

SYNTHESIS OF NEW AROMATIC MANNICH POLYOLS FOR RIGID POLYURETHANE FOAMS

Iolanda ROTARU¹, M.IONESCU², D.DONESCU³, M.VULUGA⁴,
Violeta PURCAR⁵

Spumele poliuretanice rigide sunt polimeri celulari care se obțin prin reacția a două componente principale : un izocianat organic și o componentă poliolică, care este un amestec format din polieteri sau poliesteri polioli. Polioli Mannich sunt o nouă categorie de polieteri polioli aminici care datorită structurii aromatice imprimă spumelor poliuretanice rigide rezistență termică și la foc precum și proprietăți fizico-mecanice superioare. Datorită prezenței azotului terțiar din structura lor, polioli Mannich au un efect autocatalitic în reacția cu izocianatii, realizându-se o reducere de cost importantă prin eliminarea unei părți a catalizatorilor de reacție amine terțiare, care au un cost relativ ridicat. Articolul prezintă sinteza unor noi polieteri polioli Mannich printr-o metodă nouă bazată pe chimia oxazolidinelor.

Rigid polyurethane foams are cellular polymers prepared by reaction of two components: an organic isocyanate and a polyolic component which is a mixture between of polyethers or polyesters polyols. Mannich polyols are a novel group of aminic polyols with aromatic structure which give fire resistance, good thermal and superior physico-mechanical properties. Because of tertiary nitrogen presence in their structures, Mannich polyols have an autocatalytic effect in reaction with isocyanates, making an important cost reductions by reducing the amount of the highly priced tertiary amines used as catalysts. The paper presents the synthesis of some new Mannich polyether polyols by a new method based on oxazolidines chemistry.

Keywords: rigid polyurethane foams; aminic polyols; Mannich polyether polyols; autocatalytic effect; isocyanates.

¹ Senior Research Scientist II , Quality Control Specialist– S.C. Zentiva S.A., Romania

² Senior Research Scientist I, Ph.D. Pittsburg State University, Kansas Polymer Research Center, USA;

³ Senior Research Scientist I ,Ph.D., ICECHIM – Bucharest, Romania

⁴ Senior Research Scientist II, Ph.D., Centre for Organique Chemistry “Costin D.Nenitescu” Romanian Academy , Bucharest Romania

⁵ Chemist, ICECHIM – Bucharest, Romania

1. Introduction

Polyether polyols for rigid polyurethane foams are usually low molecular weight addition product of propyleneoxide to chain initiators, having active hydrogen atoms as: alcohols, amines, condensation product of aldehydes and phenols, acid derivatives [1-12].

Polyether polyols for rigid polyurethane foams should have two important characteristics: a high equivalent functionality, greater than 2 (usually 3-8 hydroxyl groups/mole) and a short chain derived from one hydroxyl group of 1-2 propyleneoxide (PO) or ethyleneoxide (EO) units/ hydroxyl groups [4,12].

Mannich polyols are a new type of aminic polyethers polyols with aromatic structure, which give good thermal properties, fire resistance and superior physico-mechanical properties to the resulted rigid polyurethane foams [11,12].

These properties are explained by the low mobility and high thermostability of aromatic structures comparative with the aliphatic structures of conventional polyether polyols.

For the synthesis of Mannich polyols produced currently by different company like Dow Company and Hunstmann in USA, Synthesia in Spain, S.C.OLTCHIM in Romania the most used raw materials are phenol, para-nonylphenol, formaldehyde and diethanolamine. The starter with aromatic triazinic ring structure, like melamine, also leads to highly thermostable and high fire resistant rigid polyurethane foams [12,13].

Polyethers polyols are alkyleneoxide adducts of propyleneoxide and/or ethyleneoxide to polyfunctional compounds with active hydrogen atoms such as polyols (e.g. glycerol, sorbitol, sucrose etc.) or polyamines (ethylene diamine, diethylene triamine, toluene diamine etc.).

Mannich bases are condensation compounds of three components: a carbonylic compound, a primary or secondary amine and an organic compound with enolizable acidic hydrogen (phenols, ketones etc.) [14-17]. The Mannich bases can be used as starters for alkoxylation reactions with PO or EO leading to aminic polyether polyols, named "Mannich polyols".

