terephthalamide (4T4) and N,N' -Bis(6-aminohexyl) terephthalamide (6T6) were prepared by the reaction of dimethyl terephthalate (DMT) with tetramethyldiamine (TMDA) and hexamethylenediamine (HMDA) respectively [7]. Structures of the obtained oligomers were confirmed by FTIR method. A series of di-(ω -aminoalkyl) terephthalamides were also made from DMT and α,ω -diaminealkanes [8]. The alkanes were used as ethane, propane, butane, hexane, heptane and octane. The formation of higher oligomers, such as pentamer 6T6T6-diamine and heptamer 6T6T6T6-diamine was also proposed.

All the above publications have been reported on the common "bottom-up" approach, or the preparation of polyamides and oligomers from commercial monomers. By using another method, called as "top-down", polymers are firstly degraded to oligomers and then these oligomers are converted to polymers by functional group transformation. This is a useful method of chemical recycling of polymers. Aminolysis of poly(ethyleneterephthalate) (PET) to afford α,ω -aminoalkylterephthalamides, for example, is one of several methods of PET recycling in order to use waste material as a source of chemicals. The effective organocatalysis of the aminolytic depolymerization of waste PET producing a broad range of crystalline terephthalamides was reported [9]. The melting points of PET aminolysis products were determined by DSC. Trimer N,N' -bis(2-aminoethyl)terephthalamide

and pentamer were prepared from waste PET bottle and their thermal properties were identified by DSC and TG [10].

As a result of having reactive amino end groups, N,N' -bis(2-aminoethyl)terephthalamide prepared from PET waste can be used as an epoxy resin hardener [11].

Generally, the melting points of α,ω -aminoalkylterephthalamides were determined by DSC as endothermic peak and reported in other research papers [8, 9]. By combining DSC and TG methods we can find out the specific thermal properties of α,ω -aminoalkylterephthalamides prepared from aminolysis of waste PET bottle with ethylene diamine (EDA) [10], TMDA and HMDA [12]. These thermal properties are useful for solid state polymerization (SSP) to form polyamide.

MATERIALS AND METHODS

Materials

Trimers and pentamers of N,N' -bis(4-aminobutyl)terephthalamide and N,N' -bis(6-aminohexyl)terephthalamide were prepared from waste PET bottle [12].

Thermal characterization methods

Differential scanning calorimetry (DSC) was performed with a METTLER STARe SW 11.00 instrument. Samples were heated from room temperature to 400 °C or 450 °C, with the heating rate of 10 °C min⁻¹ in nitrogen atmosphere.

Thermogravimetric analysis (TGA) was carried out on a Q500 Universal V4.5A TA Instrument, heating from room temperature to 800 °C with the heating rate of 10 °C min⁻¹ in nitrogen atmosphere.

RESULTS AND DISCUSSION

General chemical structures of α,ω -aminoalkylterephthalamides are shown in Fig. 1. Values m, p and names are defined in Table 1.

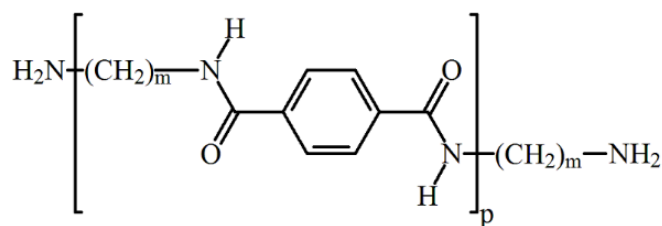


Fig. 1 Chemical structures of α,ω -aminoalkylterephthalamides. Ethyl ($m=2$), butyl ($m=4$), hexyl ($m=6$), trimer ($p=1$), pentamer ($p=2$), heptamer ($p=3$)

Table 1. Values of m , p and names of α,ω -aminoalkylterephthalamides corresponding to the chemical structure shown in Fig. 1

m	p	Names	-mer	Abbreviations
2	1	<i>N,N'</i> -Bis(2-aminoethyl)terephthalamide	Trimer	BAET
	2	α,ω -Bisaminoligo(ethylene terephthalamide)	Pentamer	AOET*
4	1	<i>N,N'</i> -Bis(4-aminobutyl)terephthalamide	Trimer	BABT
	2	α,ω -Bisaminoligo(tetramethylene terephthalamide)	Pentamer	AOBT*
6	1	<i>N,N'</i> -Bis(6-aminohexyl)terephthalamide	Trimer	BAHT
	2	α,ω -Bisaminoligo(hexamethylene terephthalamide)	Pentamer	AOHT*

Note: *AOXT (X: E, B, H) is an abbreviated name for the methanol insoluble part A, that is a mixture of major pentamer and minor heptamers, etc. ($p \geq 2$).

