

# Study of Reaction Between $N,N,N',N',N''$ -Pentakis(hydroxymethyl)melamine and Ethylene or Propylene Oxide

JACEK LUBCZAK

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

Received 18 October 1996; accepted 21 January 1997

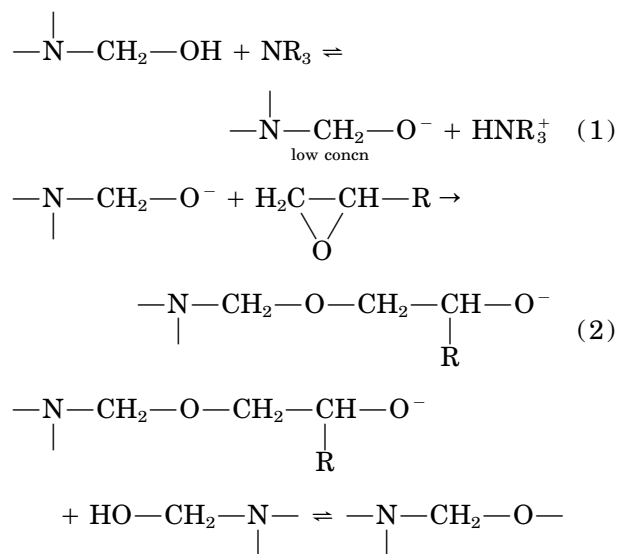
**ABSTRACT:** The effects of the kind and amount of oxirane (propylene or ethylene oxide), the amount of triethylamine catalyst, and the temperature on the reaction with  $N,N,N',N',N''$ -pentakis(hydroxymethyl)melamine (PHMM) in DMSO solution were studied. The changes in the content of reactive groups in the reaction mixture and in the final product were analyzed. The oxirane addition was shown to be accompanied by the condensation of hydroxymethyl groups in the PHMM. Optimal conditions for the synthesis and the structural formula of the *s*-triazine ring containing polyetherols were established. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 2589–2602, 1997

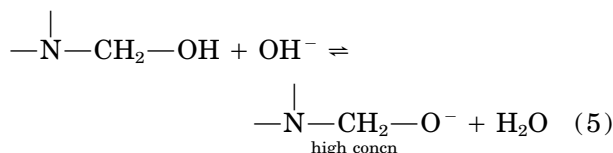
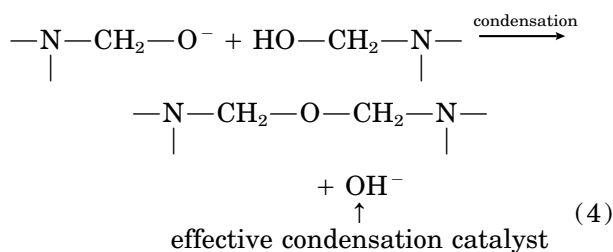
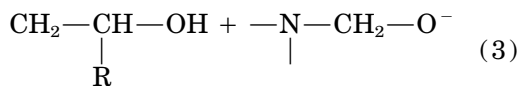
**Key words:** oxiranes; triethylamine catalyst;  $N,N,N',N',N''$ -pentakis(hydroxymethyl)-melamine; ethylene oxide; propylene oxide

## INTRODUCTION

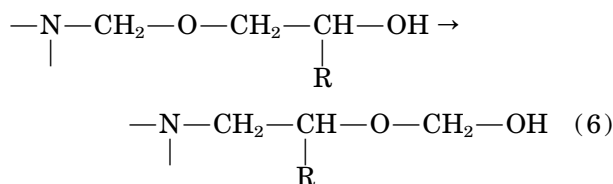
In the reaction between melamine and an excess of oxiranes, such as ethylene (EO) and/or propylene oxide (PO), one obtains polyetherols with *s*-triazine rings that are suitable components of polyurethane foams having improved thermal stability.<sup>1</sup> Although these materials seem very useful and relatively cheap, little is known about their synthesis.<sup>2–5</sup> The reason seems to be the poor solubility of melamine and the lack of suitable solvents in which to carry out the reaction. In DMSO, which seems to be the best solvent, the solubility of melamine<sup>6</sup> is only ca. 6 g/100 cm<sup>3</sup> at 30°C. Much better solubilities are exhibited by the hydroxymethyl derivatives of melamine. These compounds also react readily with oxiranes to yield *s*-triazine ring-containing polyetherols. The problem is their tendency to polymerize through condensation of hydroxymethyl groups with themselves or with amino groups, leading to high

molecular and eventually crosslinked products.<sup>7</sup> The condensation is facilitated by the catalytic effect of alkoxylate anions that are formed in the reaction of oxiranes with hydroxymethyl groups in the presence of tertiary amines used as addition catalysts.<sup>8,9</sup>





As reported previously,<sup>10</sup> the best results in polyetherol syntheses are obtained by using hydroxymethyl derivatives containing at least four hydroxymethyl groups per melamine ring and by applying a large excess of oxirane: 12 mol/mol derivative. The reaction should be carried out at 45–70°C. By determining the presence of formaldehyde, both in the final reaction mixture and after distilling off the solvent (DMSO) and catalyst (triethylamine, TEA), we were able to establish the amount of formaldehyde blocked by oxirane units and that remaining at the end of oxirane chains in the form of semiacetal. The latter is formed by the rearrangement



In this article we report on some of the details of the course of the reaction between *N,N,N',N',N''*-pentakis(hydroxymethyl)melamine (PHMM) and oxiranes. The main aim of the study was to find a relation between the excess of oxirane used at the optimal synthesis conditions and the content of semiacetal groupings in the reaction products. This allowed us to establish the approximate structural formula of the melamine based polyetherols.

## EXPERIMENTAL

### Preparation of PHMM

PHMM was obtained from melamine (pure, Kędzierzyn Nitrogen Plants, Poland) and formaline

(pure, 36 wt % aqueous solution of formaldehyde, Tarnów Nitrogen Plants, Poland) according to the procedure described elsewhere.<sup>10</sup>

### Reaction of PHMM with Oxiranes

PHMM 13.8 g, 0.05 mol and 50 g of DMSO (pure, Harmful, U.K.) were introduced into a 250-mL heavy-wall glass reactor. The content was heated until all PHMM dissolved and then it was cooled down to 10°C before the predetermined amounts of TEA (pure, Fluka, Switzerland) and EO or PO (pure, Fluka, Switzerland) were introduced. The amount of TEA was 1.25, 2.5, or 5 mL and the molar ratio of PHMM : oxirane was 1 : 3, 1 : 6, or 1 : 12. The content of the reactor was brought to reaction temperature (30, 40, 50, or 60°C) within 3–4 min. The extent of reaction was followed by measuring the epoxy and alkaline numbers (see the next paragraph for definitions) as well as the content of formaldehyde. After the reaction was completed, the solvent and catalyst were distilled off under reduced pressure (2.5–10.5 hPa, at 75–90°C) and the product was analyzed by <sup>1</sup>H-NMR.

