

bis-Mannich Polyether Polyols with Aromatic Structures

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The paper presents the synthesis of bis-Mannich polyolic compounds with high aromatic content and thermostable structures. Synthesis of bis-Mannich polyolic bases was performed by the reaction of acidic substrates such as phenols with the Mannich precursor reagent, such as bis-1,3-oxazolidine derivate compound, followed by alkoxylation in the absence of a catalyst. Applications of these polyols are poured and "spray" rigid polyurethane foams synthesis with high thermostability and enhanced flame retardancy properties.

Keyword: N,N'-hydroxyethyl-bis-1,3-oxazolidine; bis-Mannich polyether polyols; rigid polyurethane foams

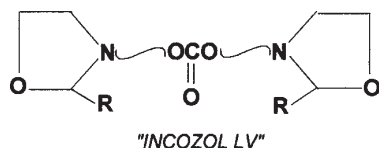
The demand for reducing volatile organic compounds ("VOC") in polyurethane foams, determine the research for synthesis of new reactive polyols with improved reactivity, removing partially or entirely quantity of specific amine catalysts of reaction between polyols and polyisocyanates [1-12].

The presence of cycloaliphatic and aromatic rings in the polyether polyols structures improves also, the chemical and physico-mechanical properties of rigid polyurethane foams, due to low mobility of rings and of high rigidity degree obtained.

Derivated compounds of 1,3-oxazolidines are utilized for polyurethane synthesis, with low VOC [13,14] for instance, for coatings, adhesives due to the fact that they improve reaction with polyisocyanates, reacting with residual water from polyurethane formulations [13,14] and eliminate formation of foam in a monocomponent system [14].

Incozol LV, a research product of Industrial Copolymers Ltd.[13], is a bis-1,3-oxazolidine, with two oxazolidine rings linked by a carbonate bridge, that can afford low viscosity by restricting intermolecular hydrogen bonding. *Incozol LV* can replace 1-30% polyol from 2-pack polyurethane coatings.

This product is activated during spraying application, by ring opening hydrolysis, as a result of reaction with low quantity of water present in polyolic components or atmospheric humidity, resulting two hydroxyl and two amino groups [13].



Due to these characteristics bis-1,3-oxazolidine derivate compounds can be used as Mannich precursor reagent for the synthesis of polyethers polyols with bis-Mannich structure or mixed with Mannich polyether polyols.

The autocatalytic reactivity due to tertiary nitrogen content of bis-Mannich polyethers polyols with aromatic structures enables green technology applications.

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Mannich polyols can be obtained, by classical Mannich reactions or using a preformed Mannich reagent and different acid substrats [8,9,11,14-16].

This paper presents the synthesis of a bis-Mannich polyols by a new method, based on the utilization of a Mannich precursor reagent such as N,N'-hydroxyethyl-bis-1,3-oxazolidine.

Experimental part

Materials

Reagents were utilized without further purification.

Diethanolamine (Fluka), purity > 98.2%; water content 1.5% (Karl-Fisher method)

Glyoxal (Merck): Glyoxalhydrat trimer, 80% glyoxal content.

Phenol (Fluka): 99.9% content.

Para-nonylphenol (Fluka): 98.7% content;

Propyleneoxide (PO): donated by S.C.Oltchim S.A.Romania; 99.2 % content

Synthesis of N-hydroxyethyl-bis-1,3-oxazolidine, the Mannich reagent precursor and synthesis of Mannich base was performed in a one litre four-neck angled round-bottom flask with stirrer, thermometer, dropping funnel and condenser.

Synthesis of N-substituted-bis-1,3-oxazolidine (Mannich reagent precursor)

A mixture of N,N'-hydroxyethyl-1,3-bis-oxazolidine and water was obtained (*1*) from 2 mols of diethanolamine with 1 mol of glyoxal at 65°C during 1-2 h. Bis-1,3-oxazolidine compound was anhydridized by vacuum distillation, 1-2 h at 80-95°C and 15-20 mmHg until content of water decreases to 1.5-2% .

