

Synthesis and Properties of Thermoplastic Polyisocyanurates: Polyisocyanuratoamide, Polyisocyanurato(Ester-Amide) and Polyisocyanurato (Urea-Ester)

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Abstract: It has been proved that introducing isocyanurate into polymer chains could improve the flame retardancy of polymers. We describe in this work the synthesis and the thermal property study of three thermoplastic polyisocyanurates, which are polyisocyanuratoamide (PICA-6), polyisocyanurato(ester amide) (PICEA-6) and polyisocyanurato(urea ester) (PICUE-6). These polymers show similar and improved thermal stability with the existence of isocyanurate rings. PICA-6 is more crystalizable than the rest two and the melting temperature is found to be around 240°C but it still crystallizes slowly. For PICEA-6 and PICUE-6, only glass transition can be observed on the DSC traces. The glass transition temperature follows the order of PICA-6 > PICEA-6 > PICUE-6 (101.9, 77.9 and 28.7°C, respectively).

Keywords: Thermoplastic polyisocyanurate; polyamide; poly(ester amide); poly(urea ester)

1 Introduction

Isocyanuric acid (cyanuric acid) is one of the most important derivatives of urea. Since urea is obtained from human daily urine or from the recyclable carbon dioxide and ammonia, urea and isocyanuric acid both are renewable. It is usually synthesized by trimerization of urea at high temperature (180–290°C) [1–6]. The NH groups in isocyanuric acid (ICA) are relatively reactive, which makes it possible to perform further chemical modifications. For instance, ICA is able to react with acrylate or acrylonitrile via Michael addition [7]. The existence of isocyanurate ring generally offers excellent thermal stability for isocyanate compounds or polymers [1,8,9]. More interestingly, isocyanurate ring absorbs large amount of heat beyond 380°C, which therefore makes isocyanurates feasible to be applied in the area of flame retardation [10,11]. In most cases, isocyanurates are prepared from trimerization of isocyanates or from ICA directly. Since there are three equal NH groups in ICA, most ICA derivatives are trifunctional, for example, tri(hydroxyethyl) isocyanurate, tri(epoxypropyl) isocyanurate, tri(2-carboxyethyl) isocyanurate, etc,



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[7,12–14]. Polymers obtained from these trifunctional ICA derivatives are cross-linking, rather than thermoplastic. The isocyanurate polymers (also known as polyisocyanurates) exploited so far are impossible to be recycled or reprocessed, which limits their further applications. Thermoplastic linear polyisocyanurates are of more interests to researchers nowadays, compared with cross-linking polyisocyanurates.

Bis(2-carboxyethyl) isocyanurate (BCI) from which thermoplastic polyisocyanurates can be prepared is one of the commercially available difunctional isocyanurates. The synthetic process of BCI is quite unique but the yield is acceptable (67%) [15,16]. Polyesters based on BCI was used in the treatment of fibers at high temperature and high pressure, restraining the formation of fluff, swaying yarn and tar [17]. Even BCI-based oligoesters can be used in radioresistant coatings [18,19]. In our previous study, it was found that BCI-based polyesters (namely polyisocyanuratoesters PICEs) are flame-retarding [20]. However, the glass transition temperature of those PICEs is around 20–50°C, which is rather low for most applications. In order to obtain thermoplastic polyisocyanurates with better thermal and mechanical properties, we proposed in this study to synthesize polyisocyanuratoamide (PICA), polyisocyanurato(ester amide) (PICEA) and polyisocyanurato(urea ester) (PICUE), based on BCI and hexamethylene diamine, 6-amino-1-hexanol and di(6-hydroxyhexyl) urea, respectively. Amino group is able to react with urea [21] so that (6-hydroxyhexyl) urea can be prepared from urea and 6-amino-1-hexanol [22], rather than from diisocyanates [23]. Therefore, di(6-hydroxyhexyl) urea is also a urea-based monomer. Different from other poly(ester amide) reported [24], the amide and ester groups of the poly(ester amide) designed in this work distribute alternatively, rather than randomly.