### Determination Procedures

The epoxy number was determined by using hydrochloric acid in dioxane.<sup>11</sup> The amount of free and bound formaldehyde in the form of *N*- and *O*-hydroxymethyl groups was determined iodometrically.<sup>7</sup> The alkaline number is defined as the number of milligrams of HCl that react with 1 g of a substance. This was used to correct the epoxy number. One-half gram of sample was dissolved in 25 mL of aq. HCl followed by titration with KOH solution.

<sup>1</sup>H-NMR spectra were recorded on a 80-MHz spectrometer (BS-487C Tesla, Czechoslovakia) in *d*<sub>6</sub>-DMSO solution with HMDSO internal standard.

## RESULTS AND DISCUSSION

The course of reaction between PHMM and oxiranes was initially estimated by comparing <sup>1</sup>H-NMR spectra of the hydroxymethyl derivative and the reaction products (Figs. 1 and 2). The characteristic bands are shown in Table I.<sup>10,12–14</sup> As the reaction progressed, the intensity of signals in the spectra due to methylene and hydroxy groups in the PHMM at 4.9 + 5.3 and 5.9 ppm, respectively, decreased. Thus, the oxiranes reacted first with the hydroxymethyl groups of PHMM; the reaction with the amino proton was much slower. The

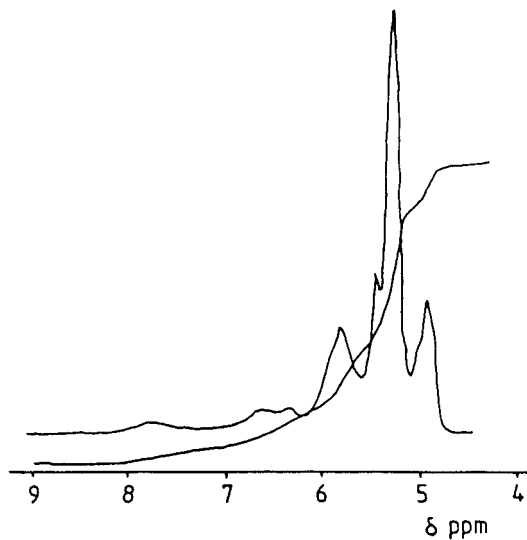


Figure 1  $^1\text{H-NMR}$  spectrum of PHMM.

amino protons were found even in the products with the PHMM : oxirane ratio of 1 : 12.

The hydroxymethyl groups vanished not only in the reaction with oxirane but also in the condensation reactions as well. As evidence consider the signal at 4.4 ppm from the dimethylene ether

groups:  $\text{N}-\text{CH}_2-\text{O}-\text{CH}_2-\text{N}$ . We found

the same signals in the spectra of melamine-formaldehyde resin obtained from PHMM subjected to gradual polycondensation. The intensity of this signal increased during condensation.

In the spectra of reaction products obtained at low oxirane excess, that is, at a PHMM : oxirane ratio of 1 : 3 and 1 : 6, it was possible to observe signals from secondary and even primary amino groups (Fig. 2). The reason why they were present is explained later in this article.

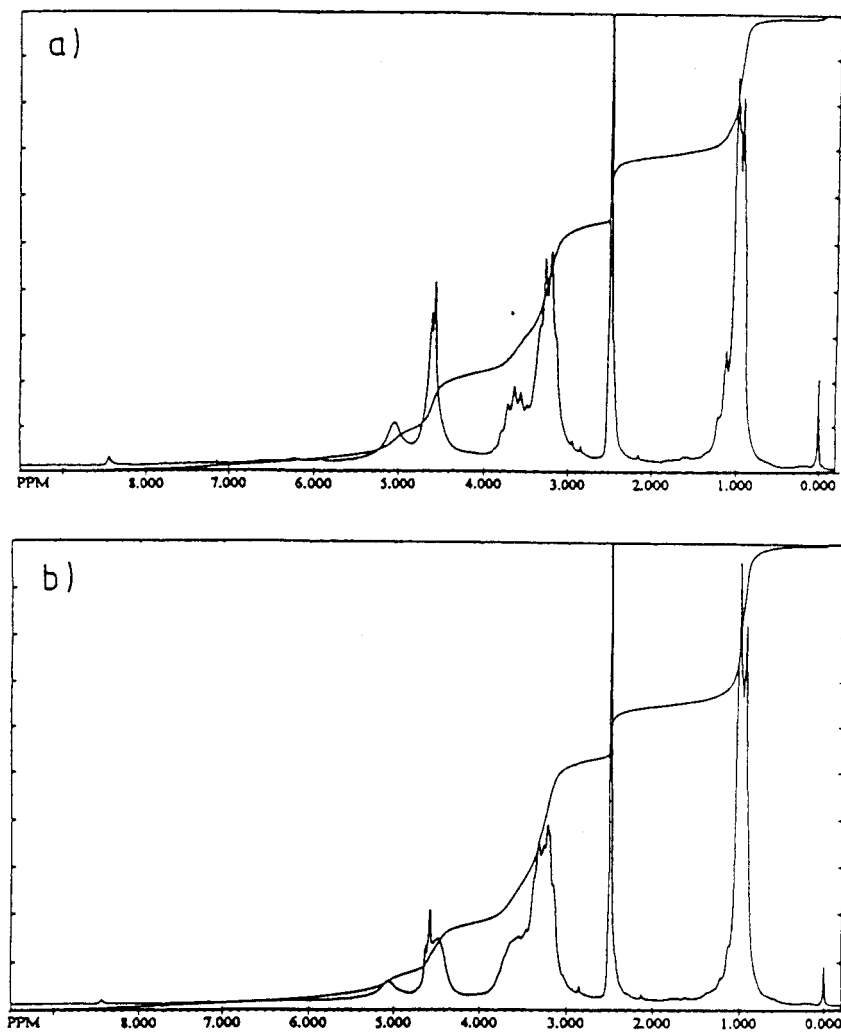


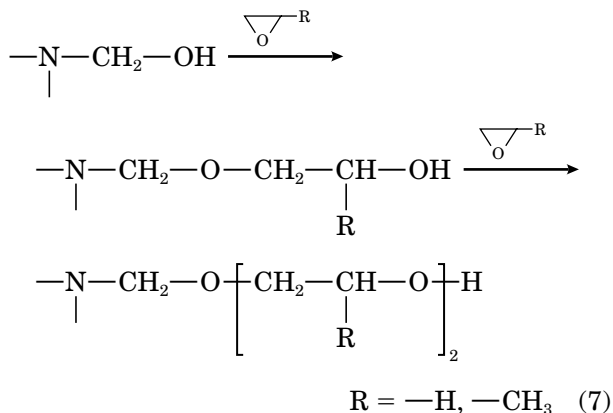
Figure 2  $^1\text{H-NMR}$  spectrum of the reaction product of PHMM with (a) 6 mol or (b) 12 mol PO.