Thermal properties of α,ω -aminobutylterephthalamides

The reaction of waste PET bottle with excess of TMDA had transformed PET into two isolated solid materials including methanol insoluble part A, containing pentamer (90 %) and heptamers (10 %), and methanol soluble part B, containing principally trimer BABT (94.3 %) and a minor quantity of pentamer (5.7 %) as determined by HPLC-MS. The structures of these α,ω -aminobutylterephthalamides were also confirmed by FTIR, ^1H - and ^{13}C -NMR [12].

The prepared part B-BABT and part A-AOBT were subjected to DSC and TG analysis (Figs. 2 and 3).

DSC curve of part B-BABT (Fig. 2A) from room temperature to 400 °C showed almost one

broad endothermic process with a peak temperature at 187 °C. This thermal occurrence could be the melting process of trimer BABT. According to Fukushima K et al. [9], the melting point of BABT is 217 °C. This higher melting temperature could be explained as the BABT sample isolated by Fukushima K et al had higher pentamer content.

The DSC curve of part A-AOBT (Fig. 2B) showed a broad endothermic peak at 72 °C. A quite sharp peak at 295 °C could be a melting point of pentamer. A broad endothermic peak at 380 °C could come from a decomposition process.

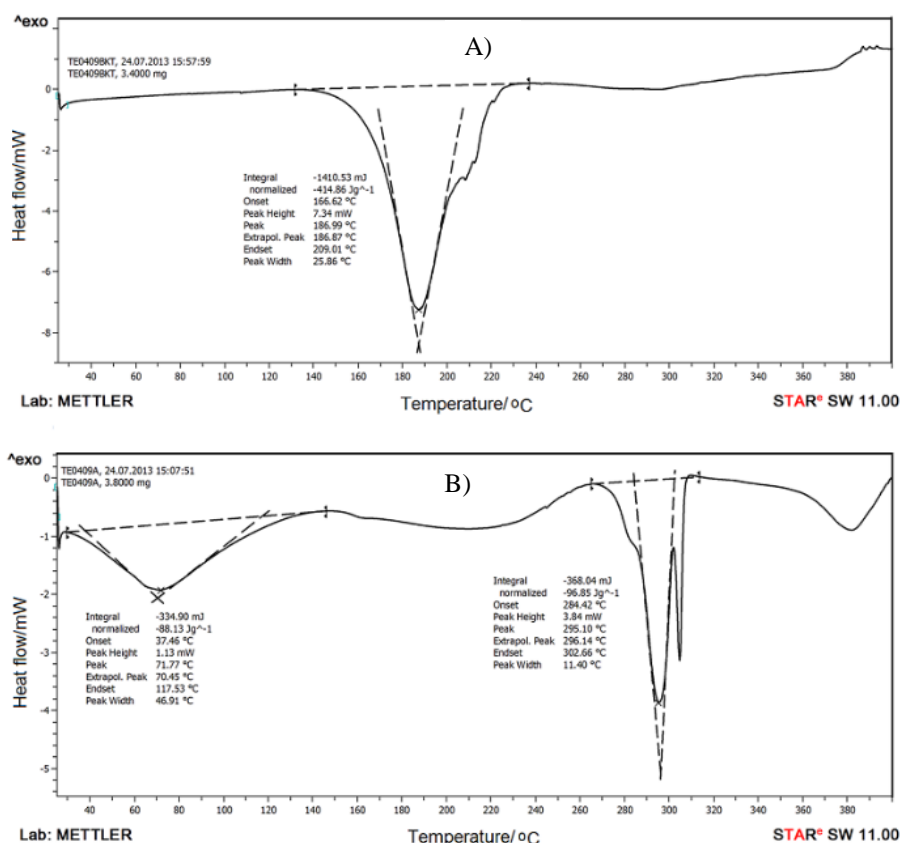


Fig. 2 DSC curves of (A) part B-BABT and (B) part A-AOBT of α,ω -aminobutylterephthalamides

The TG curve of part B-BABT (Fig. 3A) showed that the moisture absorbed was 1.23 %. The temperature range from 120 to 220 °C with a loss of 13.01 % in TG coincided with the endothermic peak from DSC with a peak temperature at 187 °C (Fig. 2A). This decomposition range could be at first melting process and then transamidation of amino end group of one BABT molecule with amido group of other BABT molecule to form a pentamer and release TMDA as depicted in Fig. 4.

