

Synthesis of *s*-Triazine Polyetherols from Bis(methoxymethyl)melamine and Oxiranes

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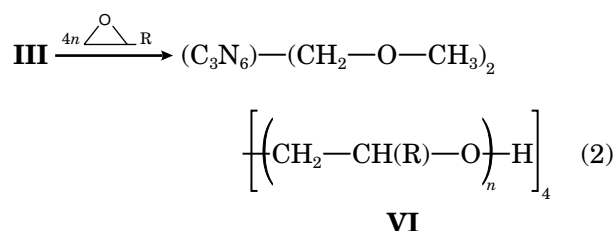
ABSTRACT: Polyetherols containing *s*-triazine rings can be obtained in reactions of oxiranes with melamine derivatives. A report on the attempt to replace pentakis(methoxymethyl)melamine with bis(methoxymethyl)melamine in the synthesis is presented. The replacement simplified the procedure by eliminating the stage of transesterification with ethylene glycol. The oxirane addition was carried out without a solvent. The course of the reaction was studied and some properties of the resulting polyetherols determined. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 423–433, 1997

INTRODUCTION

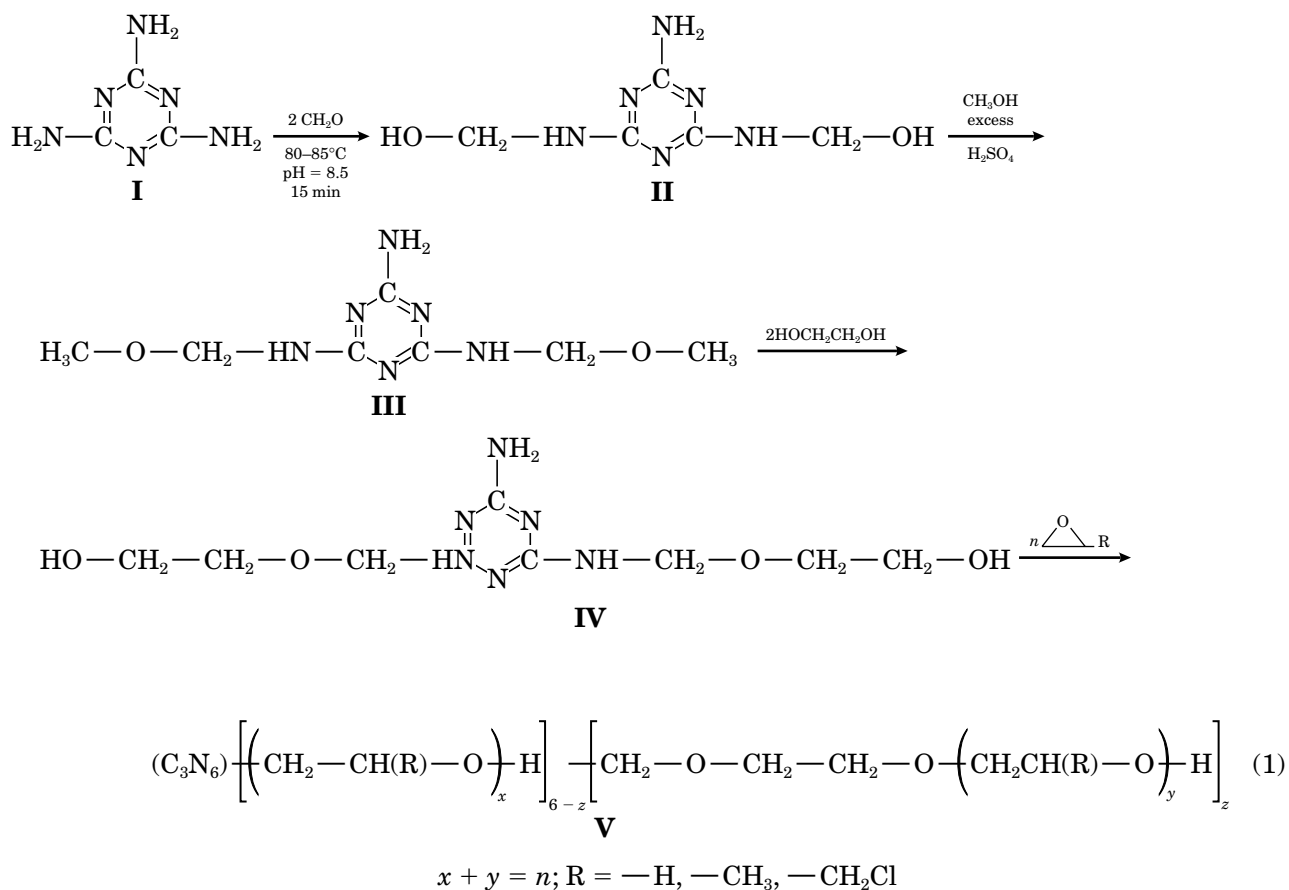
In the reactions of melamine and some of its derivatives with an excess of oxiranes, such as ethylene (EO) or propylene oxide (PO), one obtains polyetherols containing *s*-triazine rings.^{1–4} The polyetherols react with typical polyisocyanates and water to yield polyurethane foams of improved thermal stability.⁵ The known methods of synthesis of *s*-triazine polyetherol require application of harmful solvents, such as dimethylformamide or dimethyl sulfoxide, which have to be distilled off after completing the reaction. It is therefore of interest to seek different methods of synthesis, such as the one where a melamine derivative is directly dissolved in oxirane before it reacts. This approach has been already presented⁶ for the system consisting of *N,N,N',N',N''*-pentakis(methoxymethyl)melamine (PMMM), ethylene glycol (EG), and EO or PO. Although simple, the latter method had serious disadvantages. Among them were the necessity of carrying out the reaction in several stages and the poor quality of the resulting products contaminated with unreacted substrates (PMMM, EG). The main problem was that the reaction could not be carried out to completion in one of the stages due to crosslinking of the products.