**Table I** Substituent Chemical Shifts in  $^1\text{H-NMR}$  Spectra of PHMM and Its Reaction Products with Ethylene and Propylene Oxides

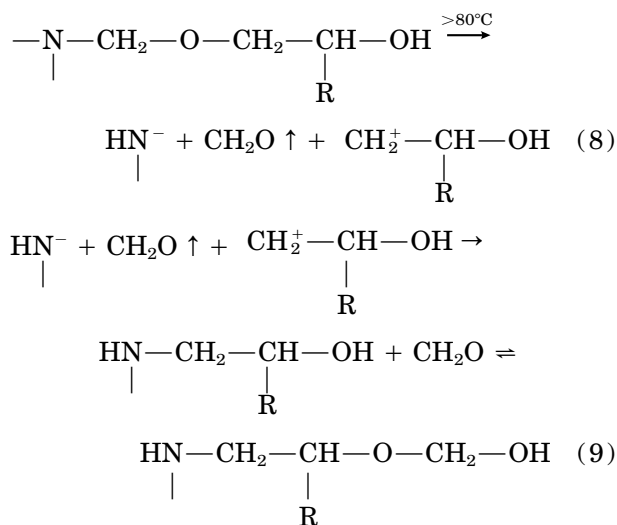
Substituent	Chemical Shift [ $\delta$ in ppm]	Reference
$\text{CH}_2\text{O}$ (free)	8.3	Lubczak <sup>10</sup>
$-\text{NH}-$	7.6–7.1	Duliban et al., <sup>12</sup> Sato and Maruyama <sup>13</sup>
$-\text{NH}_2$	7.0–6.1	Duliban et al., <sup>12</sup> Sato and Maruyama <sup>13</sup>
$-\text{OH}$	6.0–4.5	Duliban et al., <sup>12</sup> Sato and Maruyama <sup>13</sup>
$-\text{NHCH}_2\text{OH}$	5.0–5.2	Duliban et al., <sup>12</sup> Sato and Maruyama <sup>13</sup>
$>\text{N}(\text{CH}_2\text{OH})_2$	4.9–4.8	Duliban et al., <sup>12</sup> Sato and Maruyama <sup>13</sup>
$>\text{CH}_2\text{OCH}_2\text{N}<$	4.4–4.3	To be published
$>\text{CH}-$	3.8–3.7	Lubczak <sup>14</sup>
$-\text{CH}_2-$ (PO addn. product)	3.3	Lubczak <sup>14</sup>
$-(\text{CH}_2)_2-$ (EO addn. product)	3.4–3.3	Lubczak <sup>14</sup>
$-\text{CH}_3$	1.1	Lubczak <sup>14</sup>

By taking the signal at 1.1 ppm or that at 3.3–3.4 ppm as a reference in the spectra of addition products of PO or EO, respectively, it was possible to estimate the content of amino groups as well as that of dimethylene ether bridges in the reaction products (Table II).

The kind and amount of oxirane, the temperature, and the amount of catalyst were changed during the study. In all cases the rate of disappearance of hydroxymethyl groups was faster than that of oxirane. This confirmed that considerable condensation was taking place during the reaction. One should bear in mind that unreacted oxirane could react not only with hydroxymethyl groups, but also with hydroxyalkyl ones formed from the previously reacted oxirane.



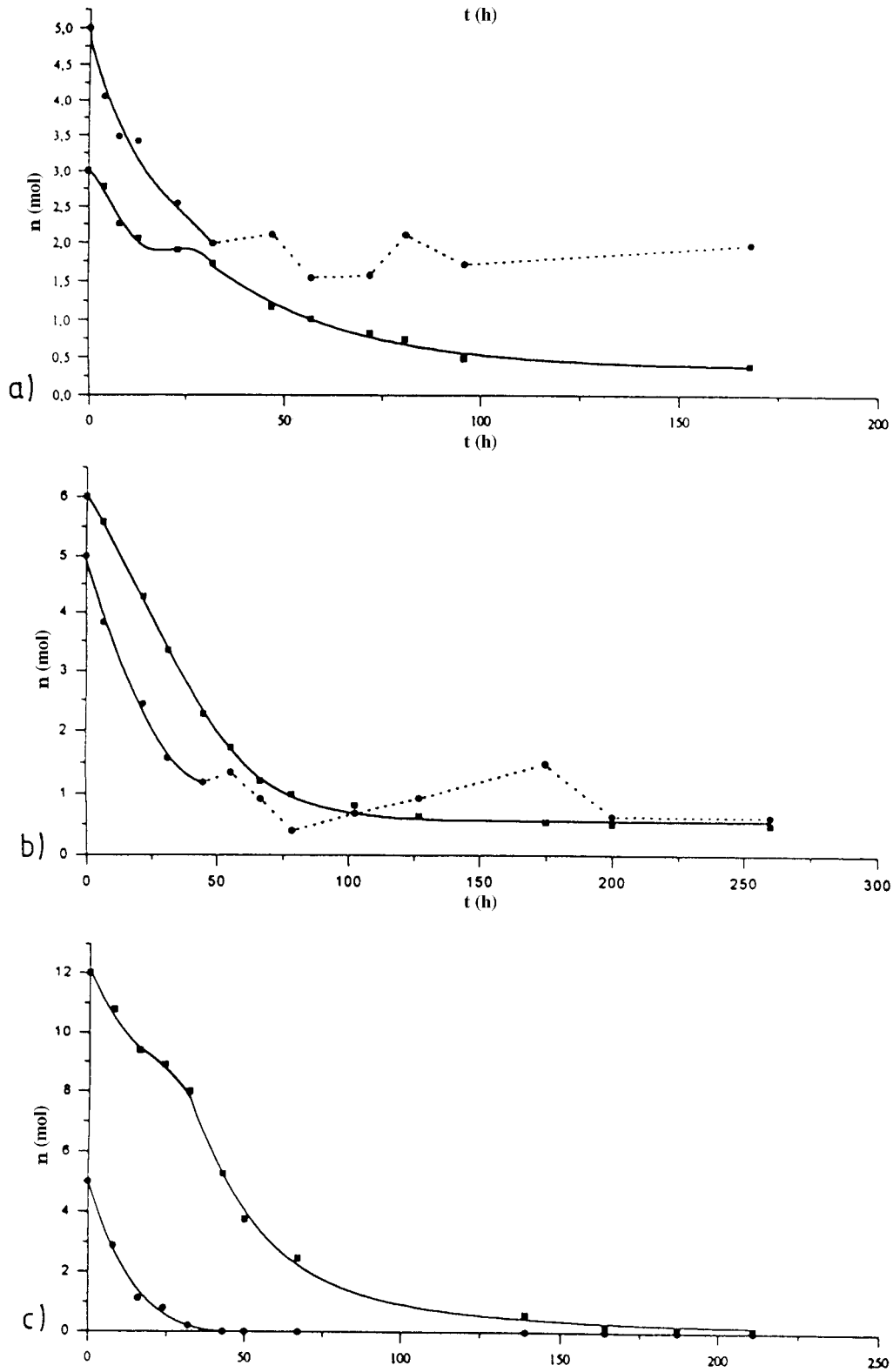
In the mixture consisting of PHMM : PO = 1 : 3 [Fig. 3(a)], a small increase of formaldehyde content was observed after ca. 1.5 mol of PO had reacted. Its concentration fluctuated as further molecules of PO reacted. As was shown previously,<sup>10</sup> formaldehyde blocked by just one oxirane molecule [cf. eq. (6)] could be relatively easily subtracted at elevated temperature, for example, during solvent removal. It was accompanied by a decomposition of the polyetherol chain and a transfer of the formaldehyde molecule to the end of the chain where it formed the unstable hemiacetal link.



