

¹H-NMR Study of Reaction of Melamine with Oxiranes

JACEK LUBCZAK

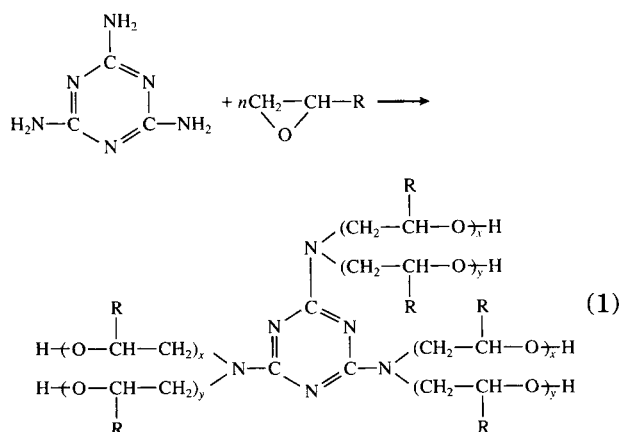
Department of Organic Chemistry, Faculty of Chemistry, Rzeszów University of Technology, 35-959 Rzeszów, Poland

SYNOPSIS

This work describes results of investigations relative to composition and structure of the initial products of the addition of oxiranes to melamine analyzed by ¹H-NMR spectrometry. The work Algebraic equations are shown that describe changes of contents in the functional groups of intermediate products in the function of the number of moles of oxirane that were attached. Reactivity of individual function groups of intermediate products are also discussed. The structure of polyetherols with an *s*-triazine ring that forms in the reaction of melamine with oxiranes is proposed on the basis of these investigations. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The reaction of melamine with an excess of oxirane yields liquid hexafunctional polyetherols containing an *s*-triazine ring¹⁻⁵:



where

$$R = \text{—H, —CH}_3; 3(x + y) = n.$$

The presence of the melamine ring in polyetherols makes them suitable for preparation of polymers, for example polyurethanes, of improved thermal stability.^{6,7} Both the methods of preparation and some properties of the polyetherols have been described.⁵

However, information is lacking on the reaction carried out at the ratio of melamine to oxirane smaller than ca. 1 : 8 as well as on the structure of products. Preliminary results published elsewhere^{4,5} revealed that mixtures rather than individual hydroxyalkyl derivatives were formed in the reaction. The products contained various amounts of unreacted amino groups. The mixtures of this kind are rather difficult to separate chromatographically; the standard chemical determination of primary and secondary amino groups is also not very reliable. Hence, a more convenient analytical tool has to be sought from spectroscopic methods. The proton NMR technique seems to be one of the convenient methods because the signals from protons at primary amino groups are sufficiently separated from those of secondary groups.⁸

In this article the results are presented on determination of average content of various groups (—NH_2 , —NH— , —N(ROH)_2 , —OROH) in the products of reaction of melamine with ethylene oxide (EO) and propylene oxide (PO) as well as on the reactivity of protons in these groups. The aim of this work was to gain a comprehensive view on the reaction between melamine and oxiranes in a broader range of molar ratios than previously.

EXPERIMENTAL

Syntheses

To a 250-mL, heavy wall glass reactor equipped with a stirrer and heating jacket, were added 6.3 g (0.05

Table I Composition of Reaction Mixtures and Time to Completion for Reactions of Addition of Oxiranes to Melamine

Melamine:Oxirane Ratio	Reaction Time (h) at 75°C	
	Ethylene Oxide	Propylene Oxide
1:1	30	35
1:2	40	48
1:3	46	60
1:4	50	68
1:5	54	—
1:6	60	80
1:8	65	90
1:10	71	100
1:12	76	115
1:14	—	124
1:18	82	—
1:20	—	140
1:24	95	—

mol) of melamine (Merck), 2–3 g of 60% aqueous solution of tetrabutylammonium hydroxide (TBAH, Fluka), 110 g of dimethylsulfoxide (DMSO, Harmful) kept over 4-Å molecular sieves prior to use, and a predetermined amount of EO or PO. The molar ratio of oxiranes to melamine was from 1 to 24 (Table I). The mixture was heated while stirring up to 75°C ($\pm 1^\circ\text{C}$) and kept at this temperature until reaction was completed. The extent of reaction was followed by measuring the epoxy number with a dioxane solution of hydrochloric acid. The solvent was then distilled off (at 75–89°C, 2.7 kPa) and the raw product analyzed.