The crosslinking problem could be avoided if another melamine derivative were used instead of PMMM. Thus, following the same procedure,⁶ bis(hydroxymethyl)melamine (BHMM) was obtained. Then, it was converted into bis(methoxymethyl)melamine (BMMM) with methanol and the product reacted with ethylene glycol and, finally, with oxirane, according to Scheme 1.

The stage involving transesterification of BMMM with ethylene glycol was also expected to be avoidable, since, instead of dissolving the transesterification product in oxirane, BMMM could directly be used (PMMM was soluble in oxiranes). Tetrafunctional polyetherols could then be obtained by addition of amino groups, rather than by hydroxyethyl ones to oxiranes (the same route was not possible for the monofunctional PMMM):



The synthesis of polyetherols would then simplify to the following stages: (i) synthesis of BHMM, (ii) its etherification with methanol, and (iii) the reaction with oxiranes. In this article, we



Scheme 1

report on the results of our work on the proposed route.

EXPERIMENTAL

Syntheses

Preparation of BHMM

BHMM was obtained in the reaction of melamine (pure, Kędzierzyn Nitrogen Plants, Poland) with the appropriate amount of formalin (pure, 36.3 wt % of CH_2O), Tarnów Nitrogen Plants, Poland) according to the procedure described in Ref. 7.

Preparation of BMMM

BHMM 279 g (1.5 mol), 1215 mL (30 mol) of methanol (pure, POCh, Poland), and 1.5 mL of H_2SO_4 (98%) was placed in a 2 L three-neck round-bottom flask equipped with a condenser, stirrer, and thermometer. The content was kept boiling (62–70°C) until all BHMM had dissolved (about 1 h) and for an additional 30 min. Then,

the mixture was cooled and neutralized with 10% aqueous NaOH; the precipitate of sodium sulfate was filtered out and the excess of methanol and water distilled off in a rotary evaporator at below 70°C (under 2.7 kPa).

Other procedures were also tested including further etherification of the compound obtained as described above with a 15-fold excess of methanol. A variation of the procedure with successive removal of water as an azeotrope with chloroform was also tested.

Transesterification of BMMM with Ethylene Glycol

BMMM 42.8 g (0.2 mol), 24.8 g (0.4 mol) of EG (pure, POCh), and 100 mL of heptane (for azeotropic removal of methanol) were introduced into a 250 mL three-neck round-bottom flask equipped with a Dean-Stark separator, stirrer, and thermometer. The mixture was kept boiling (95–100°C) until the stoichiometric amount of methanol was collected in the Dean-Stark separator. Practically, the reaction was stopped when the amount of methanol in the separator did not

change for a 0.5 h. The excess of heptane was distilled off in a rotary evaporator at below 80°C (under 2.7 kPa).

Reaction of BMMM with Glycerin Epichlorohydrine (ECH)

BMMM, 21.4 g (0.1 mol), and 37 g (0.4 mol) of ECH (reagent grade, Fluka, Switzerland) were placed in a 250 mL three-neck round-bottom flask equipped with a condenser, stirrer, and thermometer. The mixture was heated to 70°C to dissolve BMMM and then kept at 80–90°C until the epoxy number of the mixture dropped down to the predetermined value. In other experiments, the molar ratio of BMMM : ECH was 1 : 6, 1 : 8, or 1 : 12.

Reaction of BMMM with ECH and PO

The reaction of BMMM with ECH at the molar ratio 1 : 4 was carried out as described above. Then, 2 mL of triethylamine (TEA, reagent grade, Fluka) were introduced to the product (catalyst) and PO (reagent grade, Fluka) added through the condenser in such portions that the reaction temperature remained at 60–80°C. The extent of reaction was controlled by measuring the epoxy number and the total weight of the system.

Reaction of BMMM with ECH and EO

The reaction of BMMM with ECH at the molar ratio 1 : 4 was carried out as in the subsection reaction of BMMM with ECH. The product was then placed in an autoclave equipped with heating-cooling jacket and stirrer and EO (reagent grade, Fluka) was added in the amount so that the molar ratios of BMMM : ECH : EO were 1 : 4 : > 4. The autoclave was then sealed and heated to 80–100°C. The pressure was increased to ca. 0.6 MPa (at BMMM : ECH : EO = 1 : 4 : 6). The extent of the reaction was monitored following the reduction of pressure inside the reactor.