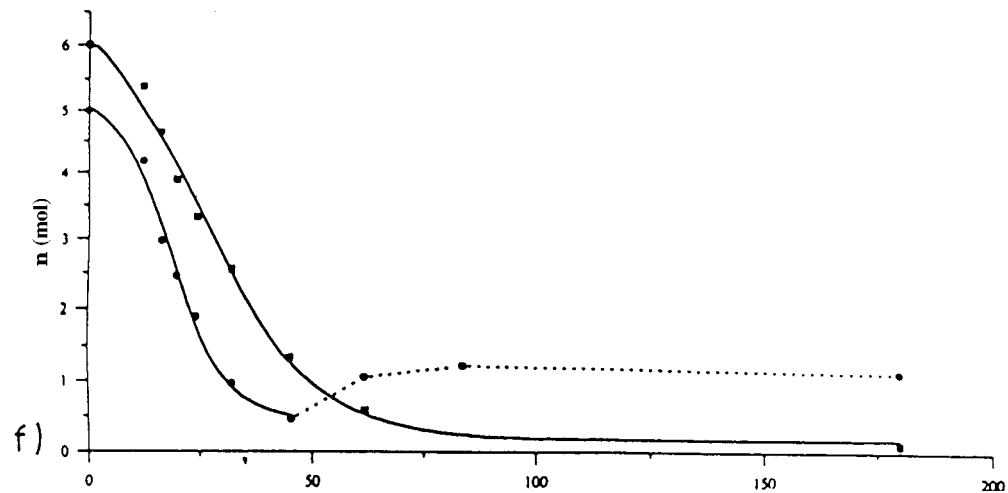
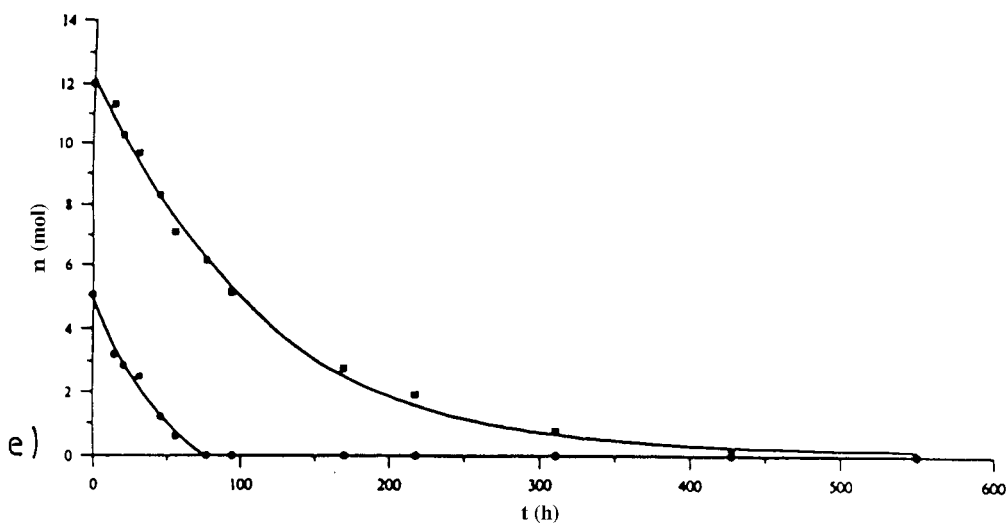
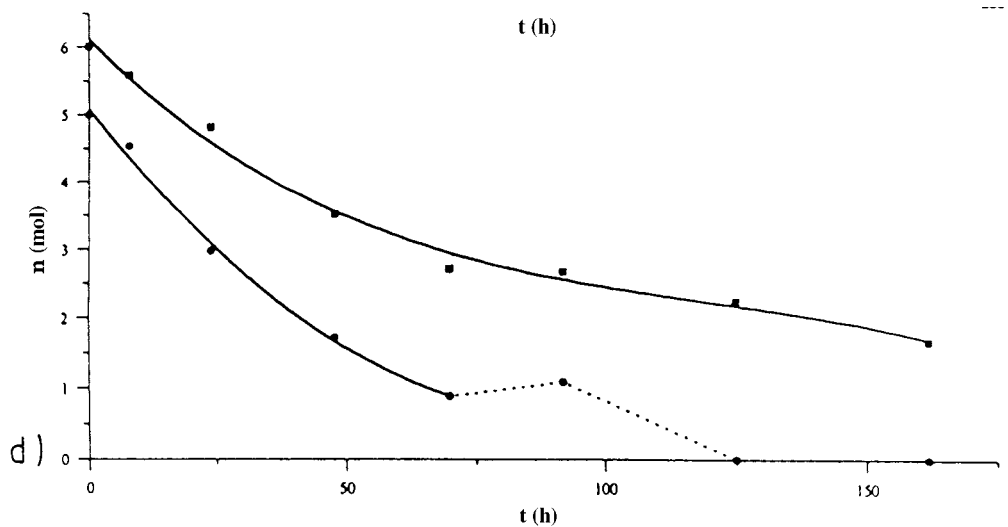
**Table II**  $^1\text{H-NMR}$  Spectra of Reaction Mixtures and Isolated Products of Reaction Between PHMM and Oxiranes