Analyses

The reaction products were dissolved in d_6 -DMSO and $^1\text{H-NMR}$ spectra of the solutions were recorded at $29.8 \pm 0.2^\circ\text{C}$ in the range 0–10 δ ppm on a BS-587A 80-MHz spectrometer (Tesla, Czechoslovakia) with trimethyl silane internal standard.

RESULTS AND DISCUSSION

In the $^1\text{H-NMR}$ spectrum of melamine there is only one signal at ca. 6.6 ppm due to all amino protons. Addition of successive oxirane molecules produces shifting of the signal to 6.2–5.9 ppm in the spectra, and the signal at ca. 6.4–6.1 ppm [Fig. 1(a–c)] is ascribed to the proton in the secondary amino groups: $-\text{NH}-\text{CH}_2-\text{CHR}-\text{O}-$. Similar peaks appear

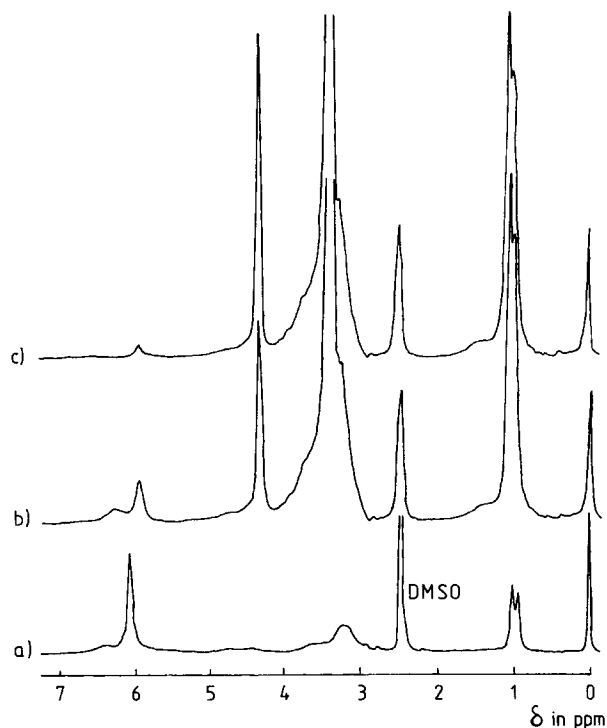


Figure 1 $^1\text{H-NMR}$ spectra of the products of reaction of melamine with propylene oxide, molar ratio 1 : 1: (a) 1 : 4, (b) and (c) 1 : 4 after addition of D_2O .

in the spectra of hydroxymethyl derivatives of melamine [except for hexakis(hydroxymethyl) melamine] due to $-\text{NH}-\text{CH}_2-\text{OH}$ groups.⁸ A rapid exchange of protons makes the signal disappear after addition of D_2O [Fig. 1(c)]. The same can be observed for the signals at 5.5–5.8 ppm from protons of hydroxyl groups formed in the reaction. The signals from protons from the alkyl groups are also present in the spectra of products of EO or PO addition (Fig. 1, Table II). The protons of the methylene groups in the struc-

Table II Chemical Shifts for Protons at Structural Elements of (Hydroxyalkyl)melamines

Structural Element	Chemical Shift (δ ppm)
$-\text{NH}-$	6.40–6.10
$-\text{NH}_2$	6.20–5.90
$-\text{OH}$	5.00–5.20
$\text{>N}-(\text{CH}_2)_2-\text{O}$	3.50–3.40
$-\text{O}-(\text{CH}_2)_2-\text{O}$	3.50–3.40
$\text{>N}-\text{CH}_2-\text{CH}<$	3.50–4.20
$-\text{CH}_3$	1.05

tures $-\text{O}-\text{CH}_2-\text{CH}_2-\text{OH}$ and $-\text{NH}-\text{CH}_2-\text{CH}_2-\text{OH}$ have been found to have the same chemical shifts. Hence, the induction effects of both the ether oxygen and hydroxy group in the first structure seem to be similar. In the second structure, the methylene groups vicinal to the nitrogen atom become unshielded because of the mesomeric effect:



to the same extent as the groups at the oxygen. All these effects lead to the magnetic equivalence of all methylene group protons and formation (at the magnetic field applied) of a singleton due to the lack of spin-spin interactions.