Reaction of BMMM with PO

BMMM, 107 g (0.5 mol), 5 mL of triethylamine, and 522 g (9 mol) of PO were introduced to the autoclave. The reactor was sealed and heated to 80–100°C. The extent of the reaction was controlled as in the preceding subsection.

Analytical methods

The content of hydroxymethyl groups in BHMM and BMMM was determined iodometrically,⁸ whereas the total content of formaldehyde, by

applying the method with phosphoric(V) acid.⁸ The content of the methoxy group was determined by using phthalic anhydride.⁸ The epoxy number was determined by titrating the sample with hydrochloric acid in dioxane.⁹ ¹H-NMR spectra of the semiproducts and polyetherols in *d*₆-DMSO solutions were recorded on an 80 MHz BS-487 spectrometer (Tesla, Czechoslovakia) with hexamethyldisiloxane as the internal standard. IR spectra were recorded on a Paragon 1000 spectrometer (Perkin-Elmer).

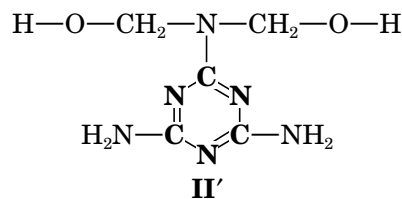
The Course of Reaction

The course of the reaction between BMMM and oxiranes was studied at 70, 80, and 90°C for ECH as an example. A fourfold or eightfold excess of this oxirane was used with respect to the melamine derivative. The content of epoxy groups was measured as it changed during the reaction. ¹H-NMR spectra of the reaction products were also examined for the molar ratios BMMM : ECH from 1 : 1 to 1 : 12.

RESULTS AND DISCUSSION

Semiproducts

BHMM was obtained in a simple reaction between 1 mol of melamine and 2 mol of formaldehyde. Formally, it is a mixture of two structural isomers: *N,N'*-bis(hydroxymethyl)-melamine (**II**) and *N,N*-bis(hydroxymethyl)melamine (**II'**):



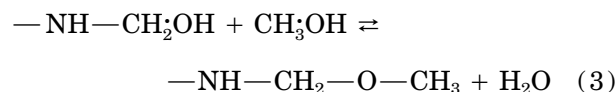
The structure was confirmed by the ¹H-NMR spectrum of the product (Table I), where, beside the signal from methylene group protons in —NH—CH₂—OH moiety at 4.80 ppm, there was another one at 5.00 ppm from two methylene groups at one nitrogen.¹⁰ The ratio of isomers calculated by integrating respective signals was found to be (**II**) : (**II'**) = 4 : 1.¹¹

As shown in Ref. 7, direct modification of BHMM with oxiranes was impossible because of the condensation of hydroxymethyl and amino groups, leading to crosslinked products. To avoid condensa-

Table I Chemical Shifts for Protons of Functional Groups in the Products and Semiproducts of the Reaction Between BMMM and Oxiranes

Compound	Substituent	Chemical Shift δ (ppm)	Reference
BHMM	CH ₂ O (free)	8.05	4
	—NH—CH ₂ —OH	7.3–7.5	10
	—NH ₂	6.3–6.5	10
	—OH	5.3–5.7	11
	—N(—CH ₂ —OH) ₂	5.0–5.2	10,11
	—NH—CH ₂ —OH	4.9–4.8	10,11
BMMM	CH ₂ O (free)	8.05	4
	—NH—CH ₂ —OCH ₃	7.3–7.5	7
	—NH ₂	6.1	7
	—NH—CH ₂ —OCH ₃	5.0	7
	—OCH ₃	3.2	7
Polyetherols	—C—H prepared with ECH and PO	3.8	12
	—CH ₂ —Cl	3.55	To be published
	—CH ₂ — PO addition	3.3	12
	—(CH ₂) ₂ — EO addition	3.3–3.4	12
	—CH ₃	1.1	12

tion, it was necessary to block hydroxymethyl groups with methanol and use the remaining amino groups to react with oxiranes. The etherification was carried out in the presence of a catalytic amount of sulfuric acid with a large excess of methanol which helped to shift the equilibrium



to the right.

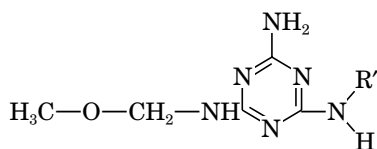
In several attempts of simplifying the synthesis of BMMM (Table II), it was found that hydroxymethylation could not be combined with etherification since, then, melamine did not react with

formaldehyde. Without success were also the attempts of avoiding isolation of BHMM from its reaction medium or at least drying it before etherification. Even with a huge excess of methanol (several tens of moles per mole of BHMM), only about one-half of hydroxymethyl groups entered the reaction. On the other hand, by dissolving the isolated from reaction mixture and the dry BHMM in methanol, one obtains after distilling off the excess of methanol a product containing a relatively small proportion of unblocked hydroxymethyl groups.