Synthesis of Mannich base and Mannich polyether polyols with aromatic structure

At 2 mols phenol (or *para*-nonylphenol) at 45-50°C , was added under stirring 1 mol N-hydroxyethyl-bis-1,3-oxazolidine (*2*) with 1,5% water content. Reaction is slightly exotherm. Reaction was conducted in the absence of a solvent. After that the whole quantity of bis-1,3-oxazolidine was added, the temperature was increased to 105-120°C and maintained for 1 h under stirring.

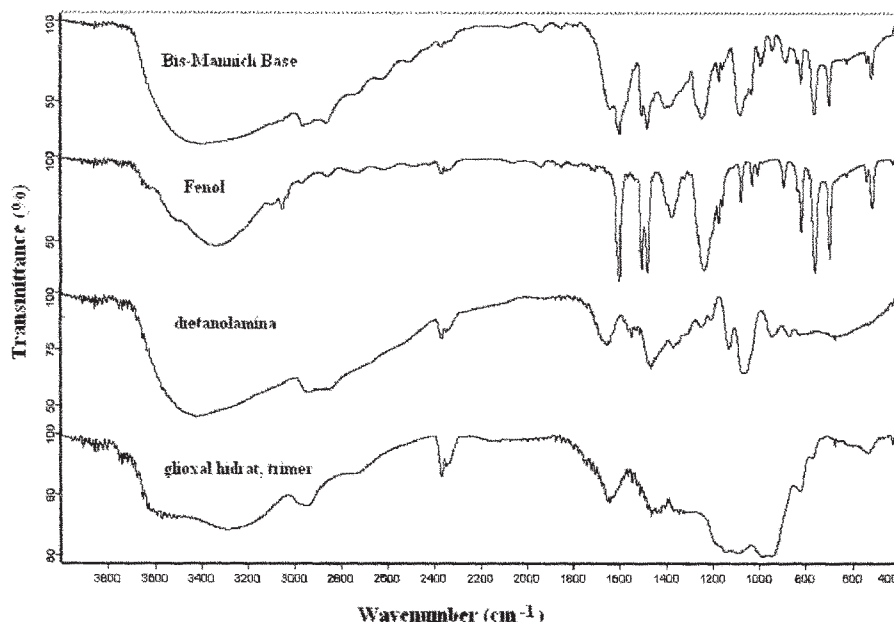


Fig.1. IR Spectrum of bis-Mannich base polyol on phenol based, as acid substrat compared with IR spectrum of raw materials

Reaction is practically quantitative (99.2% yield) after 2 h. It was observed the increasing of viscosity after mass cooling. The resulted product, bis-Mannich base from phenol, is a viscous, brown-amber liquid, with high functionality equal to 6.

Bis-Mannich polyether polyol based on phenol was obtained (3) in molar ratio 1:6 bis-Mannich base / propyleneoxide (PO) in a stainless steel pressure reactor, at a low alkoxylation temperature 80-90°C and a pressure of 1-1,5 bars, under nitrogen atmosphere, during 2-3 h. The reaction is autocatalytic, due to tertiary nitrogen atoms.

After the addition of PO, the reaction mass is maintained 1 h at 90-95°C for the consumption of the unreacted PO, than degassed by vacuum distillation.

Characterisation of synthesised compounds

Characterisation of synthesised compounds was accomplished by determination of characteristics useful for reaction with polyisocyanates, such as hydroxyl number, basicity of polyols as amine equivalent, viscosity, water content [20-26]. It was also determined IR spectrum (fig.1) of raw materials, of Mannich reagent precursor bis-1,3-oxazolidine and of bis-Mannich base polyols [20-22]. IR spectrum was performed with spectrophotometer FT-IR BRUCKER TENSOR 37. Tests are performed in KBr tablets and film.