Calculations

The intensity of signals from aliphatic protons increases following successive addition of oxirane. The intensity of signals from the amino group protons vanishes accordingly. By taking the intensity of the signals from the methylene group protons for addition products of EO, or methyl group protons for addition products of PO as a reference, one may estimate the number of primary, $n_{-\text{NH}_2}$, and secondary, $n_{-\text{NH}-}$, groups in the reaction products. For EO:

$$n_{-\text{NH}_2} = \frac{2z_0 S_{-\text{NH}_2}}{S_{-\text{CH}_2-}}; \quad n_{-\text{NH}-} = \frac{4z_0 S_{-\text{NH}-}}{S_{-\text{CH}_2-}}$$

and for PO:

$$n_{-\text{NH}_2} = \frac{3z_0 S_{-\text{NH}_2}}{2S_{-\text{CH}_3}}; \quad n_{-\text{NH}-} = \frac{3z_0 S_{-\text{NH}-}}{S_{\text{CH}_3}}$$

where S_* stands for the surface area of signals from protons in the groups shown as subscripts and z_0 is the number of oxirane moles per mole of melamine.

The change in amino group content vs. the number of moles of oxirane added is plotted in Figure 2.

The total number of unreacted amino groups, $n_{\Sigma\text{NH}}$ was calculated as $n_{\Sigma\text{NH}} = 2n_{-\text{NH}_2} + n_{-\text{NH}-}$. From the values of z_0 and both $n_{-\text{NH}_2}$ and $n_{-\text{NH}-}$ it was possible to calculate:

1. the number of moles of hydroxyalkyl groups at secondary amino groups and tertiary amino groups: n_{NHRO} and $n_{\text{N}(\text{RO}-)_2}$;
2. the number of moles of oxirane linked directly to amino groups, z_1 ;

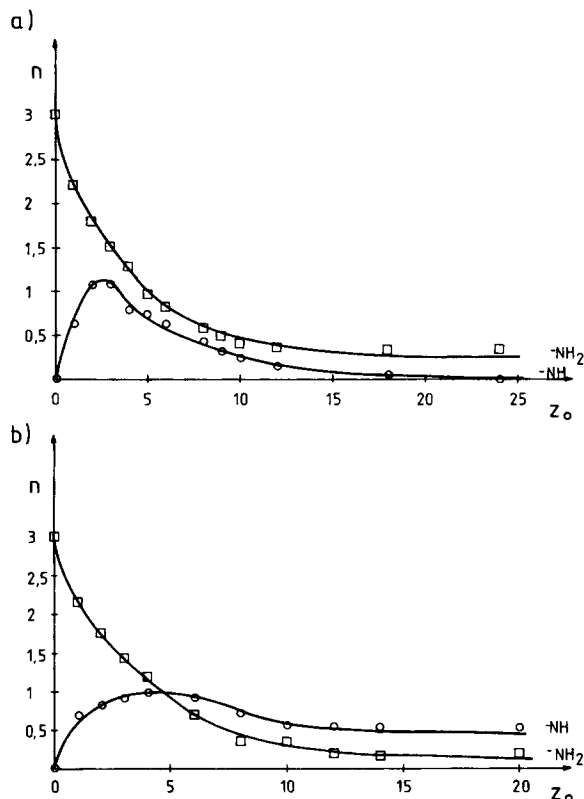


Figure 2 Changes in the content of amino groups in (a) (hydroxyethyl)melamines and (b) (hydroxypropyl)melamines.

3. the number of moles of oxirane reacted subsequently with hydroxy groups, z_2 .

The relations used in the calculations are presented in Table III and the results are shown in Table IV.

Course of Reaction

As follows from the data in Table IV, the number of moles of amino functionalities blocked by an oxirane is always smaller than the number of moles of the latter per 1 mol of melamine used in the reaction ($n_{\text{ORO}} = z_1 < z_0$). This means that oxiranes always take part in subsequent reactions, that is, in the reactions with hydroxy groups. The presence of primary and secondary amino groups can clearly be seen in the product of reaction of 1 mol of melamine with 6 mol of oxiranes. They would not be present if there were no subsequent reactions.

The amount of primary amino groups decreases as the molar excess of oxirane used increases. It does not vanish, though, even for the excess of oxirane higher than 20 : 1. The product still contains some primary groups.

