Synthetic routes to flame retardant isocyanurate of rigid polyurethane foams

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Abstract. Polyurethanes (PUs) are an important class of polymers that are widely used as thermal insulators in many areas. However pure PUs have high combustibility and low thermal stability. which thermal degradation is only 200°C. Azacyclic isocyanurate compounds have a high thermostable triazinic ring with high nitrogen content, and gives inherently flame retardant of rigid PUs. It degrades at approximate 350°C as opposed to 200°C for urethane. In this paper, we summarized the details of isocyanurate synthesis by cyclo-trimerisation and direct introduction.

1. Introduction
Polyurethanes (PUs) are an important class of polymers which covers practically all the fields of polymer applications, such as foams, elastomers, thermoplastics, adhesives, coatings, sealants, fibres and so on. Unfortunately, many people lost their lives, and many valuable buildings, constructions and materials were destroyed due to the high combustibility and low thermal stability of the polymers at high temperatures. The thermal degradation of PUs can begin to occur at processing temperatures above 180°C. The development of flame retardant PUs is an inevitable requirement for applications, such as construction, transportation, appliances, packaging, coatings, adhesives, sealants and thermal insulation etc.

Flame-retardant PUs are prepared by the addition or incorporating reactive flame retardants into the PU formulation. Additive type flame retardants, such as phosphorus-based flame-retardant, organic halogen compounds, organic nitrogen compounds, inorganic metal compounds and so on [1], often result in poor dispersibility and compatibility with the raw materials of PUs, and poor mechanical properties of PUs owing to dispersing them in the composition by physical means. Instead, most of reactive type flame retardants are organic compounds that have active functional groups, which can form covalent bonds with PUs [2]. The flame retardants do not degrade the mechanical properties of the PUs because the flame retardant group is a part of the PU molecules. They possess better compatibility with the raw materials of PUs and better fire-retardancy using small amount or low concentration [3].

A number of investigators have found that the chemical modification of the PU backbone through the introduction of thermally stable heterocyclic isocyanurate is a viable method for improving flame retardancy and thermal stability [4-7]. Isocyanurate compounds have a high thermostable triazinic ring with a high nitrogen content, which gives inherently flame retardant of rigid PUs [8-12]. It degrades at
approximate 350 °C as opposed to 200 °C for urethane, and are the more stable structure [13,14]. It can be obtained from both the trimerisation of an excess of –NCO groups against the hydroxyl groups (isocyanate index of 200-600) and direct isocyanurate into the polyols for PUs.

The present paper only goes into the details of isocyanurate synthesis through cyclo-trimerisation and direct introduction.

2. Synthetic Routes of Isocyanurate

2.1. Cyclo-trimerisation of isocyanates

Cyclo-trimerisation of isocyanate to isocyanurate has been extensively used in PU chemistry to improve flame retardancy, thermal stability, chemical resistance and film-forming characteristics.

2.1.1. By-product. The cyclo-trimerisation with formation of dimer uretdione has been well documented [15], which is known to occur spontaneously (Figure 1).

![Figure 1. Isocyanate cyclo-oligomerisation.](image)

The formation of high purity isocyanurate while avoiding uretdione contamination has become a significant challenge, because uretdione known to significantly hamper the activating ability of isocyanurate. The formation of trimers is highly dependent on the specific reactivity of the particular isocyanate.

2.1.2. Catalysts. Catalysts are a key factor for a controlled trimerization to produce materials with excellent properties. The most common catalysts are Lewis-bases, such as tertiary amines, phosphines, metal or quaternary ammonium salts of alkoxides or Lewis acids, such as various organic metal compounds, in particular metal carboxylates. For trimerization in the bulk, the catalyst system should be molecularly soluble in the diisocyanate monomer to produce materials with high optical quality.

Although many studies have been found that conventional amines can catalyse the reaction, however significant levels of uretdione by-products are observed [16]. The discovery of the strong non-ionic bases proazaphosphatranes heralded the possibility of producing isocyanurates in an unprecedentedly high purity [17]. Proazaphosphatranes effectively catalyse cyclo-trimerisation of isocyanates, giving isocyanurate with very low levels of the cyclic dimer uretdione, quickly and at low catalyst loadings (typically 0.1 mol%) [18].

Trimerisation of -NCO groups is generally produced in the presence of special catalysts, such as potassium acetate, tris (dimethylaminomethyl) phenol, etc (Scheme 1). The PUs containing triazinic ring are in fact hybrid structures having both groups urethane groups resulting from the reaction of -NCO groups of isocyanates with hydroxyl groups of polyols and isocyanurate groups. The formation of poly(urethane- isocyanurate) generally takes place at high temperatures such as 120–140 °C and in
the presence of catalyst [19]. The reaction is used for the manufacture of isocyanurate foams and urethane-isocyanurate foams.

Sendijarevic et al. used 2,4,6-tris(dimethylaminomethyl)phenol as a catalyst for the preparation of poly(urethane-isocyanurate) by the trimerization of an NCO-terminated urethane prepolymer [20]. The trimerization reaction can also be carried out at room temperature using an epoxy compound (ethylene, propylene or butylene oxide) and a tertiary amine catalyst.

Alkaline ions can catalyse the trimerisation reaction of isocyanate groups to isocyanurate rings, which is extremely undesired reaction for prepolymers (polyethers with isocyanate end groups), especially those used in elastomers and flexible foams (MDI based flexible PU foams). However, if the potassium content in the prepolymer is higher than 10-15 ppm, there is a marked tendency towards prepolymer gelification during storage. For some special applications, it is recommended that polyethers with a very low content of potassium ions, maximum 2 ppm, are used in the prepolymer synthesis.