2 Experimental

2.1 Materials

6-amino-1-hexanol (AHO, 95%), 1,6-diaminohexane (DAH, 99%) and 1,5,7-Triazabicyclo [4.4.0]dec-5-ene (TBD, 97%) were purchased from Energy Chemical Corporation (Shanghai, China). Urea (99.5%) was purchased from Aladdin Industrial Corporation (Shanghai, China). Bis(2-carboxyethyl) isocyanurate (BCI, 98%) was purchased from TCI (Shanghai) Development Company, Ltd. Titanium(IV) butoxide (TBO, 98%) was bought from Sigma Aldrich Fluka Company. Hydrochloric acid (AR, 36–38 wt%), acetone (AR) and methanol (AR) were purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China). Dimethyl sulfoxide-d6 (DMSO-d6, 99.9%, containing 0.03% tetramethylsilane) was from Cambridge Isotope Laboratories, Inc. (MA, USA). 1,6-diaminohexane was recrystallized in methanol. Urea was dried *in vacuo* before use. All chemicals mentioned above were used as received without further treatment. Bis(2-carbomethoxyethyl) isocyanurate (BCMI) was prepared with the method reported previously [20].

2.2 Characterizations

¹H- and ¹³C-nuclear magnetic resonance (NMR) were detected at 25°C on a Bruker AVANCE III HD 600 (600 MHz) spectrometer (Germany) and the chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. Solid-state ¹³C-NMR spectra were measured by a Bruker Avance III (400 MHz) by CPMAS (298 K, spinning rate of 13 kHz) equipped with a 4 mm probe. FT-IR spectra were taken by a Bruker Vertex 70 spectrometer (Germany). The measurements were taken out with an accumulation of 32 scans. Thermogravimetric analysis (TGA) was conducted on a Netzsch TG 209 F3 Tarsus instrument (Germany) (the weight of sample is 7–10 mg) at a heating rate of 10°C/min under nitrogen atmosphere (40 mL/min). Differential scanning calorimetry (DSC) was carried out at a heating rate and a cooling rate of 10°C/min by using a DSC analyzer Netzsch DSC 204 F1 (Germany) (the weight of sample is 3.5–3.8 mg). Limiting oxygen index (LOI) value was tested by JF-3 oxygen index apparatus (Jiangning Analytical Instruments, China) with the sample size of 80 × 10 × 4 mm according to ISO 4589.

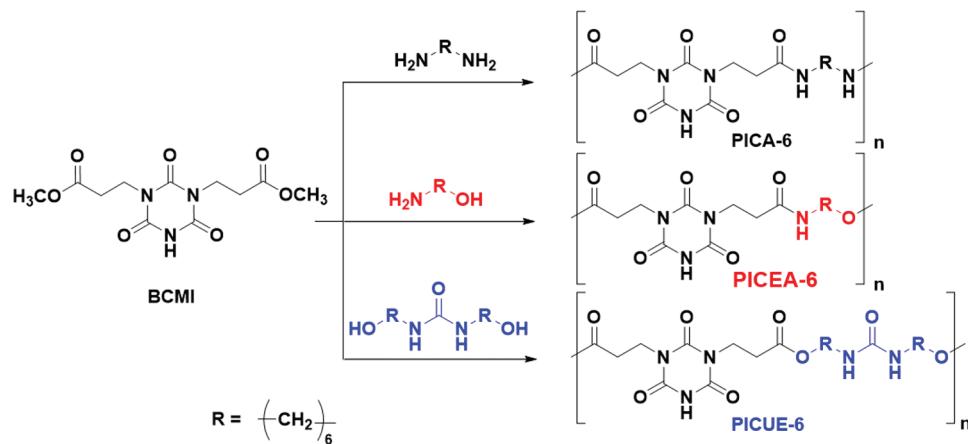
2.3 Synthesis of PICA-6, PICEA-6 and PICUE-6

Bis(2-carbomethoxyethyl) isocyanurate (BCMI, 30.10 g, 100 mmol) which was prepared with the method reported previously [20], DAH(or AHO, or DHAU-6 [22], 100 mmol) and TBD (or TBO, 5 mmol) were added into a three-neck flask equipped with an argon inlet, a mechanical stirrer and a Vigreux column connected to a Dean-Stark trap. In the first step, the reaction was performed at a certain temperature for a certain time with stirring under argon to form oligomers. Then in the second step, vacuum was applied and the temperature was gradually raised further for another period to achieve a higher molecular weight. The product was collected and dried in *vacuo* at 70°C overnight. PICA-6: first Step 130°C for 6 h, second Step 150°C for 6 h; PICEA-6: first Step 130°C for 12 h, second Step 150°C for 12 h; PICUE-6: first Step 130°C for 12 h, second Step 150°C for 12 h.