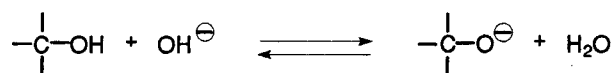
Table III Equations of Functional Dependence of Content of Structural Elements (mol/mol Melamine) on Initial Molar Ratio of Oxirane to Melamine in (Hydroxyalkyl)melamines

Structural Element	Oxirane	Equation	Correlation Coefficient	Applicability Range
Unreacted —NH— groups, —NH—R—O— groups formed ($n_{\text{NHRO-}}$)	EO	$0.014 + 1.097 \exp\left[-0.5\left(\frac{\ln z_0/2.355}{0.861}\right)^2\right]$	0.990	$1 \leq z_0 \leq 12$
	PO	$0.002 + 0.976 \exp\left[-0.5\left(\frac{\ln z_0/3.580}{1.069}\right)^2\right]$	0.988 1.000	$1 \leq z_0 \leq 10$ $z_0 > 10$
Unreacted —NH ₂ groups ($n_{\text{-NH}_2}$)	EO	$0.288 + 2.653e^{-z_0/3.661}$	0.996	$1 \leq z_0 \leq 24$
	PO	$0.124 + 2.819e^{-z_0/3.712}$	0.995	$1 \leq z_0 \leq 24$
Total of unreacted amino functionalities ($n_{\Sigma\text{NH}}$)	EO, PO	$2n_{\text{-NH}_2} + n_{\text{-NHR}} = 0$	—	$0 \leq z_0 \leq 24$
N(R—O) ₂ -groups formed ($n_{\text{N(RO)}_2}$)	EO, PO	$3 - (n_{\text{-NH}_2} + n_{\text{-NHRO}})$	—	$0 \leq z_0 \leq 24$
Total of >N—R—O— groups ($n_{\Sigma\text{NRO-}}$), —OH groups ($n_{\text{-OH}}$) oxirane units (z_1) reacted with amino functionalities; $n_{\Sigma\text{NRO-}} = n_{\text{-OH}} = z_1$	EO, PO	$6 - n_{\Sigma\text{NH}}$	—	$0 \leq z_0 \leq 24$
—ORO—groups ($n_{\text{OR-O}}$), oxirane units (z_2) reacted with —OH groups; $n_{\text{-OR-O}} = z_2$	EO, PO	$z_0 - z_1 = z_0 - 6 + n_{\Sigma\text{NH}}$	—	$0 \leq z_0 \leq 24$

The secondary amino groups vanish completely in the products obtained with more than 20 mol of EO per mole of melamine; for PO their amount stabilizes for the systems with more than ca. 12-fold excess of the oxirane. The differences seem to be steric caused by the presence of methyl groups in the PO. Generally, melamine is resistant against full substitution; it is hard to obtain even hexakis(hydroxymethyl)melamine despite the ease of reaction with formaldehyde.

In order to confirm the reliability of the ¹H-NMR technique in evaluating the amount of amino groups in (hydroxyalkyl)melamines, similar evaluation was performed for (hydroxymethyl)melamines obtained at various molar ratios of melamine to formaldehyde.⁹ The exact amount of hydroxymethyl groups, q , was determined by iodometric titration. The number of unreacted amino functionalities was then $6 - q$. The results were in good agreement with those obtained by ¹H-NMR spectrometric analysis (cf. Table V) essentially identical with that applied to hydroxyalkyl derivatives.

The analysis of Table IV leads to the conclusion that hydroxy groups are more reactive than amino ones. The differences seem to be due to the ease at which alcoholate ions are formed in the reacting system:



It can be observed in ¹H-NMR as a disappearance of OH protons signals (5.0–5.2 ppm) in the presence of TBAH catalyst or NaOH. No changes in the signals from amino protons are observed in that condition.

To verify whether or not the addition of oxirane to melamine was accompanied by side reactions, such as isomerization of oxirane or its polymerization, the number-average molecular weight of (hydroxyalkyl)melamines was determined by cryoscopic method in dioxane solutions. The analyses were made for the products with oxirane to melamine ratio higher than 8, that is, for those soluble in dioxane. The results presented in Table VI in-

Table IV Changes in Content of Functional Groups in Reaction Products of Melamine with Oxiranes (mol/mol Melamine)

