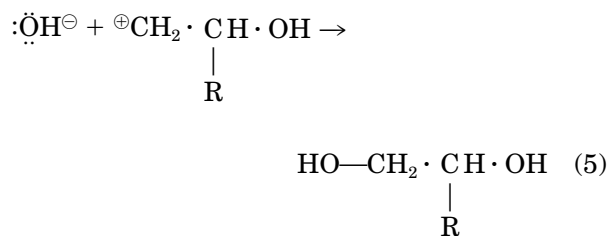
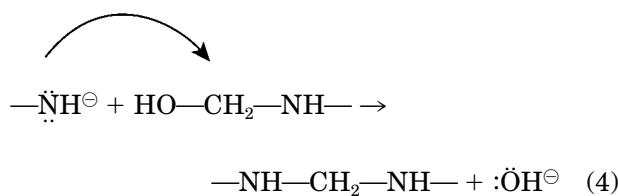
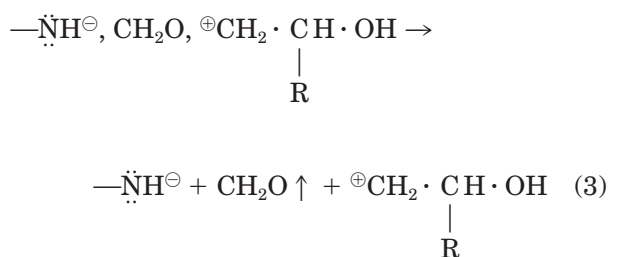


with simultaneous cross-linking and formation of the appropriate glycol:



Formaldehyde molecules are permanently blocked at amino groups only when at least two molecules of oxirane are linked to the hydroxymethyl group.¹

The relative simplicity of PHMM preparation and its good solubility in warm water called for attempts of performing synthesis of the mel-

amine-based PO and EO polyetherols in aqueous medium. The method would be of practical interest if the amount of glycol by-products were kept on as low a level as possible.

EXPERIMENTAL

Preparation of PHMM

PHMM was obtained from melamine (pure, Kędzierzyn Nitrogen Plants, Poland) and formalin (pure, 36 wt % aqueous solution of formaldehyde, Tarnów Nitrogen Plants, Poland) according to the procedure described elsewhere.⁵

Reaction of PHMM with PO or EO

To a 250 cm³ autoclave reactor 13.8 g (0.05 mol) of PHMM, 10, 20, 30, or 40 cm³ of water, TEA catalyst, and PO or EO (pure, Fluka, Switzerland) were introduced. The amount of catalyst was changed in the range 0.65–5.0 cm³ for the reactions with PO, or in the range 0.30–1.0 cm³ for the reactions with EO. The molar ratio of PHMM : oxirane was 1 : 12, 1 : 15, or 1 : 20. After mixing the components, the reactor was quickly heated (within 3–4 min) to 40, 50, or 60°C, at which the reaction was carried out. The extent of reaction was followed by measuring the content of epoxy groups and formaldehyde in the reacting mixture. After the reaction was completed water was distilled off under reduced pressure (2.7–10.7 hPa; temperature of vapors 20–28°C; temperature of boiling mixture 20–80°C), and proton nuclear magnetic resonance (¹H NMR) spectra of the product were recorded.

Analytical Methods

The epoxy equivalent was measured by the hydrochloric method in saturated aqueous magnesium chloride.⁶ The amount of *N*- and *O*-hydroxymethyl groups in the form of free and unsteadily bounded formaldehyde was determined iodometrically.⁷ By measuring the amount of formaldehyde after completion the reaction and, again, after water/catalyst had been distilled off, it was possible to calculate (in moles per mole of PHMM) how many hydroxymethyl groups were blocked in reactions with oxiranes or in condensation reaction (*a*), at the end of polyether chain in the form of *O*-hydroxymethyl groups or unreacted formaldehyde (*b*), and after distillation (*c*).