Following the chemical equation (Fig. 4), the theoretical mass loss due to volatile TMDA over 2 molecules of trimer BABT was $[88.15/(2 \times 306.41)] \times 100\% = 14.38\%$. If the purity of trimer is considered, the corrected value must be $14.38\% \times 0.943 = 13.56\%$. This value approximated to the experimental value of 13.01

%. In the temperature range of 220 °C to 520 °C, two partly overlapped decomposition steps occurred as evidenced by the two consecutive peaks from dTG at 366 °C and 443 °C. At this high temperature range, the freshly formed pentamer could be transformed to higher oligomers or polymer by transamidation and readily decomposed.

Thermal property of part A-AOBT was also characterized by TG method. The mass loss in TG (Fig. 3B) from room temperature to 140 °C was just about 2 %, whereas in DSC curve (Fig. 2B) of the same temperature range, there was a broad endo peak at 72 °C. This thermal occurrence could not be explained simply by the loss of volatile materials like vapor or solvent with small quantity as determined by TG. The reason for this endothermic process could come

from a transition of crystalline structure of AOBT. This phenomenon named as Brill transition was investigated by Murthy NS et al. [13]. They had used variable-temperature XRD and NMR measurements to show that nylon 6 undergoes crystalline relaxations between the

glass transition temperature and the melting point. These relaxations brought about a crystalline transition between 80 and 170 °C from a monoclinic structure to a new crystalline structure, which was also most likely monoclinic.