Classical synthesis of Mannich polyethers polyols occurs by 3 steps [13]:

1. Synthesis of Mannich bases;
2. Anhydridization of Mannich bases;
3. Alkoxylation of Mannich bases.

The anhydridization of Mannich bases is an important part of conventional processes which leads unfortunately to secondary polycondensation by-products which increase the polyols viscosity and to a darkening effect of the final polyols.

A new method, more simple and rapid, based on oxazolidines chemistry was developed in the present paper for the synthesis of Mannich bases and

Mannich polyols, which leads to the same high yield products of low viscosity and improved color.

2. Experimental part

A new Mannich bases and Mannich polyether polyol with high aromaticity and high nitrogen content is obtained from propoxylated aniline as starter. The new process has the following important steps:

1. Synthesis of anhydrous oxazolidines;
2. Synthesis of Mannich bases;
3. Alkoxylation of Mannich bases.

Synthesis of Mannich bases takes place by simple addition of oxazolidine to the acidic component in different molar ratio depending on the expected functionality needed in order to obtain the final Mannich polyether polyols.

Mannich bases from propoxylated aniline and anhydrous oxazolidine in molar ratio 1 : 2 were synthesised at 80-90°C and alkoxylation with 2 moles of propyleneoxide at 90 -95°C, under nitrogen at 2.5 – 3 bars in 2-3 hours.

The reaction between oxazolidine and propoxylated aniline is practically quantitative (99.6 % yield) after 2 hours of reaction .

The resulted Mannich bases are viscous liquids at room temperature.

The Mannich bases derived from propoxylated aniline have hydroxyl index of 810 - 830 mgKOH/g and a viscosity of 10000 -15000 cP at 25°C .

The Mannich polyether polyol obtained by propoxylation of aniline based Mannich base has hydroxyl index in the range of 650 – 530 mgKOH/g, viscosity (at 25°C) of 1900 cP or less and a content of tertiary nitrogen of 6.8 %. Yield of propoxylation reaction is 99.85%

This polyether polyol was successfully used directly in rigid foams formulations without any supplementary purification.

3. Results and discussions

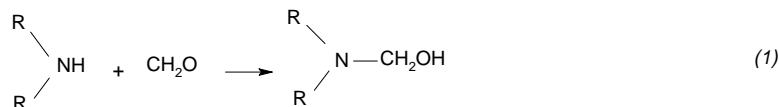
In the classical Mannich reaction the active species are immonium cations resulted by the reaction of formaldehyde (the most used carbonylic component) and a secondary amine as diethanolamine , the aminic component .

Immonium cation concentrations depend on reaction temperature, pH, and reaction time [17]. Increase of reaction temperature and acidic medium leads to increase of immonium cation concentrations and to high yield of products [17,18] .Each Mannich reaction has its optimal conditions of synthesis, depending also on the reactants structures.

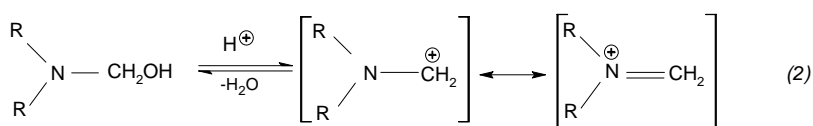
The mechanism of Mannich reaction accepted at this moment is the addition-elimination mechanism in the reaction of formaldehyde with secondary

amines (1) with the formation of an N-methylol amine derivative which give the very reactive intermediate of the reaction, the carbenium- immonium cation, in acidic medium, by water elimination [13,17], according to (2).

Addition reaction



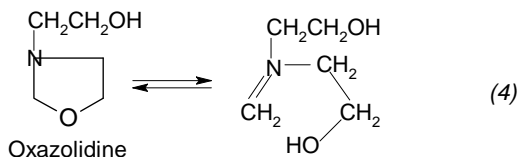
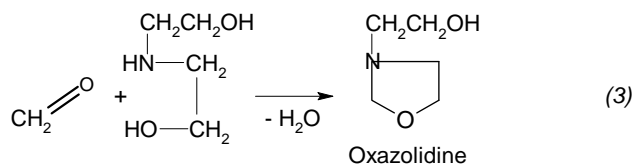
Elimination reaction



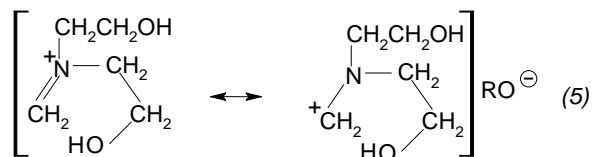
Carbenium-immonium cation

Immonium cation can react with a large number of acidic enolizable components to give Mannich bases, which can be alkoxyated (propoxyated or propoxyated and ethoxyated) thus leading to the Mannich polyether polyol.