Oxirane	Sample	PHMM : Oxirane Molar Ratio	Temp. (°C)	NEt <sub>3</sub> (mmol/g solvent)	No. Functional Groups (mol/mol PHMM)				
					—NH—	—NH <sub>2</sub>	Σ NH	—CH <sub>2</sub> OCH <sub>2</sub> —	CH <sub>2</sub> O (free)
PO	1	1 : 3	40	0.931	0.5 <sup>a</sup>	0.0 <sup>a</sup>	0.5 <sup>a</sup>	0.35 <sup>a</sup>	0.2 <sup>a</sup>
					1.3	0.3	1.9	0.35	0.2
	2	1 : 6	40	0.931	0.8 <sup>a</sup>	0.5 <sup>a</sup>	1.8 <sup>a</sup>	0.45 <sup>a</sup>	0.1 <sup>a</sup>
					0.5	0.5	1.5	0.45	0.1
	3	1 : 12	40	0.931	0.5 <sup>a</sup>	0.0 <sup>a</sup>	0.5 <sup>a</sup>	0.54 <sup>a</sup>	Traces <sup>a</sup>
					0.5	0.0	0.5	0.54	Traces
	4	1 : 6	40	0.466	2.0	0.0	2.0	0.4	0.2
	5	1 : 12	40	0.466	1.0	0.5	2.0	0.7	0.1
6	1 : 6	40	1.862	0.3	0.6	1.5	0.4	0.1	
7	1 : 6	50	0.931	2.0	0.8	3.6	0.6	0.2	
8	1 : 6	60	0.931	2.8	0.3	3.4	0.7	0.3	
EO	9	1 : 3	40	0.931	0.2	0.3	0.8	0.5	0.2
	10	1 : 6	40	0.931	0.0	0.0	0.0	0.3	0.1
	11	1 : 12	40	0.931	0.0	0.0	0.0	0.4	Traces
	12	1 : 6	30	0.931	0.0	0.0	0.0	0.3	0.1

<sup>a</sup> The reaction mixture still containing DMSO and TEA.



**Figure 3** The course of reaction of 1 mol PHMM with (a) 3 mol PO at 40°C and  $c_{cat.} = 0.93$  (molal concentration); (b) 6 mol PO at 40°C and  $c_{cat.} = 0.93$ ; (c) 12 mol PO at 40°C and  $c_{cat.} = 0.93$ ; (d) 6 mol PO at 40°C and  $c_{cat.} = 0.466$ ; (e) 12 mol PO at 40°C and  $c_{cat.} = 0.466$ ; (f) 6 mol PO at 40°C and  $c_{cat.} = 1.862$ ; (g) 6 mol PO at 50°C and  $c_{cat.}$



= 0.93; (h) 6 mol PO at 60°C and  $c_{cat.} = 0.93$ ; (i) 3 mol EO at 40°C and  $c_{cat.} = 0.93$ ; (j) 6 mol EO at 40°C and  $c_{cat.} = 0.93$ ; (k) 12 mol EO at 40°C and  $c_{cat.} = 0.93$ ; (l) 6 mol EO at 30°C and  $c_{cat.} = 0.93$ . The circles and squares denote the number of moles of formaldehyde and oxirane per mole of PHMM, respectively.