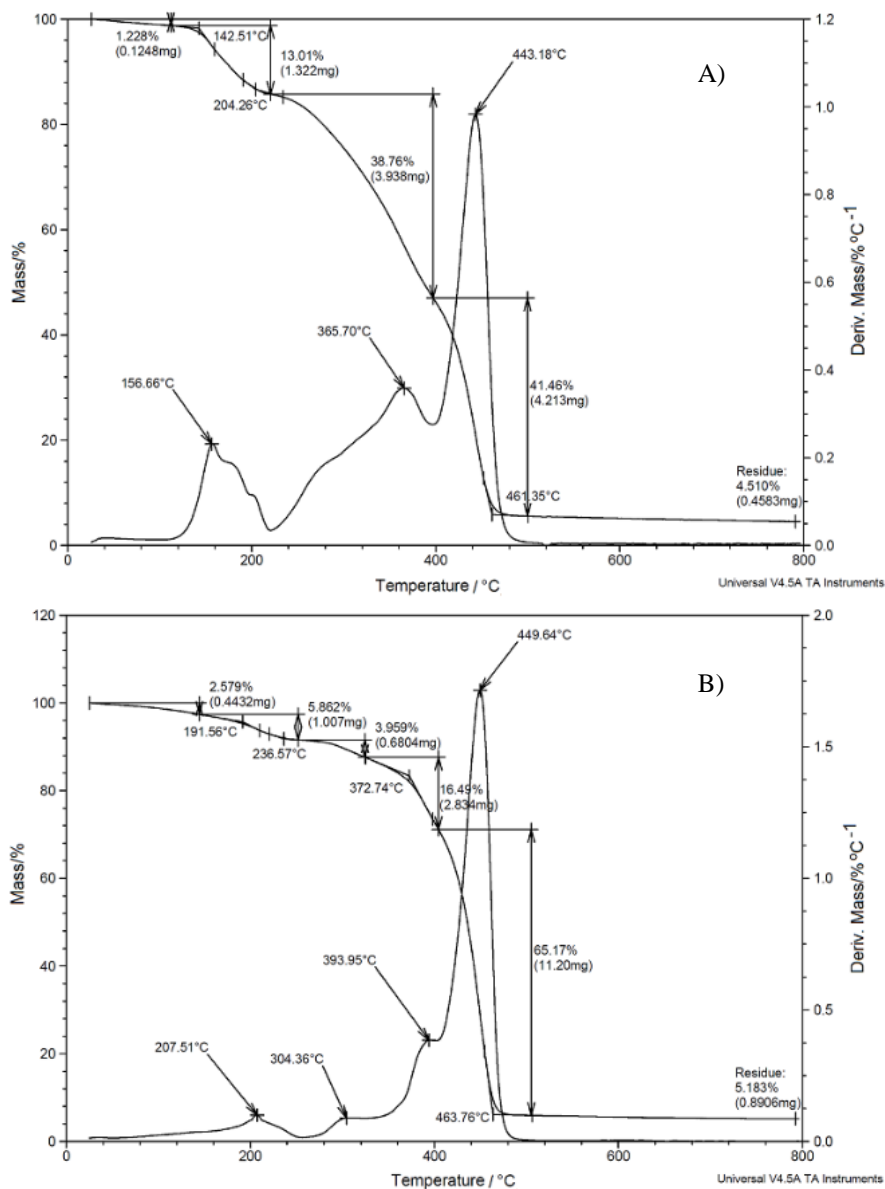


Fig. 3. TG curves of (A) part B-BABT and (B) part A-AOBT of α,ω -aminobutylterephthalamides

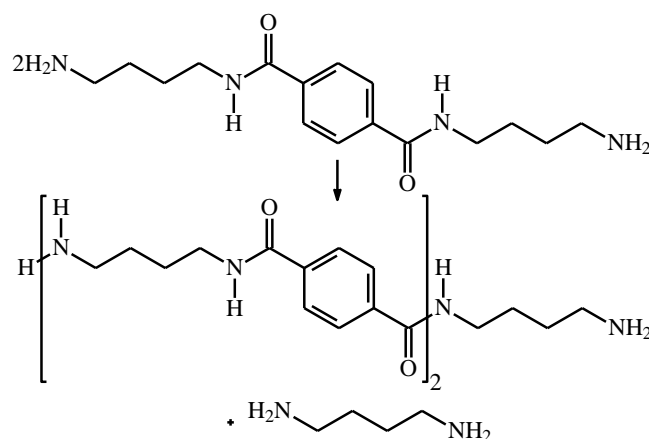


Fig. 4. Formation of pentamer from trimer BABT under TG conditions

From room temperature to 260 °C the TG curve (Fig. 3B) showed a mass loss of 8.44 % with a peak from dTG at 208 °C. Assuming that the transamidation occurred between two pentamer molecules to form a nonamer and TMDA, the theoretical mass loss due to volatile TMDA was $[88.15/(2 \times 524.66)]100\% = 8.40\%$. This value was in good agreement with the experimental loss. By comparing with the TG curve of part B-BABT (Fig. 3A), at 208 °C, the trimer had not yet completely converted into pentamer. For this reason, the transamidation of pentamer was not observed in part B-BABT. In the temperature range from 260 to 500 °C, nonamer was further decomposed as seen by three consecutive peaks at 304, 394, and 450 °C in dTG. The principal peak at 450 °C was due to polyamide decomposition. This decomposition temperature was lower than the reported value of 460 °C of PA4T prepared from salts [6].

The maximum theoretical mass loss due to transamidation of pentamers to form polyamide and TMDA ($nM5 \rightarrow \text{Polyamide} + n\text{TMDA}$) was $(88.15/524.66)100\% = 16.80\%$. The mass loss at higher temperature due to polyamide decomposition could be $100 - 16.80 = 83.20\%$. The combined experimental mass loss from 340 to 500 °C (Fig. 3B) was 81.66 %, and this value was close to the theoretical value. Therefore, we

could conclude that by thermal treatment of pentamer AOBT under TG conditions, the transamidation occurred from room temperature to 340 °C, and the newly formed polyamide decomposes at temperature range of 340 to 500 °C.

The decomposition temperature at peak of part B-BABT (443 °C) was comparable with the one of part A-AOBT (450 °C), therefore this temperature was specific for PA4T formed just before its decomposition.

Thermal properties of α,ω -aminohexylterephthalamides

The reaction of waste PET bottle with excess of 1,6-hexamethylenediamine (HMDA) was also carried out. Two parts of solid materials were isolated, identified by FTIR, ^1H - and ^{13}C -NMR methods. From HPLC-MS analysis, methanol insoluble part A-AOHT, contained mainly 89.2 % of pentamer and 10.8 % of heptamer, and methanol soluble part B-BAHT was a mixture of trimer BAHT (90.6 %), minor quantities of pentamer (7.1 %) and tetramer (2.3 %) [12].