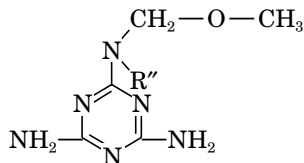
Direct analysis revealed that the product obtained within 1 h with a 30-fold molar excess of methanol contained 25.8 wt % of —OCH₃ and 6.1 wt % of —CH₂OH groups. The structure of the BMMM semiproduct can thus be expected to be

Table II Content of Methoxy Groups and Formaldehyde in BMMM Prepared in Different Ways

Preparation Conditions	—OCH ₃ Content (wt %)	Formaldehyde Content (wt %)	
		as —CH ₂ OH	Total
Once methoxylated	25.8	6.1	6.1
Twice methoxylated	29.2	5.4	9.7
Azeotropic water removal	21.3	2.5	6.8



VII



VII'

$$R' = \left[\text{CH}_2\text{-OH} \right]_{n'} \left[\text{CH}_2\text{-O-CH}_3 \right]_{m'} \quad n' + n'' = n$$

$$R'' = \left[\text{CH}_2\text{-OH} \right]_{n''} \left[\text{CH}_2\text{-O-CH}_3 \right]_{m''} \quad m' + m'' = m$$

The values of n and m as well as the molar mass of semiproduct (M) can be calculated from the set of equations

$$\begin{aligned} n + m &= 1 \\ \frac{30n}{M} \cdot 100\% &= p_{\text{CH}_2\text{O}} \\ \frac{31(n+1)}{M} \cdot 100\% &= p_{\text{OCH}_3} \end{aligned}$$

where $p_{\text{CH}_2\text{O}}$ and p_{OCH_3} are the percentages of hydroxymethyl and methoxymethyl groups in BMMM, respectively. Thus, in the present example, the calculations yielded $n = 0.47$ and $m = 0.53$. About 0.5 mol of unreacted hydroxymethyl groups remained in the product. Further heating of the product with methanol favored condensation of hydroxymethyl groups as can be found by the analysis of total formaldehyde content [by the phosphoric(V) acid method].

The attempts of increasing the yield of etherification by adding another etherification step, i.e., isolation of the product following by repeating the whole procedure, or by azeotropic removal of water (by using chloroform) did not increase satisfactory the yield of etherification (Table II). During the repeated etherification, the content of hydroxymethyl groups indeed decreased, but at the same time, the amount of dimethylether bridges increased (signal at 4.4 ppm in the $^1\text{H-NMR}$ spectrum). Furthermore, the isolated product still contained unblocked hydroxymethyl groups.

Polyetherols

The product of BMMM methoxylation obtained with a 30-fold excess of methanol was a solid resin which did not dissolve in EO or PO at room temperature. Because of the low boiling points of EO (14°C) and PO (34°C), it was therefore necessary to carry out the reaction in an autoclave. In further experiments, the system was modified to obtain homogeneous mixtures of reagents at room temperature. Initially, it was expected that, similarly as for PMMM, the transesterification with ethylene glycol should provide a product better soluble in oxiranes than in BMMM. It turned out, however, that the resulting product was still insoluble in oxiranes and, by judging from the presence of a signal in $^1\text{H-NMR}$ spectrum at 4.4 ppm, condensation took place during transesterification.

Epichlorohydrin (bp 116°C) was therefore used as the solvent of BMMM. This choice was successful; BMMM dissolved in ECH at 70°C and the resulting product was a dark brown resin soluble in water. Equally well behaved were the systems where 4 mol of ECH were added to 1 mol of BMMM at 70–80°C and then PO was added at 50–60°C. Fragments originating from both oxiranes were found in the final products (Table III). The synthesis of polyetherols with PO carried out at 70–80°C in an autoclave was also successful. A product was obtained in which the molar ratio of BMMM to PO was 1 : 18. The attempts of using EO at the same conditions failed. The reaction product was a brittle gel.

To obtain an inaccessible product directly with primary hydroxy groups, EO was reacted with the product of reaction of 1 mol of BMMM with 4 mol of ECH. In this reaction, carried out in an autoclave, a polyetherol was obtained in which the molar ratio was BMMM : ECH : EO = 1 : 4 : 6 (Table III). To conclude, it is worth pointing out that the reactions of BMMM with ECH and PO were carried out without a catalyst, whereas in the addition with PO, a triethylamine catalyst was used.