^1H NMR spectra of the products were recorded in a BSS-4872 spectrometer, 80 Hz (Tesla, Czechoslovakia) in d_6 -DMSO solution and hexamethyldisiloxane as the internal standard. The method of calculating the amount of functional groups from the spectra was described elsewhere.⁵ A mass balance was made for each run to within 0.1 g.

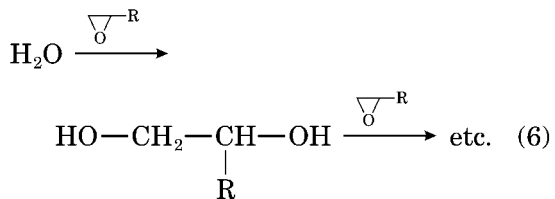
The products were also analyzed in a gas chromatograph (Hewlett Packard 5890, USA) equipped with a flame-ionization detector. The chromatograms were used to estimate quantitatively the amounts of diols and the subsequent products of reactions of oxirane with water. The conditions were: capillary column HP-FFAP of length 10 m and 0.53 mm diameter; layer thickness, 0.1 μm ; temperature profile, 50–220°C (20 deg/min), 5 min at 220°C, 220–240°C (30 deg/min), 15 min at 240°C; temperature of injection chamber, 220°C; rate of carrier gas (He), 18.3 cm^3/min ; sample volume, 0.2 μdm^3 .

The calibration was made by using cyclohexanone, which served as internal standard. The data used for calibration are presented in Table I; the retention times of the products of reaction of PO and EO with water are listed in Table II.

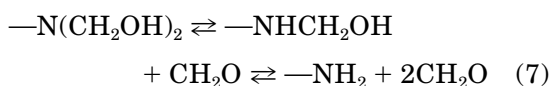
RESULTS AND DISCUSSION

The replacement of an organic solvent with water in the synthesis of polyetherols from PHMM and PO or EO results in two undesired side reactions taking place in the system:

1. Reaction of oxirane with water leading to respective diols and subsequent reactions of the diols with the excess of oxirane:



2. Dissociation of PHMM leading to melamine derivatives with a reduced number of hydroxymethyl groups:



The last reaction yields primary and secondary amino groups that react much less readily with

Table I The Diols and Subsequent Products of PO and EO Hydration Used for Calibration of Gas Chromatography

Reaction	Formula	Name	Best Line Coefficients		Correlation Coefficient	Retention Time (min)
			Slope	Intercept		
$\text{H}_2\text{O} + \text{PO}$	$\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_3$	propan-1,2-diol (PD)	0.446	0.024	0.999	3.16
$\text{PD} + \text{PO}$	$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{OCH}_2\text{CH}(\text{OH})\text{CH}_3$	4-oxaheptan-2,6-diol (OHD)	0.063	-0.001	0.992	4.49
	$\text{CH}_3\text{CH}(\text{CH}_2\text{OH})\text{OCH}_2\text{CH}(\text{OH})\text{CH}_3$	2-methyl-3-oxahexan-1,5-diol (MOHD)	0.038	-0.002	0.991	4.76
$\text{OHD} + \text{PO}$	$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{OCH}_2\text{CH}(\text{CH}_3)\text{OCH}_2\text{CH}(\text{OH})\text{CH}_3$	5-methyl-4,7-dioxadecan-2,9-diol (MDODD)	0.378	-0.005	0.999	5.87
$\text{H}_2\text{O} + \text{EO}$	$\text{HOCH}_2\text{CH}_2\text{OH}$	ethan-1,2-diol (ED)	0.110	0.008	0.996	3.35
$\text{ED} + \text{EO}$	$\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$	3-oxapentane-1,5-diol (OPD)	0.109	0.005	1.000	5.24
$\text{OPD} + \text{EO}$	$\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$	3,6-dioxaocetan-1,8-diol (DOOD)	0.111	0.005	0.994	6.91