Thermal properties of the obtained oligomers were also characterized by both DSC and TG (Figs. 5 and 6).

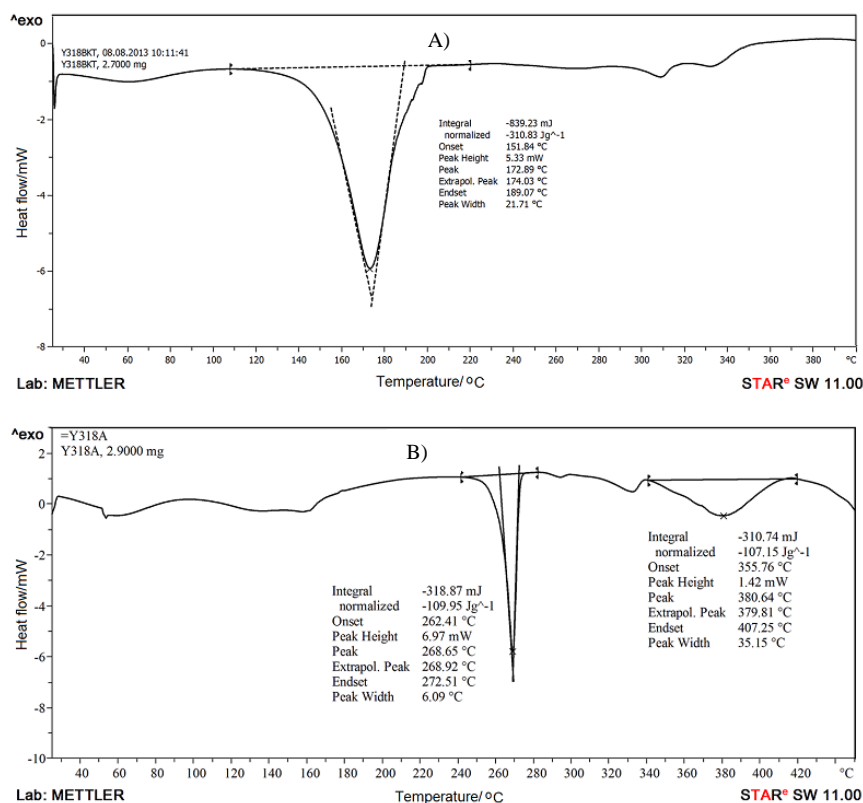


Fig. 5. DSC curves of (A) part B-BAHT and (B) part A-AOHT of α,ω -aminohexylterephthalamides

Figure 5A showed an endothermic peak at 173 °C due to the melting process of BAHT and melting enthalpy of 311 J/g. The melting point and melting enthalpy of this compound had been reported by Krijgsman et al. [8] as 178 °C and 130 J/g, respectively. Compared to our data, the melting points were equivalent, however the melting enthalpy value of our sample was much higher, it meant that our product has higher crystallinity and higher purity. Fukushima K et al [9] had also reported that the melting point of BAHT was 171 °C.

The DSC curve of part A-AOHT (Fig. 5B) displayed two major endothermic peaks at 269 and 381 °C. These thermal processes could only be explained by combining DSC and TG techniques.

From TG curve of part B-BAHT (Fig. 6A), the mass loss of 2.81 % from room temperature

to 137 °C was attributed to volatile moisture. From 137 to 340 °C, the TG curve showed two mass loss steps, one from 137 to 200 °C, and another from 200 to 340 °C with overall experimental mass loss of 30.36 %. The principal mass loss due to the decomposition of just formed PA6T occurred from 340 to 472 °C with a maximum peak at 459 °C. The residue at 472 °C was 3.21 %.

The maximum theoretical mass loss due to volatile HMDA released from trimer BAHT transamidation (Fig. 7) was calculated as $(116.21/362.52) \times 100 \% = 32.06 \%$. The experimental value in the temperature range of 137 to 340 °C is 30.36 %, after being corrected by removal of moisture and residue, it became $30.36 \% \times 100 / (100 - 2.81 - 3.21) = 32.30 \%$. These experimental and theoretical values were similar.