Selected physical properties of the polyetherols such as viscosity, density, surface tension, and refractive index were determined. The results are presented in Table IV in the form of equations relating these quantities to temperature. At room temperature, the polyetherols were thick liquids (10000–30000 cP) of density ranging from 1.05 to 1.34 g/cm³ and of surface tension 28–40 N/m. Some of them (e.g., BMMM : ECH : PO = 1 : 4 : 4; BMMM : ECH : EO = 1 : 4 : 6, and BMMM :

Table III The Stages and Conditions of Polyetherol Synthesis

	Stage	Temperature at °C		Reaction Time (h)	Catalyst	Solvent	pH	Isolation Method	Properties ^a
		Start	End						
I	BHMM synthesis	80	85	0.25		H ₂ O	8.5	Cooling and filtering	Solid; CH ₂ O (wt %): 32.8 detd, 32.3 calcd
II	Methoxylation of HM groups	62	70	1.5	H ₂ SO ₄ (98%)	30-fold CH ₃ OH excess		Distillation off CH ₃ OH under red. pressure	Hard resin; CH ₂ O (wt %): 6.1 detd, —OCH ₃ (wt %): 25.8 detd
III	ECH addition 6 mol	70	80	18					Brown resin
	ECH addition 8 mol	70	90	20					As above
	ECH addition 12 mol	70	90	45					As above
	ECH (4 mol) and PO (4 mol) addition	70	80	16					As above
		60	70	50	TEA			Distillation off TEA	
	ECH (4 mol) and PO (6 mol) addition	70	80	16					As above
	80	100	36						
	80	100	40	TEA			Distillation off TEA	As above	

^a detd = determined; calcd = calculated.

Table IV Temperature Dependence of Some Properties of Polyetherols Prepared from BMMM and Oxiranes (*T* in Centigrade)

Molar Ratios	Property												Temperature Range (°C)
	Refractive index, <i>n</i>			Density, <i>d</i> (g/cm ³)			Viscosity, $\eta \cdot 10^3$ (sPa)			Surface tension, $\tau \cdot 10^3$ (N/m)			
	Equation			Equation			Equation			Equation			
	$n = aT + b$			$d = aT + b$			$\eta = AT^{-a}$			$\tau = aT + b$			
	$a \cdot 10^4$	<i>b</i>	<i>r</i> ^a	$a \cdot 10^4$	<i>b</i>	<i>r</i> ^a	<i>A</i>	<i>a</i>	<i>r</i> ^a	<i>a</i>	<i>b</i>	<i>r</i> ^a	
BMMM : ECH = 1 : 8	-3.180	1.5446	1.000	-7.20	1.3748	0.996	$1.75 \cdot 10^{12}$	4.80	0.999	-0.0954	35.7	0.991	30-80
BMMM : ECH = 1 : 12	-3.680	1.5347	0.993	-8.08	1.3774	1.000	$7.01 \cdot 10^{10}$	4.22	1.000	-0.127	38.6	0.993	30-80
BMMM : ECH : PO = 1 : 4 : 4	-3.010	1.5317	0.999	-7.20	1.2469	0.999	$2.27 \cdot 10^{15}$	6.06	1.000	-0.0452	30.9	0.994	40-80
BMMM : ECH : EO = 1 : 4 : 6	-3.229	1.5219	1.000	-7.09	1.2809	1.000	$1.35 \cdot 10^9$	3.46	0.998	-0.0449	41.5	0.996	20-80
BMMM : PO = 1 : 18	-3.768	1.4840	1.000	-7.26	1.0721	0.999	$4.91 \cdot 10^7$	2.78	0.999	-0.0998	29.5	0.946	20-80

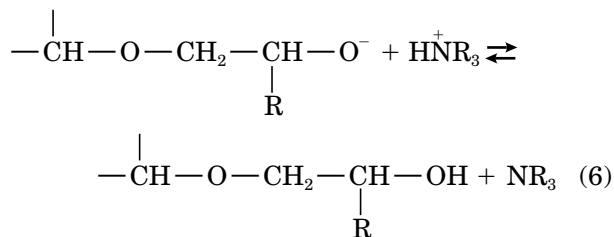
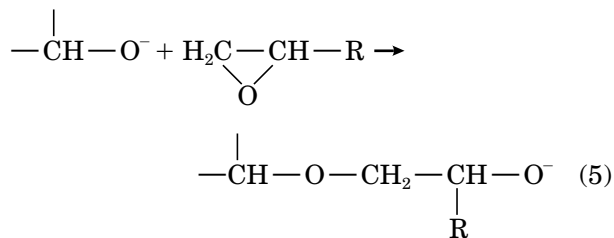
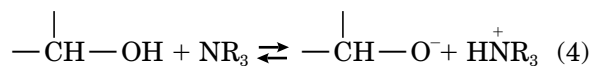
^a Correlation coefficient.

PO = 1 : 18) easily mixed with diisocyanates and water to give thermally stable foams. Detailed results on the properties of the polyetherols will be published separately.

The Course of Reaction

As follows from the results presented above, one can obtain *s*-triazine polyetherols in reactions of BMMM with oxiranes provided that the melamine derivative is dissolved in the oxirane. This requirement reduces the possibility of studying the reaction under normal pressure to the system BMMM–ECH. Therefore, this reaction was studied without any solvent at 70–90°C and at the molar ratio BMMM : ECH = 1 : 4 and 1 : 8. The rate of reaction was measured by monitoring the decrease in the relative concentration of oxirane in the reaction mixture defined as $\beta = c/c_0$, where c and c_0 are the actual and initial concentration of oxirane, respectively.