Table II The Qualitative Results of the Chromatographic Analysis of Products of PO and EO Hydration Taking Place During Polyetherol Synthesis

System	Identified Compounds	Retention Time (min)
Reaction of PO with H ₂ O at molar ratios 1 : 1 to 2 : 1	PD	3.17
	OHD	4.50
	MDODD	5.87
	Higher oligomers	5.92, 7.20, 7.27, 8.55
Reaction of PO with H ₂ O accompanying polyetherol synthesis at PHMM : PO = 1 : 15	PD	3.16–3.18
	OHD	4.50–4.52
	MDODD	5.51–5.86
Reaction of EO with H ₂ O at molar ratios 1 : 1 to 2 : 1	ED	3.35
	OPD	5.24
	DOOD	6.91
	Higher oligomers	8.51, 9.42, 11.16
Reaction of EO with H ₂ O accompanying polyetherol synthesis at PHMM : EO = 1 : 15	ED	3.35–3.37
	OPD	5.23–5.26
	DOOD	6.91–6.93

oxiranes than hydroxymethyl groups.⁸ The use of autoclave in the process was required because of the volatility of oxiranes, which were in large excess. The temperature had to be below 60°C in order to keep the condensation reactions on a low

level. The analysis of the course of reaction was based on the following data (Tables III and IV):

- mass balance of the reaction,
- formaldehyde content in the reacting mix-

Table III The Results of GLC Analysis of Reaction Products of Oxiranes With Water That are Formed During Polyetherol Synthesis From PHMM and PO or EO in Aqueous Solutions

Oxirane	Synthesis No.	PHMM : Oxirane Molar Ratio	TEA Content mol/mol PHMM	H ₂ O Content cm ³ /mol PHMM	Reaction Conditions		Products of Reaction of Oxirane with H ₂ O wt % ^a				Etherol Content wt %
					Temp (°C)	Time (h)	I	II	III	Σ	
PO	1	1 : 12	13	400	50	140	20.2	6.4	2.7	29.3	70.7
	2	1 : 15	13	400	50	150	20.2	9.8	9.5	39.5	60.5
	3	1 : 20	13	400	50	180	20.3	13.8	15.5	49.6	50.4
	4	1 : 15	13	800	50	90	29.1	7.1	2.1	38.3	61.7
	5	1 : 15	13	200	50	80	10.7	11.1	12.7	35.0	65.0
	6	1 : 15	13	400	40	170	13.4	16.8	13.3	43.5	56.5
	7	1 : 15	13	400	60	90	30.8	6.8	2.8	40.4	59.6
	8	1 : 15	25	400	50	35	13.7	12.7	11.6	38.0	62.0
	9	1 : 15	50	400	50	11	12.8	3.4	3.1	19.3	80.7
	10	1 : 15	100	400	50	5	4.2	37.2	7.8	49.2	50.8
EO	11	1 : 15	20	400	40	18	14.0	22.5	2.51	61.5	38.5
	12	1 : 15	13	400	40	21	15.6	22.6	23.0	61.2	38.8
	13	1 : 15	6	400	40	40	36.2	31.7	17.9	85.8	14.2
	14	1 : 15	20	200	40	18	12.8	20.8	25.3	58.9	41.1
	15	1 : 15	13	200	40	23	11.0	19.4	28.3	58.7	41.3
	16	1 : 15	6	200	40	45	7.5	14.9	18.5	40.9	59.1

^a The Roman numerals denote the subsequent products of oxirane reaction with water: I = PD or ED; II = OHD or OPD; III = MDODD or DOOD.