The transamidation of trimer BAHT was different from BAET and BAPT. Due to having longer chain, lower active amine content, the transamidation of BAHT occurred in a broad temperature range (137 to 340 °C), and the formation of pentamer was overlapped by the formation of higher oligomers and polymers. This finding is useful for the polymerization of

trimer in a solid state system. For example, the trimer BAHT sample should be heated slowly from room temperature to 290 °C under an inert atmosphere and kept at this temperature for a period of time to convert trimer into PA6,T.

Consequently, the sharp endothermic peak at 269 °C in DSC (Fig. 5B) was assigned to the transamidation and evaporation of HMDA.

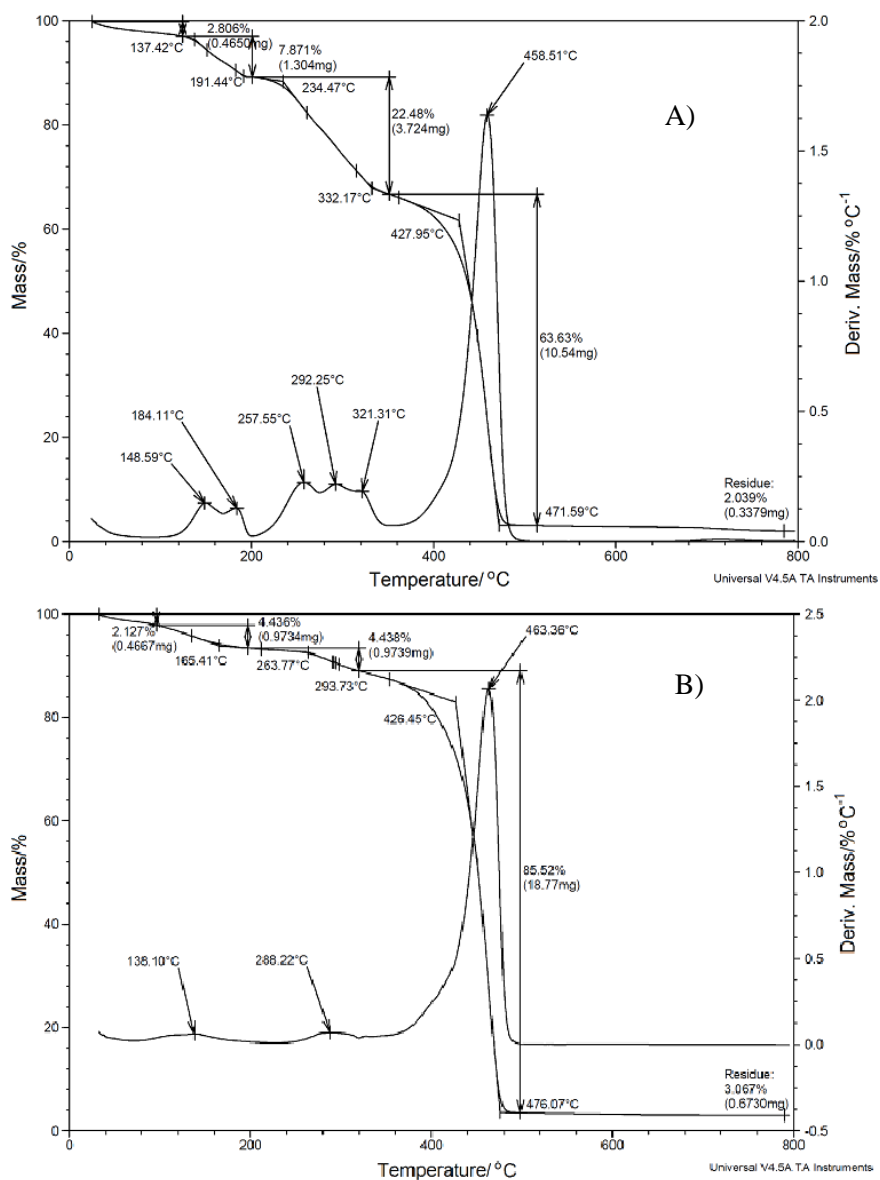


Fig. 6. TG curves of (A) part B-BAHT and (B) part A-AOHT of α,ω -aminohexylterephthalamides