Oxirane	Melamine:Oxirane Ratio	$-\text{N}(\text{RO})_2$	$-\text{NHRO}-$	$\Sigma > \text{N}-\text{R}-\text{O} =$	$-\text{OH}$	$-\text{NH}_2$	$-\text{O}-\text{R}-\text{O}-$
TE	1:1	0.01	0.68	0.70	2.31	0.30	
	1:2	0.09	1.09	1.31	1.82	0.69	
	1:3	0.47	1.07	1.99	1.46	1.01	
	1:4	0.90	0.92	2.84	1.18	1.16	
	1:5	1.28	0.76	3.38	0.96	1.62	
	1:6	1.58	0.62	3.78	0.80	2.22	
	1:8	2.00	0.41	4.37	0.59	3.63	
	1:9	2.15	0.34	4.62	0.51	4.38	
	1:10	2.26	0.28	4.81	0.46	5.19	
	1:12	2.41	0.20	5.08	0.39	6.92	
	1:18	2.61	0.08	5.31	0.31	12.70	
	1:24	2.67	0.04	5.42	0.29	18.60	
TP	1:1	0.22	0.50	0.74	2.28	0.26	
	1:2	0.39	0.84	1.63	1.77	0.37	
	1:3	0.66	0.96	2.32	1.38	0.68	
	1:4	0.95	0.97	2.89	1.08	1.11	
	1:6	1.45	0.87	3.72	0.68	2.28	
	1:8	1.81	0.74	4.32	0.45	3.68	
	1:10	2.07	0.62	4.85	0.31	5.15	
	1:12	2.22	0.55	4.99	0.23	7.01	
	1:14	2.26	0.55	5.07	0.19	8.93	
	1:20	2.31	0.55	5.17	0.14	14.80	

R = $-(\text{CH}_2)_2-$, $-\text{CH}_2-\text{CH}(\text{CH}_3)-$.

dicates that no side reactions accompany the addition of oxirane to melamine.

In conclusion one can state that in the reaction of melamine with an excess of oxirane, the subsequent growth of oxyethylene (oxypropylene) chains

plays an important role. This growth takes place at the expense of the reaction of amino groups. As a result, one should expect a structure where a long polyetherol chain substitutes the "first" amino proton, whereas the "second" amino proton is left un-

Table V Results of Amino Groups Analysis in (Hydroxymethyl)melamines (HMM) Carried out Chemically and Spectroscopically

Content of CH_2O in HMM (wt %)	Molar Ratio Melamine: CH_2O in HMM	Content of Amino Groups (mol/mol) of Melamine Calcd. from	
		CH_2O Content	$^1\text{H-NMR}$ Spectra
31.39	1:1.92	4.08	3.91
32.30	1:2.00	4.00	4.00
35.50	1:2.31	3.69	3.92
37.31	1:2.50	3.50	3.60
37.84	1:2.56	3.44	3.45
50.00	1:4.20	1.80	1.50
50.72	1:4.32	1.68	1.40
53.48	1:4.83	1.07	1.05
54.40	1:5.00	1.00	0.83
54.84	1:5.10	0.90	0.95

Table VI Molecular Weights of (Hydroxyalkyl)melamines

Oxirane	Melamine: Oxirane Ratio	Molecular Weight	
		Calculated	Measured
EO	1:20	566	580
	1:12	654	680
	1:18	918	937
	1:24	1182	1225
PO	1:8	590	614
	1:12	822	881
	1:14	938	954
	1:20	1286	1181

substituted or substituted with relatively shorter polyetherol chain [$x_i > y_i$ in eq. (1)]. From Figure 2 one may also conclude that EO, as a more reactive compound, reacts more indiscriminately than PO and the differences in lengths of polyoxyethylene chains at the same nitrogen atom are expected to be smaller than for PO.

REFERENCES

1. J. Langrish and R. Marklow, Br. Pat. 1,049,288 (1966); *Chem. Abstr.*, **66**, 38960p (1967).
2. D. Kaiser and J. Zane, U.S. Pat. 3,256,281 (1966); *Chem. Abstr.*, **65**, 10698c (1966).
3. D. Mathieson, Fr. Pat. 1,386,574 (1965); *Chem. Abstr.*, **62**, 14895g (1965).
4. J. Lubczak and M. Kucharski, *Chemia Stos.*, **29**(3-4), 277 (1985).
5. M. Kucharski and J. Lubczak, *Acta Polym.*, **42**(4), 186 (1991).
6. Z. Wirpsza and J. Brzeziński, *Aminoplasty*, WNT, Publishers, Warsaw, Poland, 1970.
7. M. Kucharski and J. Lubczak, *Polimery*, **29**(7), 264 (1984).
8. K. Sato and K. Maruyama, *Makromol. Chem.*, **182**, 2233 (1981).
9. A. Bachmann and G. Köhler, Ger. Pat. 1,054,459 (1959); *Chem. Abstr.*, **55**, 6508d (1961).

Received February 8, 1995

Accepted March 28, 1995