Table IV The Composition of Postreaction and Product Mixtures in Reactions of PHMM With PO or EO as Determined From Formaldehyde Analysis, GLC, and ¹H NMR

Oxirane	Sample (Nos. as in Table III)	CH ₂ O Content Mol/ Mol of Product			Introduced	Reacted	Introduced	Oxirane Content Mol/Mol PHMM			Functional Group Content Mol/Mol PHMM					
		a	b	c				Reacting with Water to Side Products ^a			Reacting with PHMM					
								I	II	III	—NH—	—NH ₂	ΣNH	—CH ₂ OCH ₂ —	CH ₂ O ^b	
PO	1	4.6	0.4	0.0	22.2	4.10	12	2.71	1.30	0.42	7.57	1.4	0.9	3.2	0.6	0.1
	2	4.0	1.0	0.0	22.2	6.73	15	3.19	1.76	1.78	8.27	2.1	0.8	3.7	0.8	0.1
	3	3.6	1.4	0.0	22.2	8.84	20	4.05	3.12	3.67	9.16	0.3	1.0	2.3	0.8	
	4	4.2	0.8	0.0	44.4	6.37	15	4.67	1.29	0.41	8.63	1.0	0.9	2.8	0.6	0.13
	5	3.9	1.1	0.1	11.1	3.40	15	1.65	1.95	2.33	9.07	2.0	0.8	3.6	0.8	+
	6	3.3	1.7	0.0	22.2	4.42	15	2.07	3.08	2.41	7.44	1.0	0.9	2.8	0.6	+
	7	4.2	0.8	0.0	22.2	5.76	15	4.96	1.24	0.53	8.27	0.5	1.0	2.5	0.6	0.1
	8	5.0	0.0	0.0	22.2	2.98	15	2.20	2.32	2.22	8.26	1.0	1.0	3.0	0.7	0.1
	9	4.4	0.6	0.0	22.2	2.46	15	1.97	0.60	0.57	11.86	0.0	0.0	0.0	0.7	0.1
	10	4.2	0.8	0.0	22.2	4.49	15	0.66	6.68	1.46	6.20	0.0	0.0	0.0	0.7	0.2
	11	4.6	0.3	0.1	22.2	5.78	15	2.36	4.44	5.25	2.95	1.1	0.9	2.9	0.7	+
	12	5.0	0.0	0.0	22.2	6.50	15	2.64	4.48	4.84	3.04	1.0	0.7	2.4	0.8	+
	13	4.6	0.4	0.4	22.2	11.30	15	6.58	6.76	1.58	0.10	0.9	0.3	1.5	1.0	+
	14	4.5	0.5	0.4	11.1	5.87	15	2.15	4.09	5.29	3.47	0.8	0.7	2.2	0.8	+
	15	4.8	0.2	0.0	11.1	5.70	15	1.84	3.80	5.87	3.49	1.1	0.7	2.5	0.5	+
	16	4.8	0.2	0.0	11.1	3.87	15	1.22	2.83	3.72	7.23	1.2	0.4	2.0	0.6	—

^a The Roman numerals have the same meaning as in Table III.

^b + = presence; — = absence of free formaldehyde in the product.

ture during the process, in the postreaction mixture, and after distilling water and catalyst off,

- epoxy equivalent in the aqueous medium with or without PHMM present,
- ^1H NMR spectra of the reaction mixture at each stage of the synthesis, and
- content of the side and subsequent products of reactions of oxirane with water as determined by gas-liquid chromatography (GLC).

The reaction route was determined by analysis of ^1H NMR spectra of reaction products mostly in the range of 4–9 ppm. The signals present in the spectra have been listed in Table I of Lubczak.¹ Table IV summarizes the results of calculations of formaldehyde content at different reaction states, i.e., the formaldehyde in the form of hydroxymethyl groups blocked with at least two oxirane molecules or engaged in dimethylether links (referred to as *a*), formaldehyde O-linked or free formaldehyde in the postreaction mixture (*b*), and the same as in *b*, but in the product after water/catalyst have been distilled off (*c*).

The assumption was made that during distillation of water/catalyst only the formaldehyde in *N*- or *O*-hydroxymethyl group leaves the system and that reaction 3 does not occur. The latter condition is met when distillation temperature does not exceed ca. 40°C. Then *N*-hydroxymethyl groups blocked with just one oxirane molecule remain stable. The groups blocked with more than one oxirane molecule are stable at any temperature.