A small amount of TEA often used as a catalyst of oxirane reactions added at the beginning was found in this case to hinder the process (Fig. 1). Its activity relies on the subtraction of mobile protons from hydroxy groups and the formation of an anion which then reacts with oxirane¹³:



In the system BMMM–ECH (the latter used with a small excess), TEA does not act as a catalyst since it does not affect hydrogens of amino groups in BMMM; no equilibrium represented by the equation

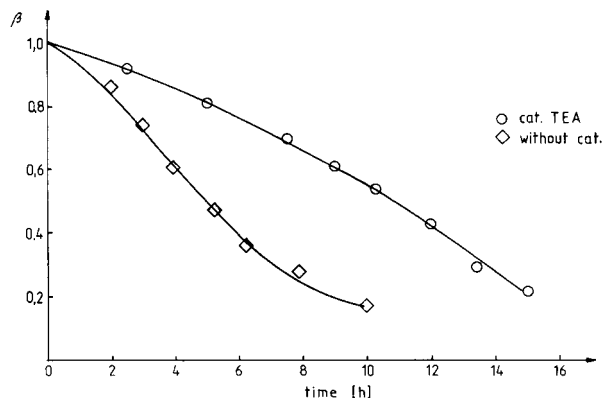
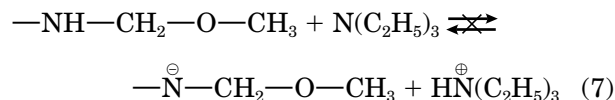
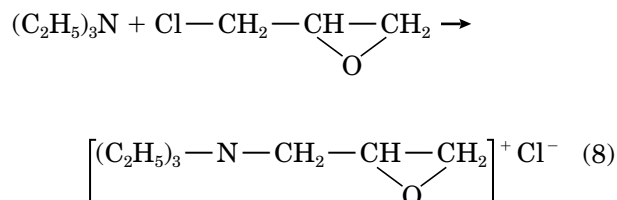


Figure 1 The effect of catalyst (TEA) on the course of reaction between 1 mol of BMMM and 4 mol of ECH at 90°C.



was detected by ¹H-NMR to exist in the system. In fact, TEA itself may deactivate the oxirane ring of ECH by formation of the ammonium salt



When ECH reacts with the product of addition (BMMM : ECH = 1 : 4), TEA regains its catalytic activity, since, then, equilibrium (4) exists (Fig. 2). Application of TEA is therefore justified for the reaction of BMMM with PO only (EO is reactive enough without any catalyst), although it does accelerate the reaction of the semiproducts containing hydroxy groups with the excess of oxirane according to reactions (4) and (5).

The reaction of BMMM with ECH at the molar ratio 1 : 4 (i.e., at amino protons : oxirane rings = 1 : 1) proceeds with a weak autocatalytic effect (Fig. 3). The plot of β vs. time has the characteristic inverted-S-shape. It can particularly well be seen at 80°C. The reaction was initially slow and accelerated at the conversion of 30–40%. It seems that both the autocatalytic effect of the BMMM substrate and that of the product were operative. Thus, just after hydroxy groups appeared in the system, nitrogen atoms of BMMM started to play

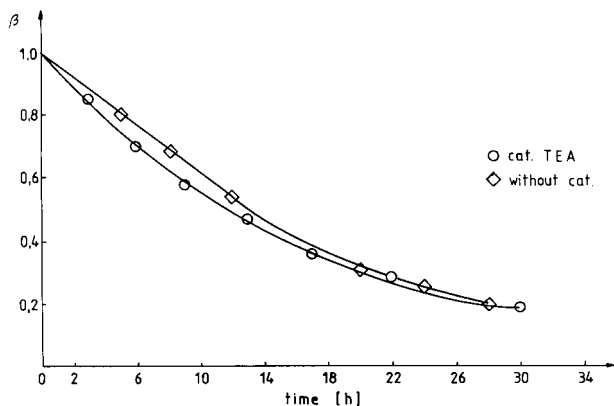
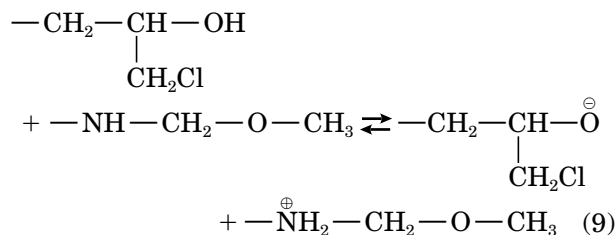


Figure 2 The effect of catalyst (TEA) on the course of reaction between 1 mol of BMMM and 8 mol of ECH at 90°C.

a similar role as that of the TEA catalyst, taking over hydroxy protons [cf. eq. (4)]:



The acceleration of the process measured as the more rapid consumption of oxirane was the result of subsequent reaction of oxirane with the alcoholate anion as follows from (9) [cf. eq. (5), too]. The higher reactivity of hydroxy groups than that of amino ones was observed for the reaction with molar ratio of BMMM : ECH = 1 : 8 (Fig. 4). At ca. 50% conversion, where hydroxy groups started