3 Results and Discussion

3.1 Polyisocyanurate Synthesis

Polyisocyanuratoamide (PICA), polyisocyanurato(ester amide) (PICEA) and polyisocyanurato(urea ester) (PICUE) were prepared via polycondensation of bis(2-carbomethoxyethyl) isocyanurate (BCMI) with 1,6-diaminohexane (DAH), 6-amino-1-hexanol (AHO) and di(6-hydroxyhexyl)urea (DHAU-6), respectively (see Scheme 1). All the hydroxyl or amino functional monomers are based on hexylene diamine or amino alcohol. Therefore, the polymers obtained are referred as PICA-6, PICEA-6 and PICUE-6. The synthesis of BCMI and DHAU-6 was performed by following the methods reported previously [20,22]. Compared with diacid, BCMI exhibits lower melting temperature which enables the reactions to be performed in bulk at a lower temperature. The activity of amino group is higher than hydroxyl group, when reacting with BCMI. Therefore, the reaction time for PICA-6 is shorter than that for PICEA-6 and PICUE-6. The proton NMR spectra of PICEA-6 and PICUE-6 are shown in Fig. 1. Since PICA-6 doesn't dissolve in any deuterated solvent, the NMR spectrum is not available to show here. It is worth to note that trace amount of PICEA-6 can also be found in the spectrum of PICUE-6, which might be due to the degradation of DHAU-6 into AHO. All the proton signals and carbon signals fit well with the chemical structures of both PICEA-6 and PICUE-6 (see Fig. 1). From the spectra of solid-state ^{13}C -NMR (see Fig. 2 left), the signal of all the carbon in the polyisocyanurates is distinguishable. The peaks at 173 and 151 ppm observed in all three polyisocyanurates are the signals of carbonyl $\text{C}=\text{O}$ in the ester (or amide) and the isocyanurate groups, respectively. For PICUE, there is one more carbonyl peak at 160 ppm, which is designated to the urea group. The peak found at 67 ppm for both PICEA and PICUE belongs to the signal of COOCH_2 . The FT-IR spectra of the obtained polymers



Scheme 1: Synthetic scheme for thermoplastic polyisocyanurates (PICA, PICEA and PICUE)

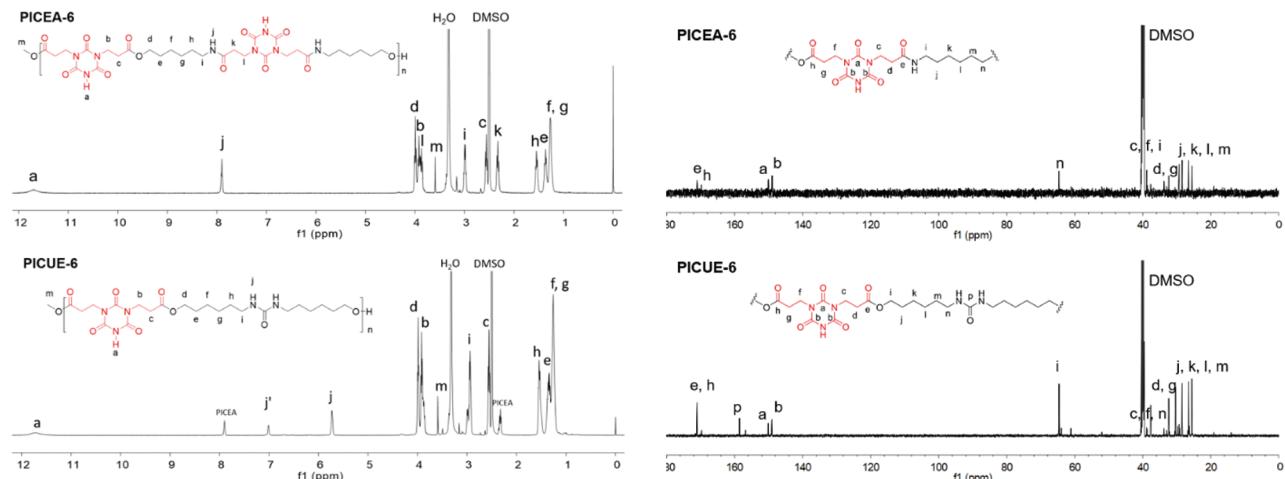


Figure 1: ¹H- (left) and ¹³C-NMR (right) spectra of soluble PICEA-6 and PICUE-6 (in DMSO-*d*6)

