# Methods of synthesis of oligoetherols suitable for obtaining of some polymers with higher thermal stability

Jacek LUBCZAK - Department of Organic Chemistry, Rzeszów University of Technology, Rzeszów

Introduction

The presence of certain heterocyclic rings with nitrogen atoms in an organic polymer may significantly improve its thermal stability. For typical polyurethane foams, the upper temperature range of save usage is usually considered to be 90-110°C [1, 2]. This limit can be improved by applying an oligoetherol component containing a thermostable heterocyclic ring with nitrogen atoms, such as 1,3,5-triazine (s-triazine) (I) [3], perhydro-1,3,5-triazine (II) [4] or purine (III) ring:


(I) (II) (III)
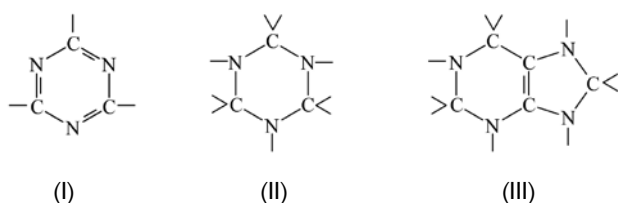
The polyurethane foams prepared from such a oligoetherol withstand temperature reaching 200°C and can permanently work at 140-150°C, and, occasionally (for up to 30 min.), at 800°C [2]. The same heterocyclic rings incorporated into the structure of other polymers, such as polyesters [6÷8] or epoxy resins [9] also improve thermal stability of the polymers and additionally enhance their chemical resistance and stability.

The oligoetherols with heterocyclic rings are usually obtained by hydroxyalkylation of the relevant heterocyclic compounds, e.g. isocyanuric acid [10], melamine [11÷15] or some of their derivatives [3,16,17] with an excess of oxiranes and/or formaldehyde. Alkylene carbonates are also used as hydroxyalkylating agents [18]. One should mention here that the reaction of amino groups with oxiranes and corresponding alkylene carbonates lead to the same products:
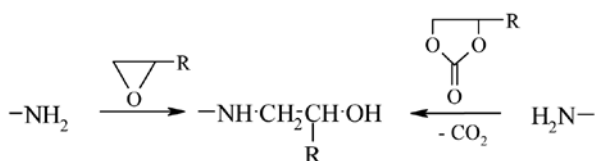

Hydroxyalkylation with oxiranes

The most common oxiranes, such as ethylene oxide, propylene oxide, or glycidyl ethers react with isocyanuric acid in a sequel of reactions to form 1,3,5-tris(hydroxyalkyl) isocyanurates (IV, x = y = z =1) [19]:


(IV)
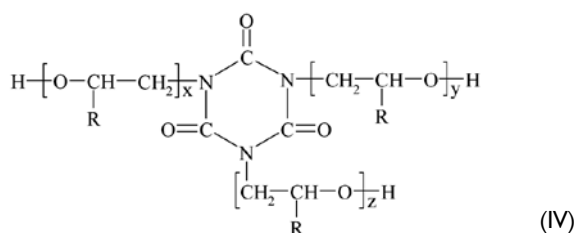
The reactions of isocyanuric acid or its derivatives with an excess of ethylene oxide or propylene oxide yield trifunctional oligoetherols (IV, x + y + z = n, n – number of moles of oxiranes/ mole of isocyanuric acid) [20, 21] comprising in their structure thermostable s-triazine ring that provide polyurethane foams with improved thermal resistance. The disadvantage of this method of preparing oligoetherols is the lack of solvents sufficiently convenient to carry out the reactions. To avoid this difficulty, an alternative method was proposed [22] consisting of replacing isocyanuric acid by 1,3,5-tris(hydroxymethyl) isocyanurate (V), its well soluble derivative. In order to eliminate solvent altogether, 5 wt.% of water was added to tris(hydroxymethyl) isocyanurate. The resulting semisolid resin was well soluble in oxiranes and was reacted with them at elevated temperature (80-120°C) in the presence of tertiary amine catalysts to afford the expected oligoeetherols (VI) [23]:

(V)

(VI)
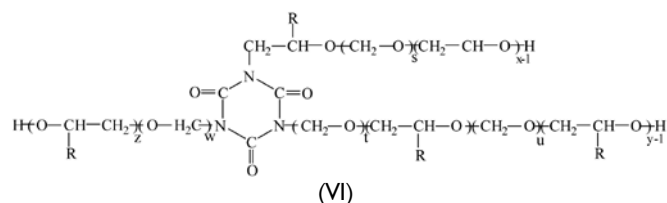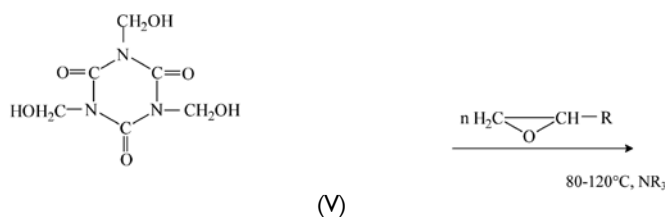
where: R = –H, -CH$_3$,   s + t + u + w = 3,   x + y+ z = n

The chemically blocked formaldehyde at nitrogen atom of the ring by one hydroxyalkyl group originating from ethylene or propylene oxides is metastable and upon heating or in solution it undergoes elimination and usually moves to the end of hydroxyalkyl chain:
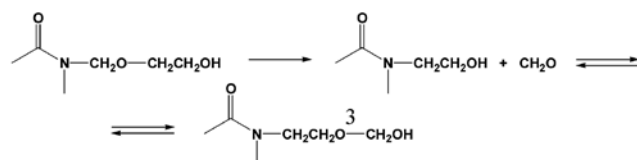
Permanent blocking of formaldehyde molecule occurs when 1 mole of hydroxymethyl groups reacts with at least two moles of oxirane.

Rather scarce patent literature on melamine (VII) concentrates mostly on the products obtained with the molar excess of oxirane exceeding six [6÷8]:

science

(VII) → (VIII)
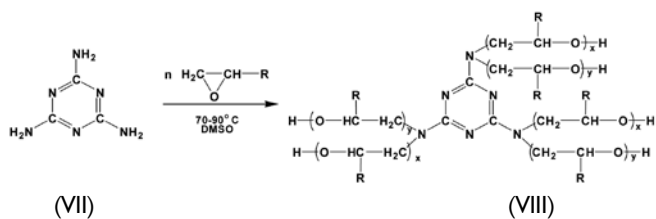
where: x + y + z = n

Liquid or resinous substances (VIII) of hydroxyl number 200÷300 are obtained. The catalysts claimed are oxides or hydroxides of metals of I and II group of the Periodic Table, most often potassium hydroxide. The latter, however, is not the most effective catalyst because of its limited solubility in organic solvents (including DMSO, which is the best solvent of melamine). Furthermore, dark-brown products are obtained in its presence, products of high viscosity. All these disadvantages were overcome when alkylammonium hydroxides were applied, such as tetrabutylammonium [24] or tetraethylammonium [25] hydroxides that dissolve in organic solvents much better than potassium hydroxide. The reaction conditions were: temperature: 60-95°C, solvent: DMSO or DMF, time: 25÷60 hrs [26]. The number of amino groups blocked by an oxirane was always smaller than the number of moles of oxirane; thus suggesting that subsequent reactions, i.e., reactions of oxirane with hydroxyalkyl groups formed earlier, do take place.