The new method based on oxazolidine chemistry, involves the very reactive species of oxazolidines obtained by (3,4). The open chain structures of oxazolidines are extremely reactive species, having a similar structure with the immonium cations in classical Mannich reaction [13].



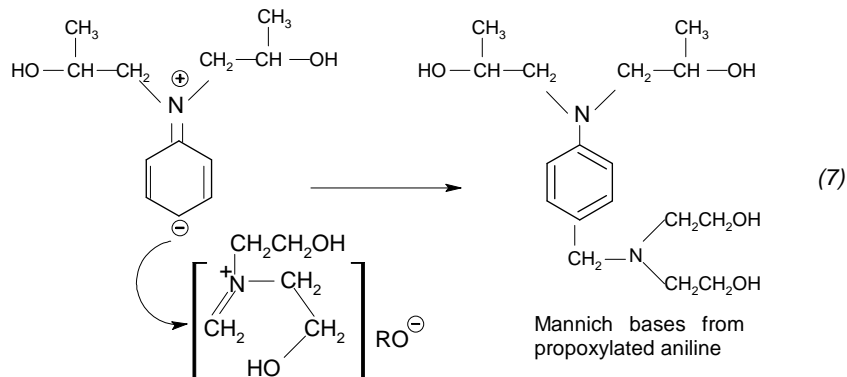
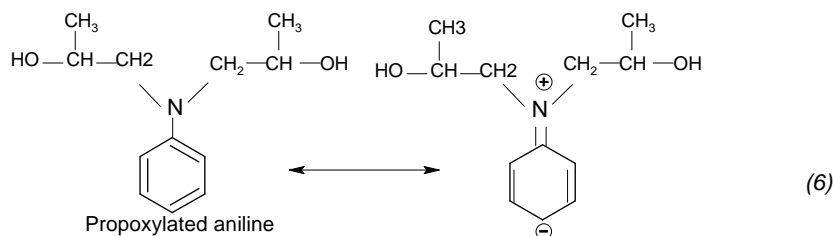
The open chain of oxazolidine (5) exhibits 2 mesomeric forms which are involved in Mannich bases synthesis as very reactive species which react with the acidic component [18,19]:



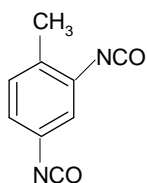
Oxazolidine is a low viscosity light yellow liquid, with the following characteristics: viscosity (at 25°C) = 25-35 cP; density: 1.12–1.13 g/cm³; refractive index (at 25°C) $n_D = 1.4765$; boiling point (at 60 mmHg) = 125–135°C.

IR spectrum of oxazolidine shows a strong absorption at 1650 cm⁻¹ (C=N imine group), proving the existence of the mentioned equilibrium between cyclic structure and open chain structure [20, 22, 23].

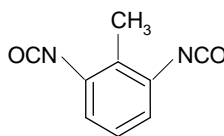
The proposed mechanism of the reaction of oxazolidines with propoxylated aniline is the following: the open chain mesomeric structures of oxazolidines react with a mesomeric form of acidic component to obtain Mannich bases (6,7).



The obtained Mannich bases can be used after the alkoxylation (propoxylation with 2 moles propylenoxide) as polyolic component in the reaction with isocyanates such as toluene diisocyanate (TDI) or especially diphenyl methane diisocyanate (MDI) to obtain rigid polyurethane foams with good physico-mechanical, thermal and fire resistant properties [13,14].