Burkus used a triethylamine and propylene oxidemixture as a trimerization catalyst for the preparation of PU–isocyanurate from an NCO-capped polyester prepolymer [21].

2.2. Direct Introduction
Cyanuric acid or 1,3,5-triazine-2,4,6-triol is a compound with triazinic ring. It is easily obtained by urea thermal decomposition. It has two tautomeric forms (Figure 2).

![Figure 2. Two tautomeric forms of cyanuric acid.](image)

1,3,5-tris(hydroxymethyl) isocyanurate (THMI) with heteroxylic triazinic structure is formed by the reaction of cyanuric acid with formaldehyde (Figure 3). As shown in Figure 3, all three hydrogen atoms of cyanuric acid can be substituted in successive reactions of formaldehyde with isocyanurate acid.

![Figure 3. Reaction of cyanuric acid and formaldehyde.](image)

The reaction is reversible in aqueous solution. When water is removed in the presence of a mineral acid, the product undergoes a reaction of condensation with formation of methylene or dimethylene ether bridges. The reaction was utilized for preparation of THMI. However, the THMI is dissolved in water, given decomposes to di- and monohydroxymethyl derivatives or to the acid itself [4]. Their proportions depend on concentration. This is the reason why THMI solutions in water become cloudy and retain acidic character of isocyanuric acid. It has been found that introduction of water (to reach 5 wt. % of THMI solution) enabled to obtain the semisolid resin well soluble in oxiranes and reacting with them at 80-120 °C in the presence of ternary amines as catalysts to form polyetherols with a triazinic ring.
Polyols with heteroxylic triazinic structure are also formed by Mannich reaction with formaldehyde and diethanolamine (Figure 4). These compounds are useful substrates to obtain PUs of enhanced thermal stability [21].

Figure 4. Reaction of cyamuric acid with formaldehyde and diethanolamine.

New heterocyclic polyols for rigid PU foams with a triazinic structure are obtained by propoxylation of the resulting polyols in the presence of a tertiary amine as catalyst, such as dimethylaminoethanol (Figure 5).

Figure 5. Propoxylation of the resulting polyols.
A well known triol, 1,3,5-tris(2-hydroxyethyl) isocyanurate (THEI) is produced industrially and currently used in PU manufacture, as a crosslinking agent (Figure 5) [22]. It can be transformed into liquid polyol by reaction with 2-3 mols of propylene oxide/mol of THEI in the presence of a tertiary amine. The polyol with 3 mols of Propylene oxide/mol of THEI has an hydroxyl number of around 375 mg KOH/g. In addition, tris(2-propene) isocyanurate and tris[2-(acryloyloxy)ethyl] isocyanurate also can be used as crosslinkers in PU formulations.

3. Discussion
As we know, PUs containing isocyanurate groups can improve the thermal stability of the polymers. The importance of evaluating the thermal stability or flame retardancy of these PUs, studying a structure–property correlation, studying thermal degradation, understanding the processes occurring during thermal stress as well as the parameters affecting the thermal stability of the polymers are essential in order to effectively design PUs having the properties suitable for the particular environment. Studying the decomposition mechanism and kinetics is also a part of these studies.

References
[1] Pinto U A, Visconte L L Y, Gallo J and Nunes R C R 2000 Polym. Degrad. Stabil. 69 257
[2] Fan H, Tekeei A, Suppes G J and Hsieh F H 2012 Int. J. Polym. Sci. 2012 8
[3] Lu S Y and Hamerton I 2002 Prog. Polym. Sci. 27 1661
[4] Sarwade B D, Wadgaonkar P P and Mahajan S S 1989 J. Polym. Sci. Polym. Chem. Ed. 27 3263
[5] Yegane H, Atai H M, Tulemi P H and Jamshidi S 2006 Macromol Mater. Eng. 291 883
[6] Yeganeh H and Shamekhi M A 2004 Polymer 45 359
[7] Sehovic H, Sendijarevic A, Sendijarevic V, Frisch K C and Wong S W 1987 J. Coat. Technol. 59 29
[8] Yeganeh H, Barikani M and Khodabadi F N 2000 Eur. Polym. J. 36 2207
[9] Levcik S V and Weil E D 2004 Polym. Int. 53 1585
[10] Wang C L, Klemper D and Frisch K C 1985 J. Appl. Polym. Sci. 30 4337
[11] Ionescu M, Mihalache I, Zugravu V and Mihai S 1994 Cell. Polym. 13 57
[12] Farrissey J W, Rose J S and Carleton P S 1970 14 1093
[13] Zhang Y, Shang S, Zhang X, Wang D and Hourston D J 1996 J. Appl. Polym. Sci. 59 1167
[14] Ashida K, Saiki K, Goto J and Sasaki K 1997 ACS Symp. Ser. 669 81
[15] Han C, Ran X, Zhang K, Zhuang Y, Dong L and Appel J 2007 Polym. Sci. 103 2676
[16] Kordomenos P I and Kresta J E 1981 Macromolecules 14 1434
[17] Gibb J N and Goodman J M 2013 Org. Biomol. Chem. 11 90
[18] Raders S M and Verkade J G 2010 J. Org. Chem 75 5308
[19] Luchkina L V, Askadskii A A and Bychk E K A 2005 Russ. J. Appl. Chem. 78 1337
[20] Sendijarevic A, Sendijarevic V, Frisch K C and Vlaic M 1991 J. Elast. Plast. 23 192
[21] John B 1961 Process of trimerizing isocyanates US, US2979485
[22] Lubczak J Polimery 2011 56 452