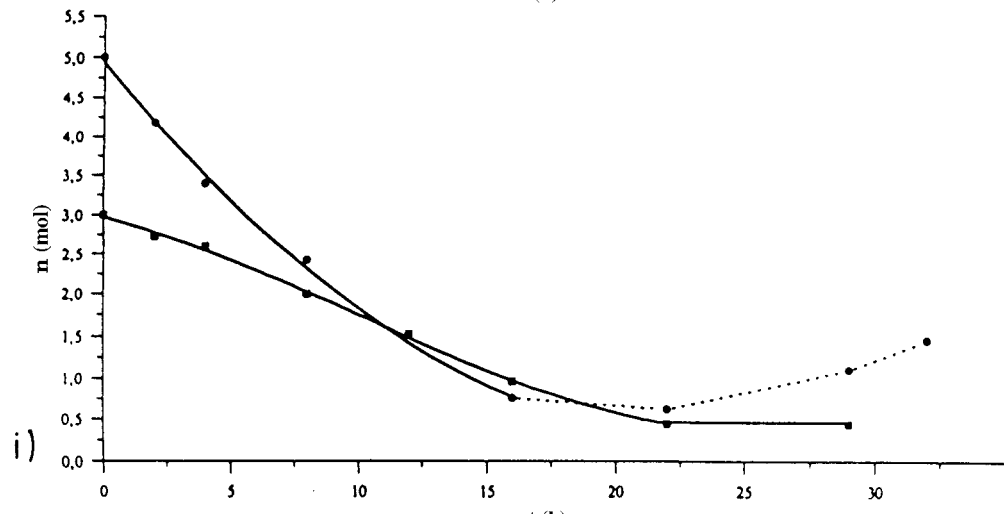
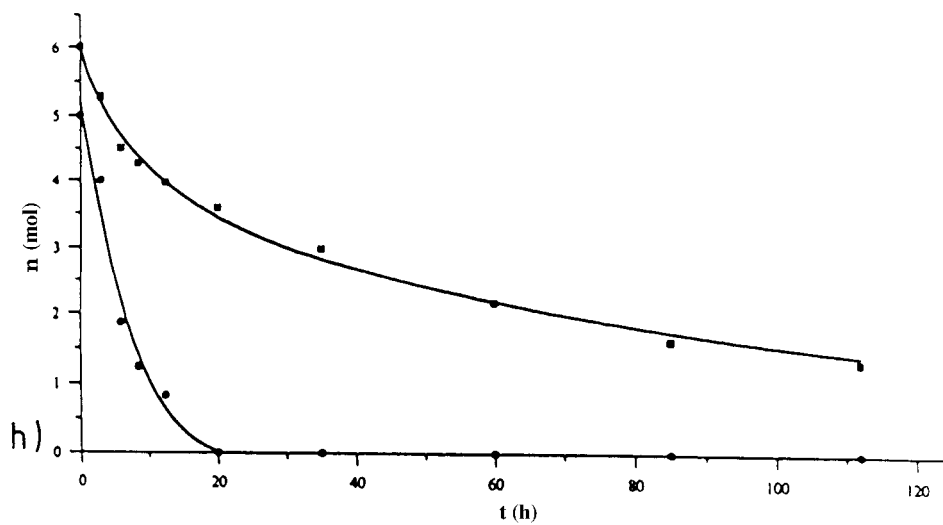
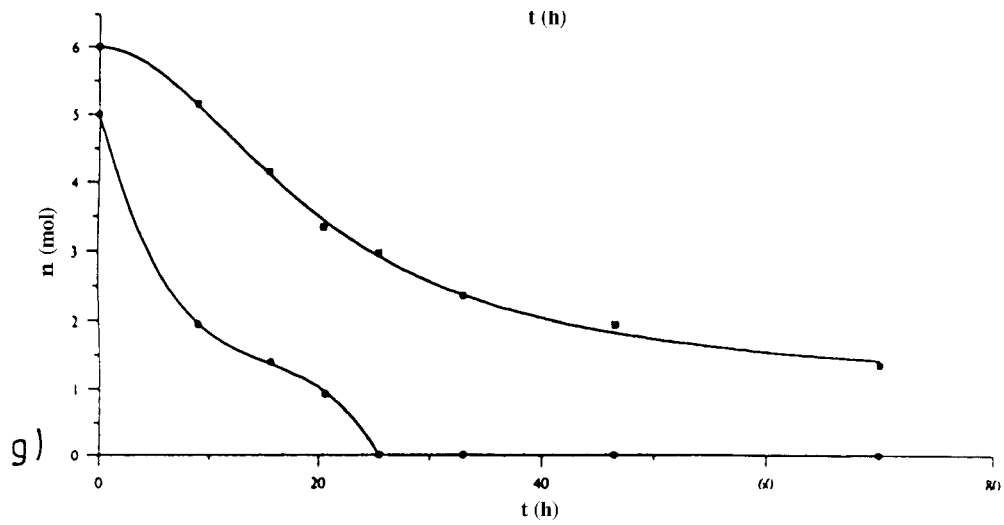


Figure 3 (Continued from the previous page)



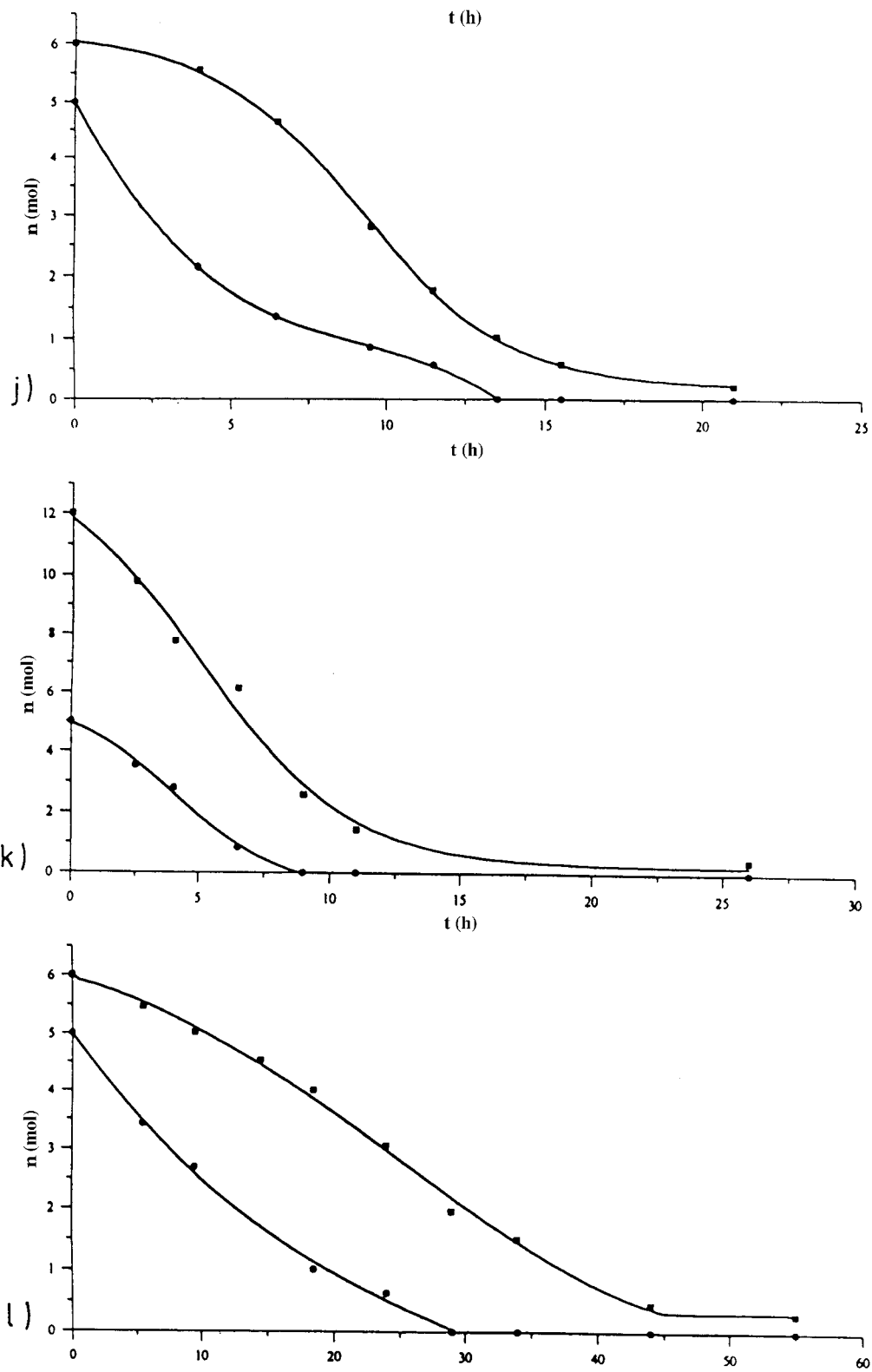
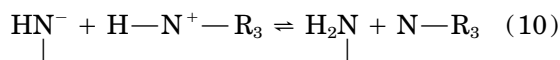