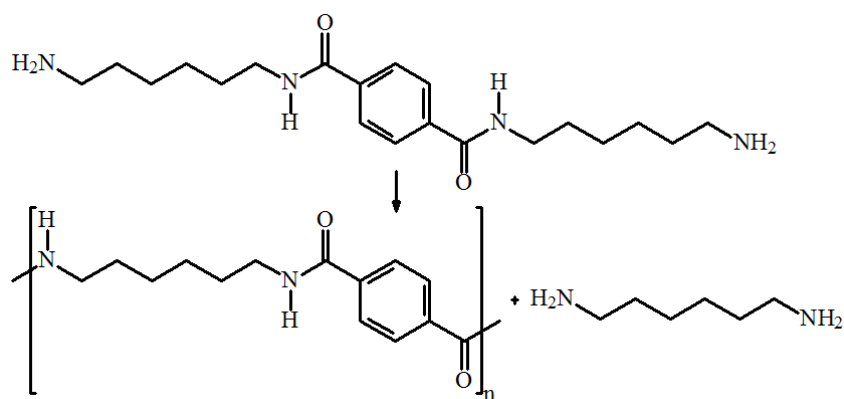


Fig. 7. Proposed transamidation reaction of trimer BAHT to form nylon-6T during heating from room temperature to 340 °C under TG conditions

TG curve of part A-AOHT is shown in Fig. 6B. The experimental total mass loss from room temperature to 100 °C due to moisture was 2.13 %. From 100 °C to 360 °C, the value was 8.87 % before polyamide decomposition. The reaction of two M5 to form a M9 and HMDA was proposed by the reaction: $2M5 \rightarrow M9 + HMDA$. From this reaction, the theoretical mass loss was $(116.21/2 \times 608.82)100\% = 9.54\%$. This theoretical value was comparable to the experimental value of 8.87 %. The maximum theoretical mass loss due to transamidation of pentamers to form polyamide and HMDA ($nM5 \rightarrow \text{Polyamide} + nHMDA$) would be $(116.21/608.82) \times 100\% = 19.09\%$. This value could not be detected in the TG curve, thus the direct polymerization of pentamer was eliminated. The formed polymer was decomposed completely in the temperature range of 476-500 °C with a mass loss of 85.52 %.

Moreover, the extrapolated main decomposition peak of pentamer at 426.45 °C was close to 427.95 °C of trimer (Fig. 6A). The temperature values at peak of pentamer (463 °C) and trimer (459 °C) were similar. These results have proven that even though the molecular weights of initial trimer and pentamer materials are different, however, due to the similarity in the structure of α,ω -aminohexylterephthalamides

with reactive amino end groups, by heating under an inert atmosphere of TG system, trimer and pentamer reacted by the same stepwise condensation mechanism to remove volatile HMDA at the ends of chains, and to form the same PA6T structure.

As reported by Lan Qu et al. [14], the melting point determined from DSC curve of PA6T was 368 °C. The DSC curve (Fig. 5B) from our experiment showed a broad endo peak from 365 to 407 °C with temperature at peak of 381 °C. The temperature difference could come from the difference in the preparation procedure, reactants, and the purity of PA6T. At the same range of temperature, the TG curve (Fig. 6B) showed the beginning of the principal decomposition step. From these observations, 381 °C was assigned as melting temperature of polyamide from AOHT.

The thermal decomposition of PA6T determined by TG was reported as 428 °C [14]. This value was much lower than our TG experimental value of 459 °C (PA6T from part B-BAHT) and 463 °C (PA6T from part A-AOHT). There are a number of possible causes for this variation in thermal decomposition temperatures. The first possibility is that the molecular weight of our polyamide sample is higher. Another possibility is that the amino end

groups in our trimer/pentamer samples have converted efficiently into PA6T with higher thermal stability by transamidation under TG heating conditions in inert gas.

Comparison of the melting/decomposition processes of trimers and pentamers

In our published research paper [10], the thermal properties of trimer and pentamer prepared from EDA-PET reaction were carefully investigated. By extending the length of aliphatic diamine to 4 (TMDA) and 6 (HMDA), in this report, the melting points and decomposition temperatures of their trimers and pentamers are compared.

The melting points of trimers or pentamers decreased with the aliphatic chain length because of weaker intermolecular forces of aliphatic moieties (Fig. 8). Obviously, pentamers with higher molecular weight have higher melting points compared to corresponding trimers.