While seeking s-triazine containing compounds better soluble in organic solvent than melamine, attempts were made of applying N,N'-diacetylmelamine (IX) as a starting material for preparation of oligoetherols [16]. It is prepared by reacting 1 mole of melamine with 2 moles of acetic anhydride [27]:

(IX)
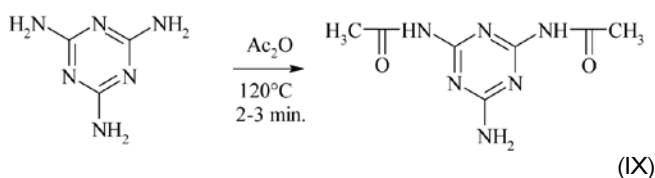
The reactions of N,N'-diacetylmelamine with ethylene oxide or propylene oxide are accompanied by nucleophilic intramolecular rearrangement that alter the structure of oligoetherols [28] with respect to the anticipated structure on the basis of the N,N'-dia-cetylmelamine formula [16]. Hence, in the reaction of 1 mole of N,N'-diacetylmela-mine with two moles of ethylene oxide N,N'-bis(acetyloxyethyl)melamine (X, R= –H) rather than N,N'-diacetyl-N,N'-bis(2-hydroxyethyl)melamine is formed:

(X)
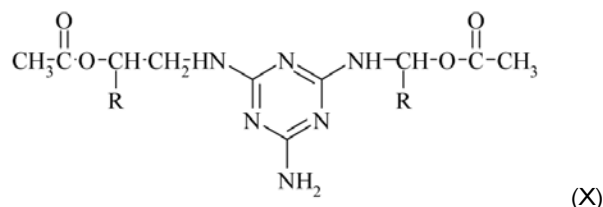
Although N,N'-diacetylmelamine was somewhat better soluble in DMSO or DMF than melamine itself, its solubility was still insufficient and the technical problems related to the solubility was not overcome. Since, as its well known, the solubility of melamine can be substantially improved by reacting it with formaldehyde to form (hydroxymethyl)melamines (for example N,N,N',N',N"-pentakis(hydroxymethyl)mela-mine, XI) that are well soluble in hot water and in DMSO [29].

(XI)
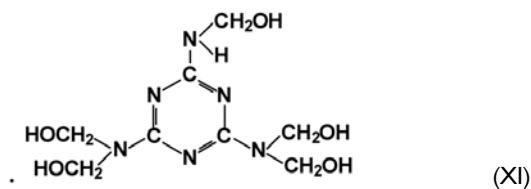
It was also found that the addition of (hydroxymethyl) melamines to ethylene oxide or propylene oxide in DMSO or DMF is accompanied condensation of hydroxymethyl groups occasionally leading to cross-linked products [30]. The amount of this product depended on the initial molar ratio of reagents and on the conditions applied [31]. The rationale of the condensation was the catalytic effect of the products of addition of oxirane [32÷34]. Formaldehyde contained in a hydroxymethyl group and blocked by a single oxirane molecule can easily be released even at temperature as low as 40°C. The etherol chain is then broken and formaldehyde molecule is moved to the end of chain where it forms an instable semiacetal link easily decomposing with formaldehyde liberation [17]. Suitable for oligoetherol synthesis are the melamine derivatives containing 4 and more hydroxymethyl groups per molecule. Otherwise, cross-linked products and products containing unreacted amino groups are formed. Following the findings, optimal conditions of the synthesis of s-triazine oligoetherols were proposed comprising reactions of N,N,N',N',N"-pentakis(hydroxymethyl)melamine with oxiranes at 45-75°C for 25÷47 hrs. [34].

A disadvantage of the method of synthesis of oligoetherols from (hydroxymethyl)-melamines was the necessity of separation the highly boiling solvent. To overcome the problem, melamine derivatives well soluble in oxiranes were sought for. Attention was focused on the products with hydroxymethyl groups blocked with methanol. The latter converted into polyols by ethylene glycol yielded substances soluble in oxiranes. This method of preparing s-triazine oligoetherols was described in [3]. The idea is illustrated below in the fragment of hydroxymethyl derivative of melamine:

product soluble in oxiranes
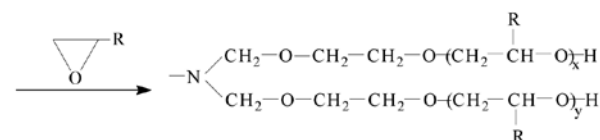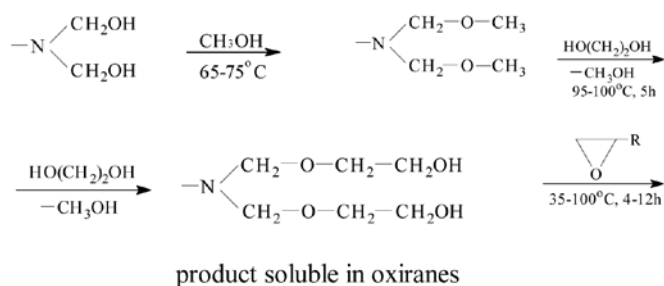
This alternative synthetic route had two disadvantages. It comprised many stages and unreacted compounds contaminated the product. The latter had no serious effect upon the thermal stability of polyurethane foams that was much higher than that of classical foams [3]. The first disadvantage was partly neutralized by replacing N,N,N',N',N"-pentakis(hydroxymethyl)melamine with disubstituted compond: N,N'-bis(hydroxymet-hyl)melamine (XII). It was possible to eliminate the transesterification stage, since bis-(methoxymethyl)melamine (XIII) disolved in oxiranes at elevated temperature [35, 36]:

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(XII)

(XIII)

$$\text{where: } x + y + p + q = n$$

(XIV)

The presence of purine ring in the structure of uric acid gives it higher thermal stability. Its temperature of decomposition is circa 400°C [37]. The simplest way of preparing oligoetherols with purine rings would be the reaction of uric acid (UA) with oxiranes. Until 1999 no information on this reaction could be found in literature. The reason is the lack of solvents of uric acid. It is insoluble even in DMSO or DMF and its solubility in water is only 0.5 g/dm³ at 99°C [37]. The solubility problem was overcome by preparing soluble hydroxymethyl derivatives (XV) of uric acid [38]. N-hydroxy-methyl derivatives of uric acid are thermally reasonably stable products, since their decomposition starts at 260°C, whereas hydroxymethyl derivatives of melamine or isocyanuric acid start to decompose as early as at 80-90°C [22, 39]. The products of addition at UA:CH_2O 1: >6, after removing water by distillation, are well soluble in cold water [38]. When a small amount of water (5 wt. %) is introduced to the product of addition at UA:CH_2O 1: ☐7 liquid products are obtained that when slightly heated (to 65-70°C) dissolve in oxiranes, ethylene or propylene oxides. In the presence of triethylamine catalyst oxiranes react with the derivative to oligoetherols (XVI) containing thermostable purine rings [40].

(XV)

(XVI)

where R = –H, –CH_3, and $K + L + M + N = n – 9$; $n \geq 12$ for ethylene oxide, $n \geq 14$ for propylene oxide, $x + y + z = 6$; $x' = 0$ for $0 < z' \geq 1$; $0 < x'$ for $z' = 0$.

The advantage of the method is that the reaction does not require any solvents.

Barbituric acid (XVII) differs from isocyanuric acid by the presence of carbon atom instead of nitrogen in the ring. Pyrimidine ring of barbituric acid is thermally stable. It decomposes starting from 270-280°C. When barbituric acid attempted to react with excess of oxiranes, tautomer (XVIII) is formed already at 40°C, and leaves the solution as precipitate instead of expected conversion into oligoetherols. This may indicate the catalytic role of epoxides in the process [41]:

(XVII) (XVIII)

The enol form is yellow solid, melting at 280°C with decomposition. It is insoluble in organic solvents, in water it slowly returns into triketo form (weeks). When hydrogens at C_5 are replaced with alkyl groups like in 5,5-diethylbarbituric acid (XIX)) the tautomerization is not possible and renders the (XIX) suitable substrate for synthesis of N-hydroxyalkyl derivatives (XX) [42÷45]:

(XIX) (XX)

where 2x = n

This strategy enables the synthesis of new derivatives; esters (XXI) and polyurethanes (XXII) with pyrimidine ring starting from 1,3-bis(hydroxyalkyl) derivatives of 5,5-diethylbarbituric acid with carboxylic acids and isocyanates [46,47], respectively:

(XXI)

(XXII)

The structure of polyurethanes, their physical and phase transitions were elucidated. It has been found that they are thermally more stable than classic polyurethanes. The ester monomers (acrylates and methacrylates) were used to obtain polymers in the radical polymerization. It has been found that the polymers with pyrimidine ring posses enhanced thermal stability and heat resistance.

Barbituric acid similarly to earlier discussed azacyclic compounds reacts with fomaldehyde [47]. These reactions are suitable way of barbituric acid modification and allow to obtain multifunctional

oligoetherols with pyrimidine ring[48÷51]. This is not possible to achieve in straightforward reaction of barbituric acid with oxiranes due to tautomerization of barbituric acid to trienol form.

Hydroxyalkylation with alkylene carbonates

As it was mentioned the hydroxyalkyl derivatives of azacycles can be obtained in straightforward reaction between alkylene carbonates, like ethylene carbonate (EC) or propylene carbonate with azacycle. Azacycles are sparingly soluble in DMSO and/or water, therefore syntheses with oxiranes were performed in DMSO; in presence of water the side reactions of oxiranes with this solvent resulted in formation of glycols or polyglycols. After completion the reaction, DMSO had to be removed under reduced pressure; nevertheless heating of post-mixture led to partial decomposition of DMSO and the product thus purified had characteristic odor. Moreover, oxiranes themselves are low-boiling, toxic and flammable compounds, and form explosive mixture with air. All these features render them hazardous chemicals [52]. The use of hydroxymethyl derivatives of azacycles instead of unsubstituted azacycles enabled to perform reaction with oxiranes thanks to better solubility of derivatives in organic solvents, sometimes in neat oxiranes. The disadvantage of this method was release of formaldehyde blocked with one oxirane, and migration of formaldehyde to the end of etherol chain. Therefore larger excess of ethylene oxide or propylene oxide used to obtain oligoetherols from hydroxymethyl derivatives was necessary, instead of straightforward reaction of azacycles with oxiranes.

Alkylene carbonates are not hazardous chemicals, because they are inflammable, non-toxic, polar [53] enough to dissolve azacycles. Thus, they can be the solvents and reagents at the same time, they do not have to be removed from post-reaction mixture, because they react to the end with azacycles. First suggestions on the use of alkylene carbonates for synthesis of oligoetherols with azacycles are dated at 1993 [54], where it was mentioned that alkylene carbonates are useful reagents for melamine to obtain oligoetherols.

In order to obtain oligoetherols with perhydro 1,3,5-triazine ring the reaction of isocyanuric acid with ethylene carbonate requires excess of hydroxyalkylating agent. As was proven in [55] the resin-like products, free of N-(2-hydroxyethyl) derivatives of isocyanuric acid (IA) are formed when initial molar ratio IA:EC is 1:>5. Reactions with ethylene carbonate were performed at 155-160°C within 3 hours in presence of potassium carbonate as catalyst. The synthesis of oligoetherols from isocyanuric acid and propylene carbonate should not be conducted in presence of potassium carbonate, because the product is always contaminated with solid potassium isocyanurate, which is formed during the synthesis of oligoetherols. The best catalyst is here 1,4-diazabicyclo[2.2.2]octane or tetrabutylammonium hydroxide, at temperature 175-180⁰C [56].

Our studies showed that at initial molar ratio of melamine to alkylene carbonates 1:<12 in presence potassium carbonate or hydroxide as catalysts recommended in the patent [57], the resin products are contaminated with lower hydroxyalkyl derivatives and melamine, which indicates the catalysts are ineffective. Instead of them 1,4-diaza-bicyclo[2.2.2]octane was proven to be a good catalyst [58, 59]. Quite pure products are in this case obtained already at melamine to ethylene carbonate ratio 1:6. Reactions were performed at 160-165°C for ethylene carbonate and 175-180 °C with propylene carbonate.