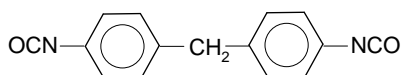


2,4 -Toluene diisocyanate



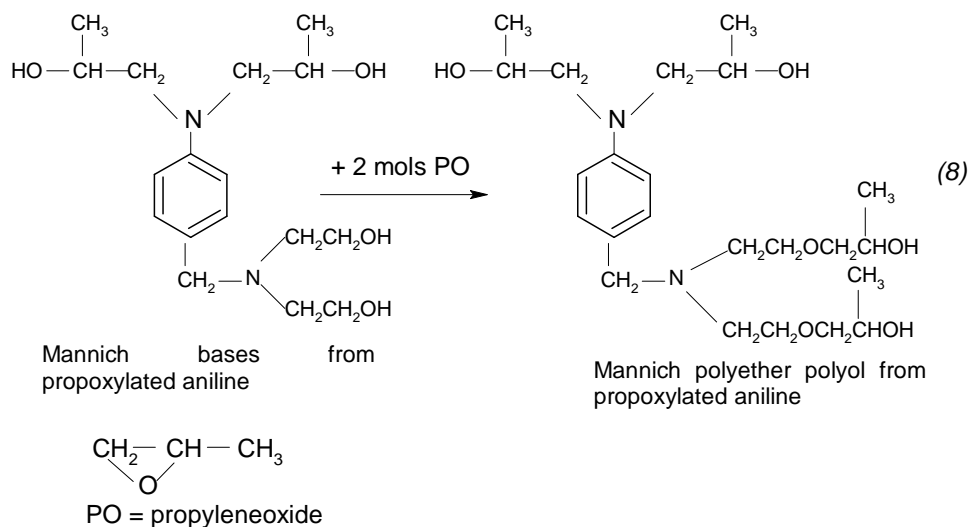
2,6 -Toluene diisocyanate

TDI = 80% 2,4 -Toluene diisocyanate + 20% 2,6 -Toluene diisocyanate



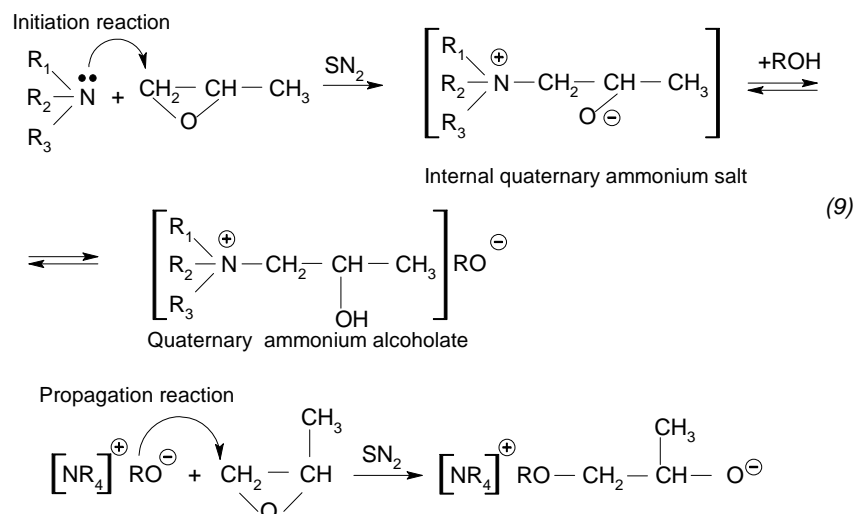
MDI = Diphenylmethane-4,4'-diisocyanate

Alkoxylation reaction of Mannich bases from propoxylated aniline (8) is a self catalytic reaction, due to the catalytic effect of the tertiary nitrogen atoms, which can open the oxiranic cycle by nucleophilic attack at less substituted carbon ($\text{S}_{\text{N}}2$ substitution), in the presence of hydroxylic groups [12,21].



This $\text{S}_{\text{N}}2$ type nucleophilic substitution reaction (9) is the main initiation reaction in case of tertiary amines used as alkoxylation catalysts.

The propagation reaction (10) is practically identical with the propagation reaction in the case of potassium alcoholate used in alkaline synthesis of polyether poyols. In fact the potassium ion is replaced by the quaternary ammonium cation [12,13].



After the addition of PO, the reaction mass is maintained 2 hours at 80-90°C for the consumption of the unreacted PO and finally is degassed by vacuum distillation, one hour at 90-100°C.

The synthesized aniline based Mannich polyol without any supplementary purification can be used directly in rigid foams formulations.

4. Conclusions

It was developed a new synthetic method for aromatic Mannich polyols based on oxazolidine chemistry which is possible to be applied to synthesise a large number of new Mannich polyols.