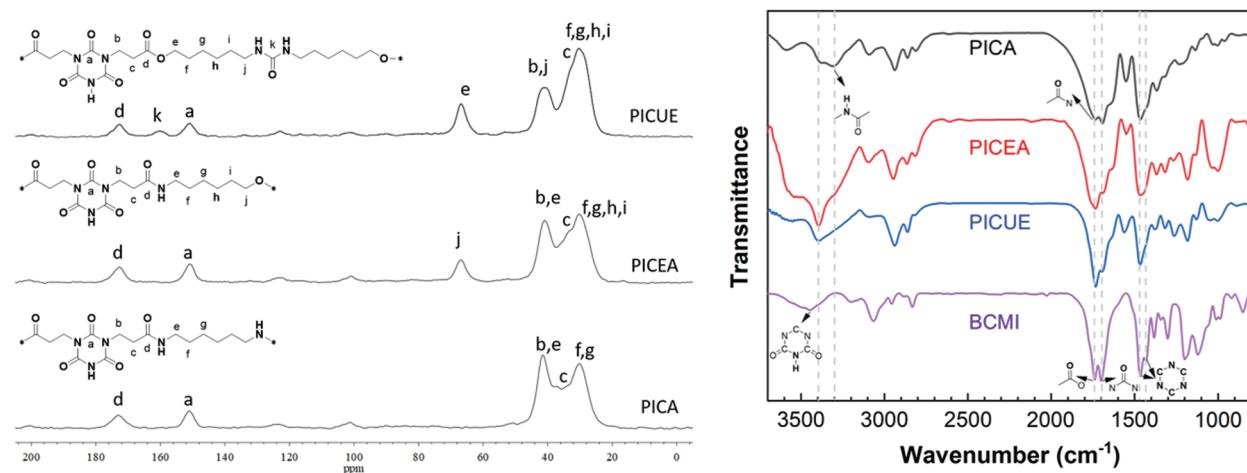


Figure 2: Solid state ¹³C-NMR (left) and FT-IR (right) spectra of PICA-6, PICEA-6 and PICUE-6

are shown in Fig. 2 (right). The signal of isocyanurate rings at 1468 and 1423 cm⁻¹ can be found for all polymers and the monomer BCMI. Compared with BCMI, the isocyanurate NH signal of polymers shifts from 3441 to 3401 cm⁻¹. The peaks of C=O in the isocyanurate ring and in the amide/ester/urea groups are observed at 1742 and 1700 cm⁻¹. The solid-state ¹³C-NMR and the FT-IR spectra indicates that the polymers synthesized are the ones as expected. All these polymers do not dissolve well in either THF or DMF and therefore, no gel permeation chromatography (GPC) data to refer to.

3.2 Thermal and Flame Retarding Properties of the Polyisocyanurates

The thermal stability of the obtained polymers was studied by thermogravimetric analysis (TGA, see Fig. 3) while the thermal transition behavior was determined by differential scanning calorimetry (DSC, see Fig. 4). The results of both TGA and DSC tests are also listed in Tab. 1. In our previous work we discovered that the thermal stability of polyisocyanuratoester (PICE) is superior to conventional aliphatic polyester, due to the existence of isocyanurate rings in the polymer backbone [20]. PICA-6 and PICEA-6 show similar thermal stability to PICE. The degradation temperature at a 5% weight loss ($T_{d, 5\%}$) is above

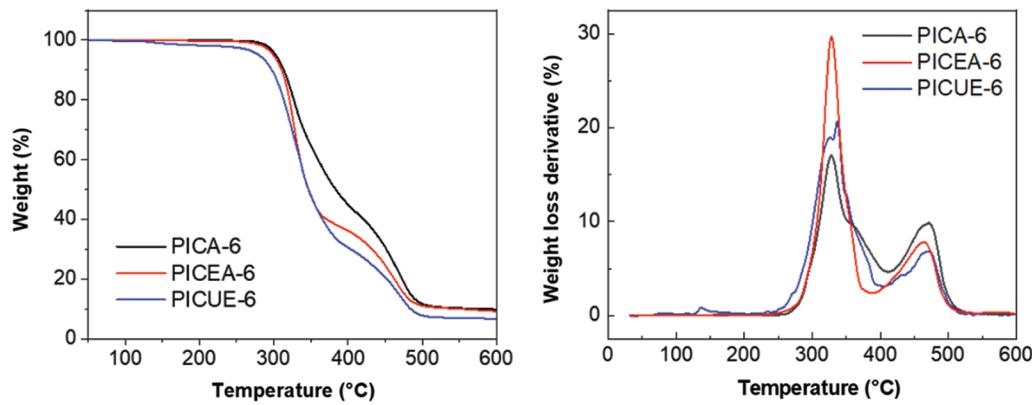


Figure 3: TGA (left) and DTG (right) curves of the polyisocyanurates (heating rate: 20 °C/min)