Studies of reaction of uric acid with alkylene carbonates showed that at excess of carbonates like ethylene or propylene carbonate slow dissolving of uric acid occurs with formation of oligoetherols with purine ring included [60, 61]. The process of synthesis of oligoetherols with purine with ethylene carbonate is usually conducted at 180°C and 1,4-diazabicyclo[2.2.2]octane catalyst, while those from uric acid and pro-pylene carbonate in presence of tetrabutylamonium hydroxide and KOH at ca. 185°C [61]. Obtained oligoetherols reveal higher thermal stability than those obtained from hydroxymethyl derivatives of uric acid and oxiranes, in which unstable oxymethylene groups are present; these can result in diminishing of thermal stability of products. Similarly, the thermal stability of polyurethane foams obtained from oligoetherols and diisocyanates is higher in comparison with those obtained from oligoetherols and hydroxymethyl derivatives of uric acid.

Preliminary studies conducted by the author showed that alkylene carbonates can be successfully used as hydroxyalkylating agents for such sparingly soluble azacyclic substrates like melamine isocyanurate, melam or melem. Especially the latter has very high thermal stability and decomposes above 660°C, which renders it a perfect candidate for obtaining polymeric material of very high thermal stability.

Unfortunately, barbituric acid cannot be directly used for obtaining of oligoetherols in reactions with alkylene carbonates as it undergoes tautomerization to trienolic form. This new form is not soluble in reaction medium and does not react with carbonates. This is the reason why there is no information in literature regarding application of barbituric acid for obtaining of oligoetherols in reactions with alkylene carbonates. The only exception are reactions with formaldehyde and oxiranes where there is no trienolic form of barbituric acid. Recently a very good way of obtaining of oligoetherols is reaction of barbituric acid with glycidol was introduced. Barbituric acid is easily soluble in glycidol at a higher temperature and also reacts with it giving hydroxyalkyl derivatives. These derivatives can react with alkylene carbonates which results in obtaining multifunctional oligoetherols with pyrimidine ring. These oligoetherols can be applied for production of polyurethanes foams with higher thermal stability.

Summary

The oligoetherols of azacyclic compounds and its hydroxymethyl derivatives can be obtained by excessive hydroxyalkylation. These oligoetherols are useful for synthesis of polymers of enhanced thermal stability. The hydroxyalkylation agents can be oxiranes like ethylene oxide or propylene oxide. Recently alkylene carbonates were introduced as hydroxyalkyl agents. When alkylene carbonates are used, it is possible to avoid traditional reagent like ethylene oxide and propylene oxide which have low boiling points (14°C and 34°C), respectively, are flammable and explosive. Instead high boiling, inflammable and non-toxic carbonates can be used, additionally pressure reactors can be avoided and reaction can be performed under reflux. An additional advantage is solubility of azacyclic compounds in these carbonates in temperature of the process.

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Translation into English by the Author

Jacek LUBCZAK - Professor (Ph.D.) works currently as Head of the Department of Organic Chemistry at the Rzeszow University of Technology. He graduated from the Faculty of Chemistry at the Rzeszow University of Technology and since that time, he has been an employee of this university. He gained his Ph.D. degree at Maria Curie – Sklodowska University in Lublin where he also received a title of professor in Organic and Polymer Chemistry. In 2011, he was awarded a title of Professor in Chemistry.

He is the author of 6 books for students and the author of over 100 articles published in national and international papers as well as in conference materials. Moreover, Prof. Lubczak was a speaker and the author of posters at around 170 conferences. He specializes in hydroxyalkylation of sparingly soluble azacyclic compounds which are applied as precursors for synthesis of polymers with higher thermal stability.

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