IR Spectrum of bis-Mannich base polyol based on phenol, shows a strong absorption at 1030 cm^{-1} (-OH hydroxyl groups), proving the existence of the high functionality and absorption at 1594 cm^{-1} due to benzenic rings, which give high aromaticity of compound. Also it was observed that absorption peak associated with C=O carbonilique bonds from glyoxal at 1650-1800 cm^{-1} , does not appear.

The aspect and colour of synthesised compounds were visually determined.

Hydroxyl numbers of polyols were determined by volumetric method [12,15] according to PURMAC [20-23] by esterification of hydroxyl groups with a solution of phthalique anhydride in pyridine, 1 hat 115 \pm 2°C. Excess of phthalique anhydride was titrated with a sodium hydroxide solution 0.5 N in the the presence of phenolphthaleine 1% in pyridine, as reaction indicator. It was also performed a blank.

Determination of Mannich bases viscosity was performed with a rheo-viscosimeter Höppler, balance type in the field 1000-100000 cP, at 25°C [20,22,24].

Basicity of Mannich polyols as amine equivalent, was determined by volumetric methode, by titration of sample dissolved in acid acetique with 0.1 N solution of perchloric acid in acid acetique, in presence of crystal violet as indicator, until colour turn from blue-mauve to green [20,22,25]. It was also performed a blank.

Water content of Mannich bases was determined by Karl-Fisher method, using automatic Mettler titrator. The titration of Mannich bases was performed in the presence of acid acetique glacial, due to aminique character of compounds. It was also performed a blank [20,22,26].

Results and discutions

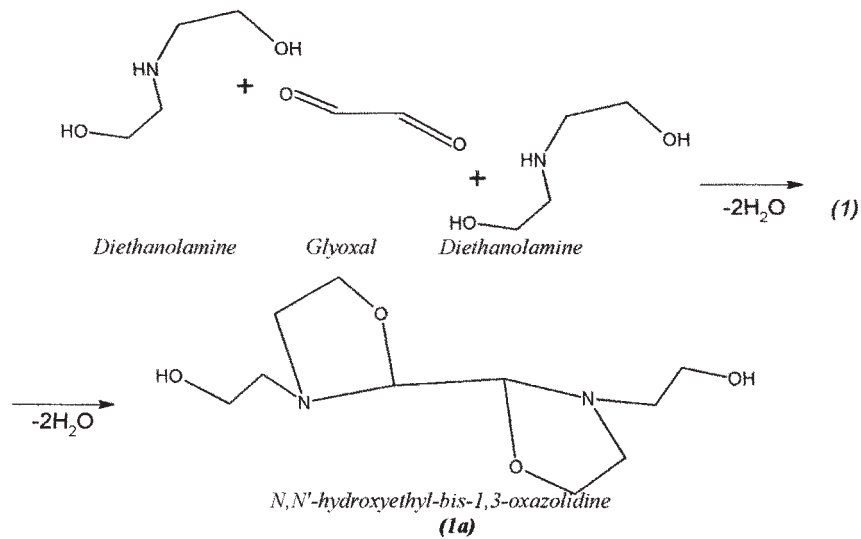
Utilisation of glyoxal as carbonilique compound in Mannich bases synthesis has the advantage of low toxicity comparative with formaldehyde. Glyoxal is readily biodegradable 82% being eliminated after 6 days [27].

Bis-Mannich polyether polyol based on phenols has characteristics that show that it can be utilized for rigid polyurethanes as sole polyolic compound or in mixture with other polyolic, polyether or polyester polyols. Hydroxyl index is in the range of 330 - 550 mg KOH/g and viscosity, at 25°C in the range of 800-14000 cP (table 1).