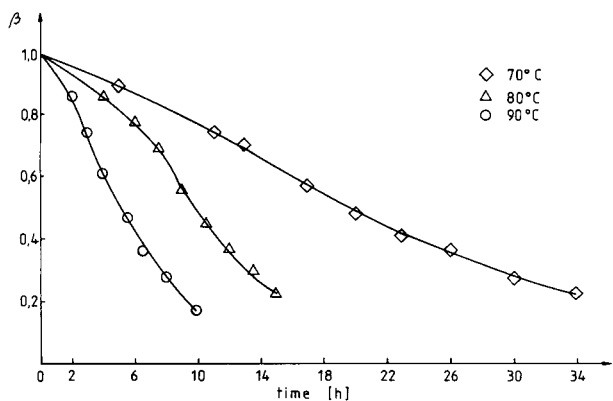


Figure 3 The course of reaction between 1 mol of BMMM and 4 mol of ECH at different temperatures.

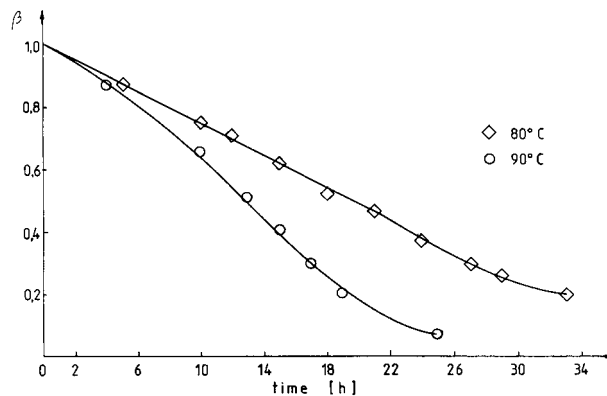
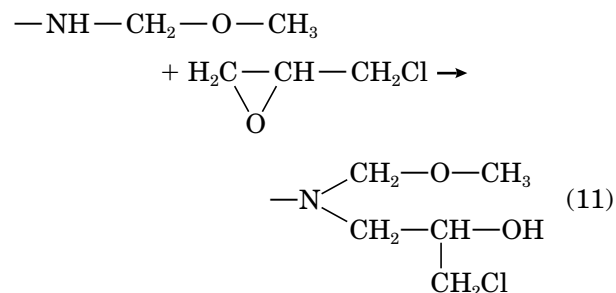
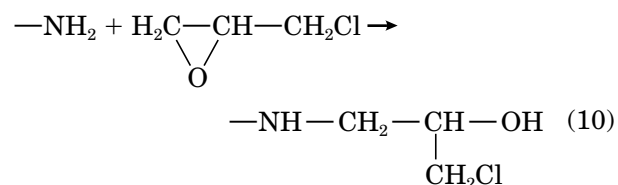


Figure 4 The course of reaction between 1 mol of BMMM and 8 mol of ECH at different temperatures.

to dominate in the system, the rate of epoxy group consumption clearly increased.

The same conclusions regarding the course of the reaction could be drawn from the analysis of $^1\text{H-NMR}$ spectra of the products obtained at different molar ratios of BMMM : ECH ranging from 1 : 1 to 1 : 8. The chemical shifts from protons of functional groups are shown in Table I. By taking the signal from methoxy groups as the reference one and knowing from direct analysis that the content of these groups in 1 mol of BMMM is 1.5 mol, it was possible to estimate the content of primary and secondary amino groups in the products of the reaction of this compound with successive ECH molecules. For example, as can be seen in Table V, in the reaction of 1 mol of BMMM with 1 mol of ECH, ca. 0.6 mol of ---NH_2 groups and the same amount of ---NH--- groups have been consumed:

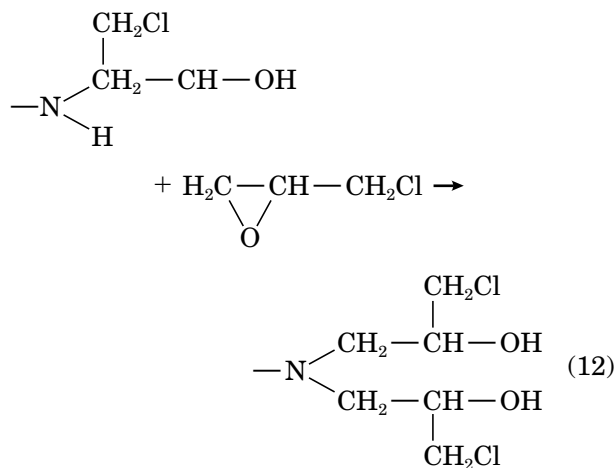


Thus, 1.2 mol of amino groups were used in all, which suggests that some proportion of