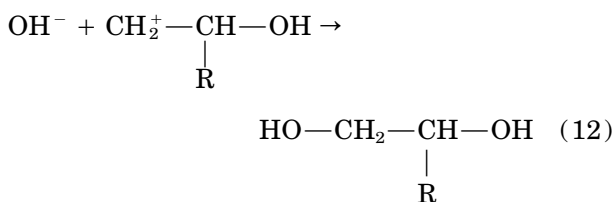
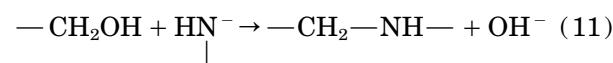
Figure 3 (Continued from the previous page)

As can be seen in Table II, formaldehyde is freed when blocked by one oxirane molecule, even at mild conditions (i.e., at 40°C).

In the  $^1\text{H-NMR}$  spectrum of the mixture obtained in the reaction of PHMM with 3 mol of PO one can find the signals from secondary and even primary amino groups (the latter is absent in PHMM itself). As was shown previously,<sup>12</sup> the amino groups could not be formed in DMSO due to abstraction of formaldehyde from the *N*-hydroxymethyl groups. The primary amino groups formed in the reaction between  $-\text{N}^-$  or  $-\text{NH}^-$  [cf. eq. (8)] with the protonized catalyst, e.g.,



Furthermore, one could not exclude a contribution from crosslinking,



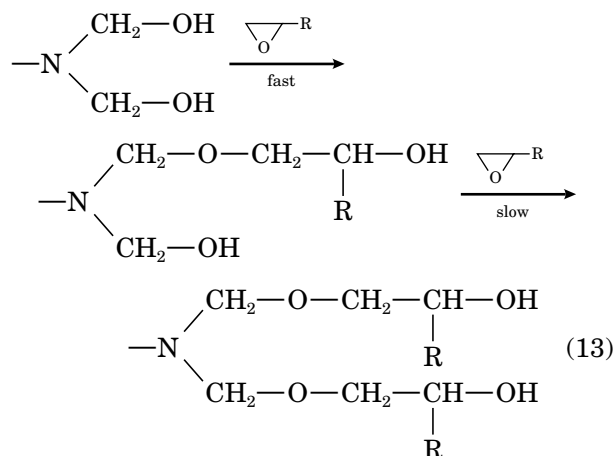
Evidence for this course of reaction, particularly at elevated temperature ( $\geq 80^\circ\text{C}$ ), was provided by the composition of distillate that was removed from the reaction mixture after 1 mol of PHMM reacted with 6 mol of PO. Propylene glycol was found to be present in the distillate.<sup>10</sup>

The distillation step led to thermal decomposition of some of the unblocked hydroxymethyl groups and to recovery of amino groups. The signal from the methylene groups in the  $^1\text{H-NMR}$  spectra diminished and the intensity of signals from the  $-\text{NH}-$  and  $-\text{NH}_2$  groups increased (Table II).

It was noticed that the rate of oxirane addition in the PHMM : PO = 1 : 3 system slowed down considerably after the first mole of oxirane had reacted. Then it slightly increased again. This can be explained in terms of the reduction in concentration of the hydroxymethyl groups due to the condensation [reaction (3)] catalyzed by alkoxylate anions formed in reaction (2). With 6 mol of

PO the extent of condensation was considerably reduced. While at PHMM : PO = 1 : 3, 2.2 mol of hydroxymethyl groups vanished from the system after 15 h of reaction, only 1.5 mol of these groups disappeared after the same time at the PHMM : PO = 1 : 6 ratio.

In fact, the release of free formaldehyde was observed only after at least three molecules of oxirane reacted with a molecule of PHMM. It was unlikely, however, that there was no formaldehyde release before that. The addition simply seemed much faster than the decomposition. After the first three hydroxymethyl groups were blocked with oxirane, the rate of addition of further oxirane molecules was reduced. The reactivity of the remaining second hydroxymethyl group at the nitrogen atom with one group already blocked was reduced due to steric hindrances.



The formaldehyde released at the PHMM : PO = 1 : 6 ratio was present in the system in the hemiacetal form. Some of it, however, remained dissolved in the resulting polyetherols, as indicated by the presence of the signal at 8.3 ppm (Table II). The hemiacetal groups did not react any further in condensation due to the lack of alcoholate anions; this catalyst was completely spent in the oxirane addition [Fig. 3(b)].

The change in reactivity of functional groups is particularly well seen in the plot illustrating the course of reaction of 12 mol PO with 1 mol PHMM shown in Figure 3(c). The initial 3 mol of PO reacted quickly (with the three most reactive *N*-hydroxymethyl groups of PHMM). Strictly speaking, only 2.5 mol PO reacted that fast because some of the hydroxymethyl groups were wasted in the condensation reaction. The next 2



**Table III** Analysis of Extent of Condensation in PHMM–Oxirane Systems

Sample <sup>a</sup>	Conditions at Maximum of $\Delta n_{\text{form}}/\Delta n_{\text{ox}}$				Range at Which $\Delta n_{\text{form}}/\Delta n_{\text{ox}} > 1$			
	Time (h)	Unreacted Oxirane, $n_{\text{ox}}$ (mol)	Unreacted Formaldehyde, $n_{\text{form}}$ (mol)	$\Delta n_{\text{form}}/\Delta n_{\text{ox}}$	Time (h)	Unreacted Oxirane, $n_{\text{ox}}$ (mol)	Unreacted Formaldehyde, $n_{\text{form}}$ (mol)	Average $\Delta n_{\text{form}}/\Delta n_{\text{ox}}$
1	22	1.85	2.67	13.3	0–32	3–1.57	5–3.96	2.12
2	1	5.97	4.77	1.91	0–22	6–4.42	5–2.32	1.70
3	1	11.75	4.67	4.10	0–12	12–10.37	5–1.92	1.89
4	1	5.97	4.99	1.67	0–42	6–3.79	5–1.94	1.38
5	1	12.24	4.94	1.42	0–13	12–11.1	5–3.48	1.69
6	2	6.03	4.73	13.5	0–11	6–5.34	5–3.46	2.33
7	2	5.95	3.57	4.98	0–10	6–4.91	5–1.84	2.90
8	4	4.87	2.87	3.03	0–17	6–3.71	5–0.36	2.03
9	1	2.87	4.49	4.22	0–15	3–1.19	5–1.11	2.15
10	2	5.87	2.88	5.83	0–5	6–5.23	5–1.85	4.09
11	3	9.37	3.35	0.77	—	—	—	—
12	2	5.99	4.41	3.53	0–14	6–4.36	5–1.71	2.01

<sup>a</sup> The samples are the same as in Table II. The total reaction time can be deduced from Figure 3.