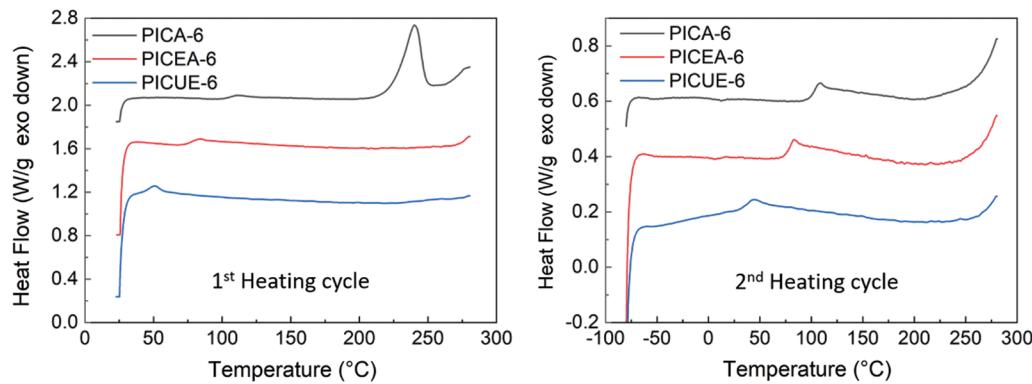


Figure 4: DSC traces of the polyisocyanurates (heating rate: 10 °C/min)

Table 1: Thermal and flame retarding properties of PICA-6, PICEA-6 and PICUE-6

Sample	T _g (°C)	T _m (°C) ^a	T _{d, 5%} (°C)	T _{d, max} (°C)	LOI (%)
PICA-6	101.9	240.2	302.9	328.7	—
PICEA-6	77.9	—	300.0	326.6	24.0
PICUE-6	38.7	—	280.3	325.7, 336.5	24.0

^a Data were recorded from the DSC first heating cycle (heating rate: 10 °C/min).

300°C. For all the polyisocyanurates, a two-stage degradation behavior is observed and the peak values are similar. In the first stage, which is at around 320°C, the obvious degradation is due to the cleavage of ester or amide bonds. For PICUE-6, another peak can be found on the DTG curve at 336°C, which is attributed to the cleavage of urea bonds. In the second stage of degradation (peak value at approximately 470°C), the isocyanurate rings set to degrade. All the polyisocyanurates show similar degradation behavior at this stage.

As seen from Fig. 4, in the DSC first heating cycle, PICA-6 behaves as a crystalizable polymer and a sharp melting peak is observed at 240.2°C. For PICEA-6 and PICUE-6, no melting peak can be found. In the second heating cycle, no melting peak is found for all of these three polymers. Polyisocyanurates crystallize slowly because of the hindrance of the isocyanurate rings so that in the cooling (at a rate of 10 °C/min) process the polymer chains do not have sufficient time to crystallize. Therefore, the signal

detected in the second heating cycle of DSC does not show any melting behavior. The glass transition temperature (T_g) of PICA-6, PICEA-6 and PICUE-6 are 101.9, 77.9 and 38.7°C, respectively. The polyamide exhibits higher T_g than the corresponding poly(ester amide), which is understandable. The poly(urea ester) seems more flexible than the poly(ester amide), even with urea groups in the backbones. The T_m of PICA-6 is similar to nylon 66 (240 vs. 253°C) and its T_g is much higher (102 vs. 45°C). Dynamic mechanical thermal analysis was also tried but failed due to the fact that the samples are too brittle.

Limiting oxygen index (LOI) was tested as well according to ISO 4589, to examine the flame retardancy of the obtained polyisocyanurates and the results are listed in Tab. 1. The LOI value of PICEA-6 and PICUE-6 are both 24.0%, which suggests that they are flame retarding materials.

4 Conclusions

Three different thermoplastic polyisocyanurates were synthesized and their thermal properties are studied in this work. The incorporation of isocyanurate into polymer chains is proved to be able to increase the glass transition temperature while keeping the melting temperature of polymers, especially for polyamide. Polyisocyanurato(ester amide) and polyisocyanurato(urea ester) are less crystallizable than polyisocyanuratoamide thus no melting peak is observed in their DSC traces. Limiting oxygen index of PICEA-6 and PICUE-6 was tested and the values are 24.0% for both polymers. Those thermoplastic polyisocyanurates are processible and have great potential contributing applications in flame retardant textiles.

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Conflicts of Interest: The authors declare that they have no conflicts of interest to report regarding the present study.

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