The melting and transamidation processes occur simultaneously to convert initial trimer or pentamer to polymer, and as a consequence, the decomposition determined by TG depended strongly on the thermal properties of newly formed polyamide. For this reason, there were almost the same decomposition temperatures of trimers and pentamers prepared from TMDA-PET and HMDA-PET as discussed above. However, in the case of trimer/pentamer prepared from EDA-PET reaction, the decomposition temperature of trimer was much lower than the one of pentamer but very close to the melting point of pentamer [10]. This result indicated that by heating at the rate of 10 °C/min, trimer from EDA-PET reaction was transformed at first to pentamer and EDA, and this pentamer could readily decompose instead of converting into polymer.

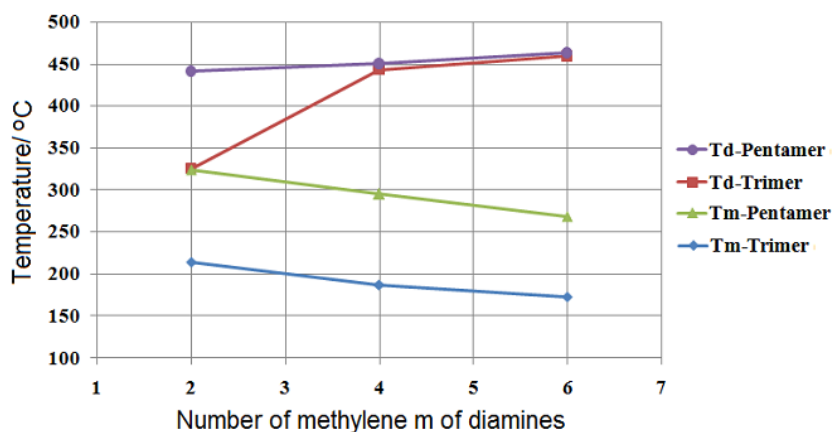


Fig. 8. Effects of the number of methylene groups of diamines on the melting points (T_m determined by DSC) and the decomposition temperatures (T_d determined by TG) of trimers (part B) and pentamers (part A) of α,ω -aminoalkylterephthalamides

CONCLUSION

The thermal properties of trimers (part B) and pentamers (part A) of α,ω -aminoalkylterephthalamides were characterized by combining both DSC and TG methods. When the methylene chain became longer (from 2 to 6),

the melting points of both trimers and pentamers decreased. On the contrary, the decomposition temperatures increased with aliphatic chain length. By heating treatment, trimers were converted firstly to pentamers and then to polymers by the same transamidation mechanism

before thermal decomposition. As a consequence of having both physical melting process and chemical transamidation at the same temperature range, trimers and pentamers prepared from aminolysis of PET by diamines had “chemical melting points”. This chemical process had converted completely these oligomers into polymer, then at the higher temperature ranges the observed decomposition temperature was just specific for newly formed polyamide, not for initial compounds.

These trimers and pentamers with reactive end groups could also be used as high molecular weight diamines for bismaleimide, polyimide, polyamide and copolyamide [15] preparation. When these oligomers were used for solid state polymerization, the heating temperature should not be over 360 °C.

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Tính chất nhiệt của α,ω -aminoalkylterephthalamide điều chế từ vỏ chai PET phế thải và các diamine mạch no

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TÓM TẮT

Trimer và pentamer của α,ω -aminoalkylterephthalamide được điều chế bằng cách amine hóa chai poly(ethylene terephthalate) (PET) phế thải với tetramethyldiamine và hexamethylenediamine. Tính chất nhiệt của các sản phẩm này được xác định bằng DSC và TG cho thấy nhiệt độ nóng chảy là nhiệt độ tại đó quá trình nóng chảy vật lý và phản ứng transamide hóa tạo thành polymer xảy ra đồng

thời. Phản ứng hóa học này đã chuyển hóa trimer và pentamer thành polyme tương ứng, do đó ở nhiệt độ cao, nhiệt độ phân hủy nhiệt thực chất là của polymer mới tạo thành chứ không còn là của chất ban đầu. Việc áp dụng khoảng TG như bình phản ứng nhỏ khá hữu ích để nghiên cứu tính chất nhiệt nhằm tìm ra điều kiện nhiệt độ thích hợp cho quá trình polymer hóa pha rắn của α,ω -aminoalkylterephthalamide.

Từ khóa: α,ω -Aminoalkylterephthalamid, nhiệt lượng kế quét vi sai (DSC), phân tích nhiệt trọng lượng (TGA), polyme hóa pha rắn, tính chất nhiệt, transamid hóa

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