The PHMM–EO system [Fig. 3(i–l)] behaved similar to PHMM–PO except that

- addition and condensation proceeded faster (EO is more reactive than PO); and
- in the products of reaction with PHMM : EO = 1 : 6, no free formaldehyde was detected [Fig. 3(i,l)] and no unreacted amino groups were found (Table II).

The reaction was accompanied by a noticeable increase in viscosity, indicating that amino groups could take part in the condensation.

To reveal at which part of the PHMM–oxirane complex reaction that the condensation became the most significant, we performed simple modeling of the reaction kinetics. As a measure of the condensation contribution we took the ratio  $\Delta n_{\text{form}}/\Delta n_{\text{ox}}$ , where  $n$  stands for the number of moles of the reagents (here formaldehyde rather than PHMM). The more this ratio exceeded unity, the higher was the contribution from condensation. The analysis was limited to the period starting at the beginning of the reaction and ending at the point at which free formaldehyde started to become detectable (in Fig. 3, broken line starts at that point). The best curves  $n_{\text{form}} = f(t)$  and  $n_{\text{ox}} = f(t)$  were computed for each set of experimental points. By using the resulting equations (usually polynomials with the poorest correlation coefficient 0.977), the ratio  $\Delta n_{\text{form}}/\Delta n_{\text{ox}}$  was calculated for time intervals  $\Delta t = 1$  h.

The data were used to detect the time and extent of reaction at which the ratio peaked (the highest rate of condensation relative to addition), as well as to establish the range of time at which

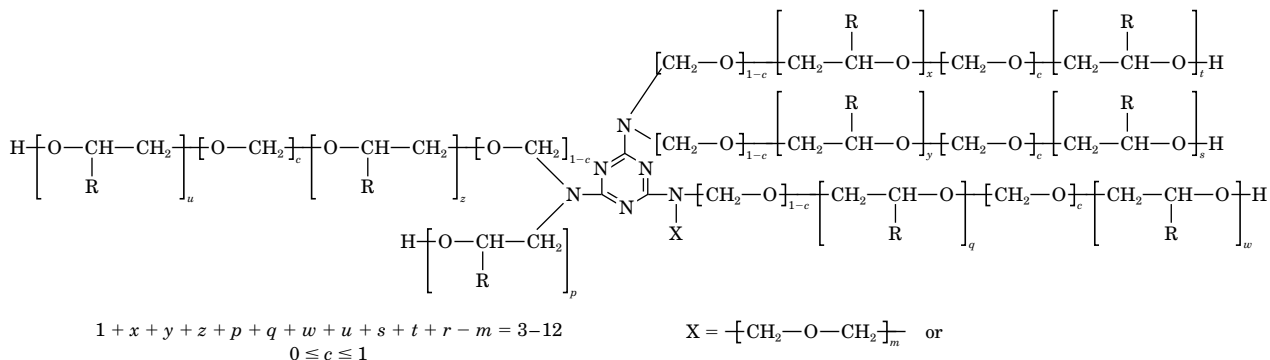
it was higher than 1. The results are presented in Table III. Their analysis led to the following conclusions:

- The highest extent of condensation was observed in the early part of the reaction. This can be explained in terms of the successive increase in alkoxylate anion concentration due to reactions (1) and (2) that act as condensation catalysts.
- A significant role in hindering condensation was played by the excess of oxirane with respect to the hydroxymethyl groups. It facilitated reaction (2) at the expense of (4).
- The TEA catalyst shifted the equilibrium (1) to the right-hand side and hence increased the concentration of  $>\text{N}-\text{CH}_2-\text{O}^-$  anions, the rate of reaction (2), and that of subsequent reactions (3) and (4). This resulted in an increased extent of condensation.

## CONCLUSIONS

The synthesis of polyetherols with *s*-triazine rings should be carried out in a closed system (in a pressurized reactor) at a large excess of an oxirane relative to PHMM ( $\geq 12$  mol oxirane/mol PHMM) at 40–50°C, irrespective of the oxirane used with the concentration of TEA catalyst used in the concentration of 0.93 mmol/g of the solvent containing 1 mmol dissolved PHMM.

The following approximate structural formula is proposed for the *s*-triazine containing polyetherols obtained from PHMM and oxirane.



The author is indebted to Prof. B. Dębska for providing a computer program used to assess the extent of condensation in the reactions of hydroxymethyl derivatives of melamine with oxiranes.

## REFERENCES

1. D. Kaiser and J. Zane, Belg. Pat. 636,694 (1964); *Chem. Abstr.*, **61**, 14856e (1967).
2. O. Mathieson, Fr. Pat. 1,386,574 (1965); *Chem. Abstr.*, **62**, 14895g (1965).
3. D. Kaiser and J. Zane, U.S. Pat. 3,256,281 (1966); *Chem. Abstr.*, **65**, 10698c (1966).
4. J. Lubczak and M. Kucharski, *Chem. Stosowana*, **29**, 277 (1985).
5. M. Kucharski and J. Lubczak, *Acta Polym.*, **42**, 186 (1991).
6. K. Sato, *Bull. Chem. Soc. Jpn.*, **40**, 1547 (1967).
7. J. Lubczak and M. Kucharski, *Polimery (Warsaw)*, **30**, 13 (1985).
8. J. Lubczak, *Indian J. Chem., Sect. B.*, **33**, 125 (1994).
9. J. Lubczak, *Indian J. Chem., Sect. B.*, **33**, 651 (1994).
10. J. Lubczak, *Polimery (Warsaw)*, **50**, 509 (1995).
11. Z. Brojer, Z. Hertz, and P. Penczek, *Epoxy Resins* [in Polish], WNT, Warsaw, 1972, p. 462.
12. J. Duliban, H. Galina, and J. Lubczak, *Appl. Spectrosc.*, **50**, 528 (1996).
13. K. Sato and K. Maruyama, *Makromol. Chem.*, **182**, 2233 (1981).
14. J. Lubczak, *J. Appl. Polym. Sci.*, **58**, 559 (1995).