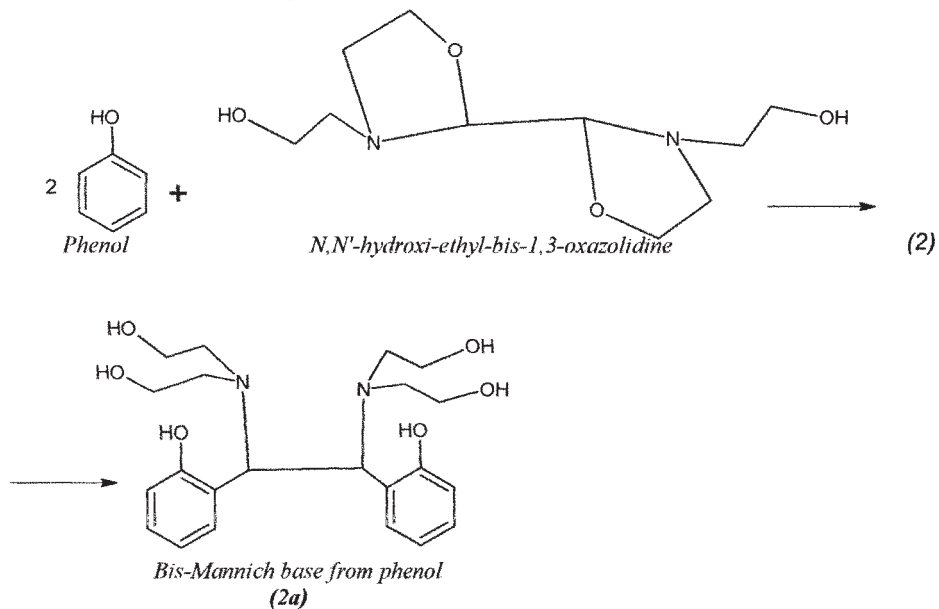
Table 1
CHARACTERISTICS OF bis-MANNICH POLYETHER POLYOL BASED ON PHENOL OR para-NONYLPHENOL

Characteristics	Bis-Mannich polyol based on phenol	Bis-Mannich polyol based on para-nonylphenol
Hydroxyl index,mg KOH/g	514.87	394,5
Viscosity,25°C,cP	9808	12989
Content of amine,%	0.268	0.223
Water content,%	1.2	1.1

Synthesis of *N,N'*-hydroxyethyl-bis-1,3-oxazolidine



Synthesis of bis-Mannich base from phenol



The bis-Mannich polyether polyols obtained from phenol has high functionality equal to 6, and a high aromaticity 19.2%.