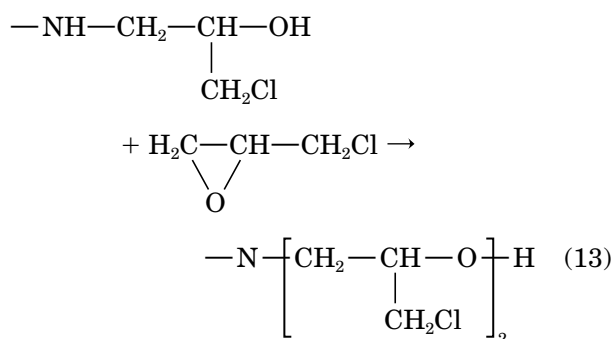
Table V Analysis of ¹H-NMR Spectra of the Products of Reaction Between BMMM and ECH

BMMM : ECH Molar Ratio	Reaction Temp (°C)	No. Amino Groups (Mol/Mol of Product)			Sum of Amino Protons
		—NH·CH ₂ —O—CH ₃	—NH·CH ₂ —O—CH— H ₂ C—Cl	—NH ₂	
1 : 1	90	1.4	0.6	0.4	2.8
1 : 2	90	1.1	0.6	0.2	2.1
1 : 3	90	0.5	0.1	0.1	0.8
1 : 4	90	0.5	0.0	0.1	0.7
1 : 4	70	0.7	0.0	0.2	1.1
1 : 6	90	0.0	0.0	0.1	0.2
1 : 8	90	0.0	0.0	0.0	0.0

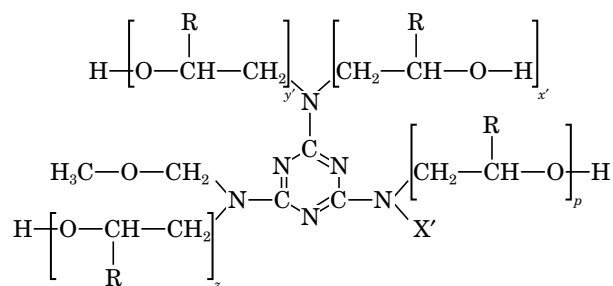
these groups was wasted in the condensation reaction involving hydroxymethyl groups present in BMMM. As the excess of ECH increased, the extent of condensation was reduced (Table V), which one can explain in terms of the faster consumption of amino and hydroxymethyl groups in the reaction with ECH than in condensation. The proportion of secondary amino groups which are formed according to eq. (10) decreased due to the subsequent reaction with ECH:



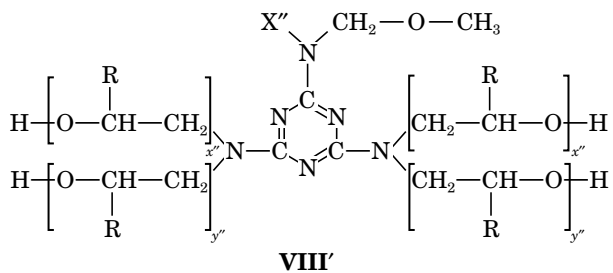
In the products of the reaction of BMMM with 6 mol of ECH, there were no secondary amino groups left and the primary ones were present in a minor amount (ca. 0.1 mol). A reduction in reaction temperature from 90 to 70°C led to a slight increase of the presence of not fully substituted amino groups. It means that this change in reaction conditions favors the subsequent reaction of oxirane with hydroxy groups:



To summarize, one can state that the polyetherols obtained in the present work had the following approximate structural formulas:



VIII
and



VIII'

where $x' + x_1'' + x_2'' + y' + y_1'' + y_2'' + z + p = q$ and q is the number of moles of oxirane that reacted with 1 mol of BMMM, $R = -H, -CH_3, -CH_2Cl$, $X' = -(CH_2OH)_{n'}$, $-(CH_2OCH_3)_{m'}$, $X'' = -(CH_2OH)_{n''}$, $-(CH_2OCH_3)_{m''}$, and $n' + n'' + m' + m'' = 1$.

These formulas are consistent with 1H -NMR spectra (Table I) as well as with IR spectra of the polyetherols. In the latter, one can observe the bands due to stretching and deformational vibrations of hydroxy groups at 3350 and 1100 cm^{-1} , respectively, and deformational vibrations of C—O—C grouping at 1050 cm^{-1} . The bands at 810 and at 750 cm^{-1} confirm the presence of *s*-triazine rings and chlorine atoms, respectively.

SUMMARY AND CONCLUSIONS

1. In the reactions of bis(methoxymethyl)-melamine with an excess of glycerin epichlohydrin or propylene oxide, one can obtain tetrafunctional polyetherols with an *s*-triazine ring. The preparation method developed in this work does not require the presence of a solvent since bis(methoxymethyl)-melamine dissolves in oxiranes at 70°C.
2. Should bis(methoxymethyl)melamine fail to dissolve in an oxirane, it may be first dissolved in glycerin epichlohydrin and then reacted with this oxirane to produce the anticipated polyetherols.
3. The reactions of bis(methoxymethyl)melamine with glycerin epichlohydrin or ethylene oxide do not require catalysts, whereas the addition of propylene oxide is facilitated by the presence of a tertiary amine, preferably triethylamine.

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