By the reaction of oxazolidines with various acidic compounds having different acidic bond C-H, N-H, O-H, P-H the Mannich bases are obtained which can be transformed in Mannich polyether polyol by alkoxylation with PO or EO.

It was successfully proved that by direct reaction of anhydrous oxazolidines with acidic enolizable compounds, the same Mannich bases with those obtained by classical Mannich reaction between acidic compounds, formaldehyde and diethanolamine are formed.

The Mannich polyether polyol synthesis by this method based on oxazolidine chemistry is very simple, rapid and reproducible leading to high quality aromatic polyols. By using this method Mannich polyols which do not need purification step are obtained, as compare with the regular polyether polyols technology (e.g. synthesis of sucrose polyols) which need the elimination of the alkaline catalyst in a complex purification step.

Due to the high content of tertiary nitrogen the Mannich polyols are extremily reactive in the foaming process. For this reason they can be used in combination with other polyether or polyester polyols in “spray” rigid polyurethane foams formulations, technology which needs very reactive polyols.

REFERENCES

- [1] *J.H.Saunders, K.C. Frisch*, Polyurethanes : Chemistry and Technology, Vol.1, John Wiley & Sons, Interscience, New York, 1962
- [2] *N.G.Gaylord*, Polyethers .Part I. Polyalkyleneoxides and other Polyethers, Wiley & Sons, Interscience, New York, 1963
- [3] *J.H.Saunders, K.C. Frisch*, Polyurethanes : Chemistry and Technology, Vol.2, John Wiley & Sons, Interscience, New York, 1964
- [4] *T.H.Ferrigno*, Rigid Plastics Foams, Second Edition, Reinhold Publishing Corp., New York, 1967
- [5] *J.M.Buist, H.Gudgeon*, Advances in Urethane Science & Technology, John Wiley & Sons, Interscience, New York, 1968
- [6] *P.F.Bruins*, Polyurethane Technology, John Wiley & Sons, Interscience, New York, 1969
- [7] *J.M.Buist*, Development in Polyurethanes, Vol.1, Applied Science, London, 1978
- [8] *G.Oertel*, Polyurethane Handbook, Hans, Munnich, 1985
- [9] *G.Woods*, The ICI Polyurethanes Book, John Wiley & Sons, Interscience, New York, 1987
- [10] *E.I.Goethls*, Telechelic Polymers. Synthesis and Applications, CRC Press 1989
- [11] *D.Klemper, K.C.Frisch*, Handbook of Polymeric Foams and Foam Technology, Hanser Publishers, 1991
- [12] *M.Ionescu, V.Zugravu, I.Mihalache, S.Mihai*, Advances in Urethane Science & Technology, Vol.14, Technomic Publishing Company, Inc., USA, 1998, p.151-217.
- [13] *M. Ionescu*, Chemistry and Technology of Polyols for Polyurethanes, RAPRA, Anglia, 2006
- [14] *B Reichert*, Die Mannich-Reaktion, Springer-Verlag, Berlin, 1959
- [15] *H Hellman, G Opitz*, Alfa-Amino-alkylierung, Verlag-Chemie, Weinheim, 1960
- [16] *M. Tramontini, L. Angiolini*, Mannich Bases – Chemistry and Uses, CRC Press, 1994
- [17] *H.Heaney*, Comprehensive Organic Chemistry, Vol.2, pag.893-980, Pergamon Press 1991
James B. Hendrickson, Donald Cram, George S. Hammond, Chimie organica, Editura Stiintifica si Enciclopedica, Bucuresti, 1976
- [18] *Heinz Becker, Werner Becker & colectiv*, Organicum - Chimie organica practica, Editura Stiintifica si Enciclopedica, Bucuresti, 1982
- [19] *Felicia Cornea*, Chimie Organica, Ed. Didactica si Pedagogica, Bucuresti, 1983
- [20] *Kurt C.Frish, Sidney L. Reegen*, Ring –Opening Polymerization, vol.2 of “ Kinetics and Mechanisms of Polymerization” M. Dekker, N.Y. 1969
- [21] *D.J.David, H.B. Staley*, Analitical Chemistry of the Polyurethanes, vol XVI, part III of “High Polymers”, Wiley- Interscience 1969
- [22] *I.Pogany; M.Banciu*, Metode fizice in chimia organica, Editura Stiintifica, Bucuresti 1972