Synthesis of bis-Mannich polyether polyol with high aromatic content

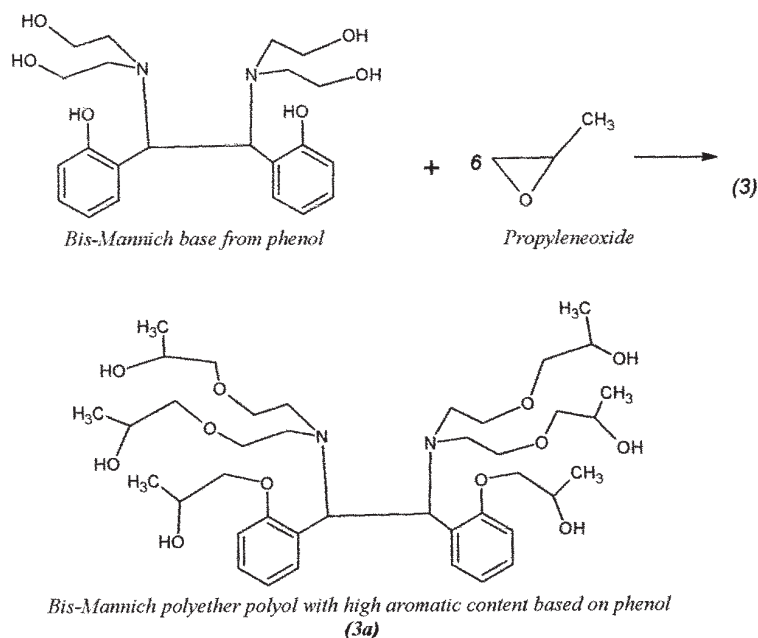


Table 2
CHARACTERISTICS OF POLYURETHANE FOAMS OBTAINED WITH DIFFERENT FORMULATIONS WITH *bis*-MANNICH POLYETHER POLYOLS

Characteristics	UM	1	2	3	4
Sucrose based polyether polyol	p.g	75	75	50	50
PM I – S3 (Phenol)	p.g	25	-	50	-
PM II- S4 (<i>para</i> -Nonylphenol)	p.g	-	25	-	50
Water	p.g	6	6	-	-
HCFC 141b	p.g	-	-	22	22
TCPP	p.g	12	12	15	15
Silicon 8433	p.g	1.7	1.7	-	-
Silicon 8461	p.g	-	-	1.5	1.5
DMAE	p.g	0.2	0.2	-	-
Dabco 33LV	p.g	0.15	0.15	-	-
DMCHA	p.g	-	-	1.25	1.25
T12	p.g	-	-	0.06	0.06
MDI Index	-	105	105	115	115
Cream time	Sec	21	23	10	10
Gel time	Sec	81	89	23	28
Rise time	Sec	109	116	31	38
Physico-mechanical					
Density	Kg/m ³	25.77	25.44	35.6	41.41
Compression strength	kPa	155	145	188	282
Tensile strength	kPa	191	183	-	-
Flexural strength	kPa	180	240	300	266
Dimensional Stability: 24h / 100 °C	% vol	-0.62	-0.61	-	-
24 h / 80 °C	%vol	-0.70	-1.07	-0.53	-1.27
24 h / -29°C	% vol	-	-	-0.87	+0.4
Flameproofing properties					
- length burn	mm	57	70	35	42
- selfextinguishing time	sec	45	55	60	50

Due to tertiary nitrogen atoms, bis-Mannich polyether polyols are sufficiently reactive to react with isocyanates without amine catalysts or in very small quantities [9-12,16-21].

Mannich polyether polyols can be used as single polyolic compound or mixed with other polyether polyols with low viscosity or other Mannich polyether or polyester polyols [20, 21].

Bis-Mannich polyether polyol based on phenol was tested for rigid polyurethane foam synthesis, by pouring and spraying technique.

Characteristics of polyurethane foams obtained with bis-Mannich polyether polyols mixed with a sucrose Mannich polyether polyol are presented in table 2.

For pouring formulations (exp.1;2) it can be observed a good dimensional stability of foams due to high aromatic contents. In case of spraying formulations (exp.3;4) can observe a good dimensional stability even at low temperature (-) 29°C.

Both pouring and spraying formulations improve flameproofing properties of polyurethane foams, thermostability, due to aromatic character of polyols which gives low mobility structures of polymeric chain, high rigidity and high char yield generated during the burning process.

In case of spraying formulations (exp.3,4) it can be observed better flameproofing properties of polyurethane foams, respectively a smaller burn length than for pouring formulations, so we can conclude that this type

of polyol Mannich can be used with good results in spraying formulations.

Conclusions

By akoxylation of bis-Mannich base synthesised from a Mannich reagent precursor such as N,N'-substituted bis-1,3-oxazolidine derivatives and phenols, it was obtained bis-Mannich polyether polyols with high aromatic structure and high functionality. Utilisation of tailored structures of Mannich reagent precursor, allows to obtain bis-Mannich base and polyether polyols with high aromaticity and high reactivity in the foaming process.

The resulted Mannich base and Mannich polyether polyol have autocatalytic properties due to the aminic tertiary nitrogen content and were tested in foaming process. This improved reactivity of polyolic compound allows to reduce VOC emission from polyurethane foams by elimination the major quantity of tertiary amine catalyst used in formulations of PU foams.

The advantage of those bis-Mannich structures is that due to the presence of high aromatic content, the rigid polyurethane foams obtained with this bis-Mannich polyols has higher physico-mechanical properties, thermostability and enhanced flame resistance relative to those based on classical aliphatic polyether polyols.

The synthesized Mannich polyols can be used for rigid polyurethane foams synthesis, without any purification and are recommended to be used for "spray" rigid polyurethane foam formulations.

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