The course of reaction between PHMM and oxiranes in water is illustrated in Figures 1 and 2. In each there are following three curves:

1. change of epoxy group concentration due to reactions of oxiranes with PHMM and water (solid line),
2. change of epoxy group concentration due to reactions of oxiranes with water in the absence of PHMM (broken line),
3. change of hydroxymethyl group concentration (as deduced from free formaldehyde content) due to their reactions with oxiranes and due to condensation (initially solid line that changes to broken one at the point when formaldehyde starts to discharge according to reaction 3).

At the very beginning of reaction the system remained heterogeneous due to limited solubility

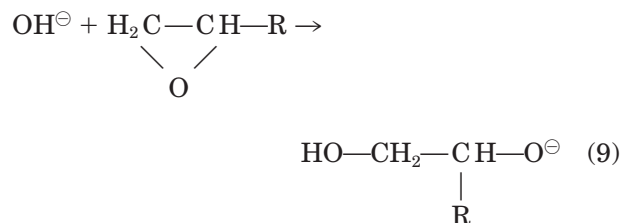
of PHMM in water. Hence, the concentration measurements were performed only after the reaction system became homogeneous. The curves extrapolated to that time are dotted lines.

One can notice that in some plots the content of hydroxymethyl groups smoothly reduces and at certain times the concentration starts to change irregularly. This happens when formaldehyde is blocked with just one oxirane molecule from having a chance to evaporate (according to reaction 3). These fluctuation in formaldehyde content occurred in the systems with the molar ratio of PHMM : PO equal to 1 : 12 or 1 : 15. In the latter case it took place only under the conditions that favored formation of propylene glycol (large excess of water, high temperature; see Tables III and IV). Formaldehyde release was observed for all PHMM : EO = 1 : 15 systems. Hence, even this large EO excess was still insufficient to block hydroxymethyl groups. The reason was the reaction of EO with water.

The presence of water affected the rate at which hydroxymethyl groups reacted. It was smaller than that observed in nonaqueous medium. Here again the competitive reaction of oxirane with water was responsible as well as the equilibrium that existed between *N*-hydroxymethyl groups and free formaldehyde (see reaction 2).

Further increase of EO excess resulted in stabilization of more and more hydroxymethyl groups but nevertheless some release of formaldehyde was observed.

A wealth of information on the reaction of PHMM with oxiranes provided the analysis of the system without the PHMM (which was replaced by the same amount of an inert component, namely dioxane). It is worth noticing that in solutions with a small amount of catalyst, oxiranes are consumed more rapidly than in the presence of PHMM (!), (see Figs. 1b, 1e, and 2d). This anomaly can be explained as follows. At low catalyst content, the main transformation that undergoes in the system is the reaction with water:



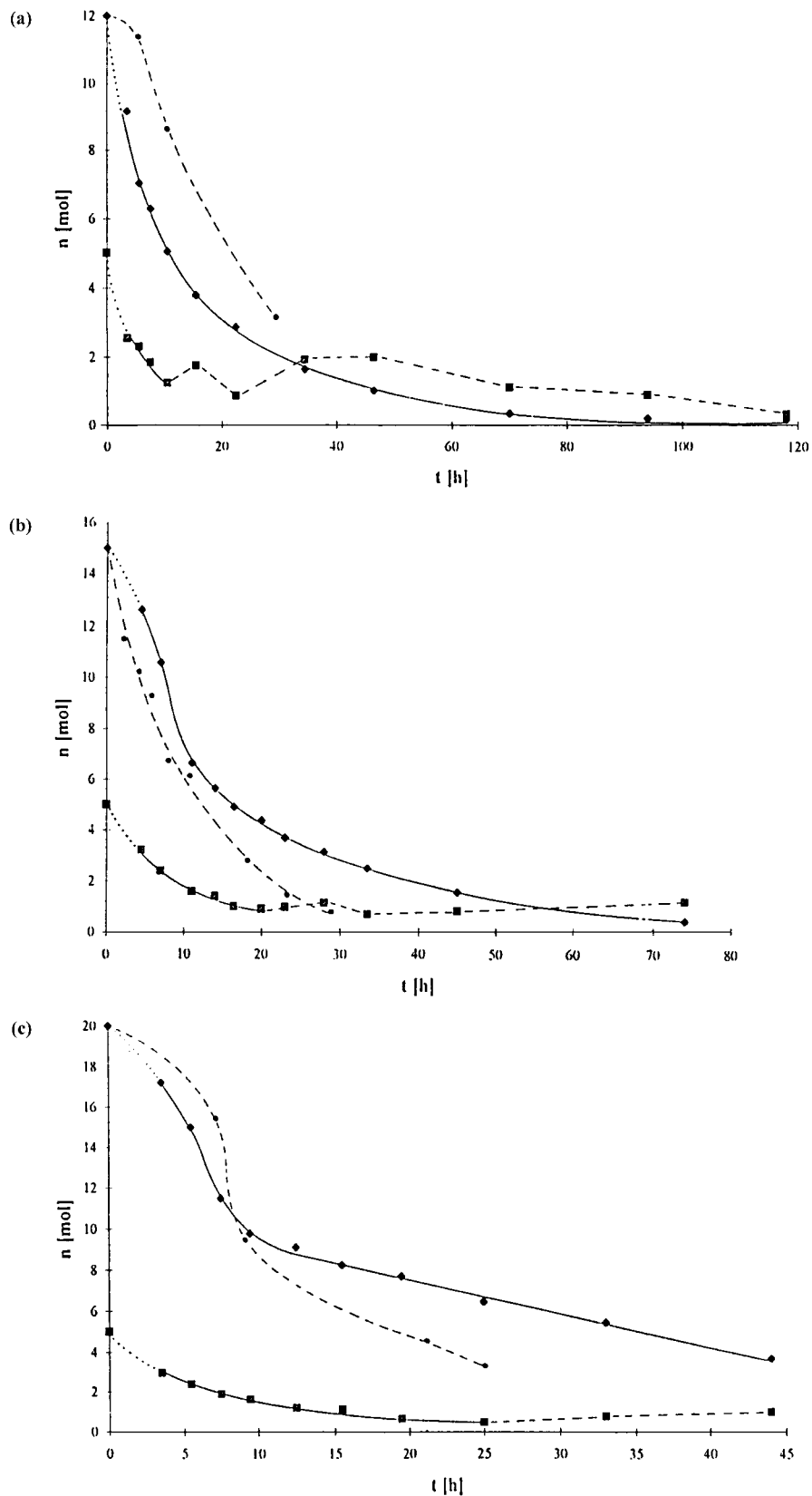


Figure 1 The course of reaction between 1 mol of PHMM and (a) 12 mol PO, 400 cm³ H₂O, and 13 cm³ TEA at 50°C; (b) 15 mol PO, 400 cm³ H₂O, and 13 cm³ TEA at 50°C; (c) 20 mol PO, 400 cm³ H₂O, and 13 cm³ TEA at 50°C; (d) 15 mol PO, 800 cm³ H₂O, and 13 cm³ TEA at 50°C; (e) 15 mol PO, 200 cm³ H₂O, and 13 cm³ TEA at 50°C; (f) 15 mol PO, 400 cm³ H₂O, and 13 cm³ TEA at 40°C; (g) 15 mol PO, 400 cm³ H₂O, and 13 cm³ TEA at 60°C; (h) 15 mol PO, 400 cm³ H₂O, and 25 cm³ TEA at 50°C; (i) 15 mol PO, 400 cm³ H₂O, and 50 cm³ TEA at 50°C; (j) 15 mol PO, 400 cm³ H₂O, and 100 cm³ TEA at 50°C.

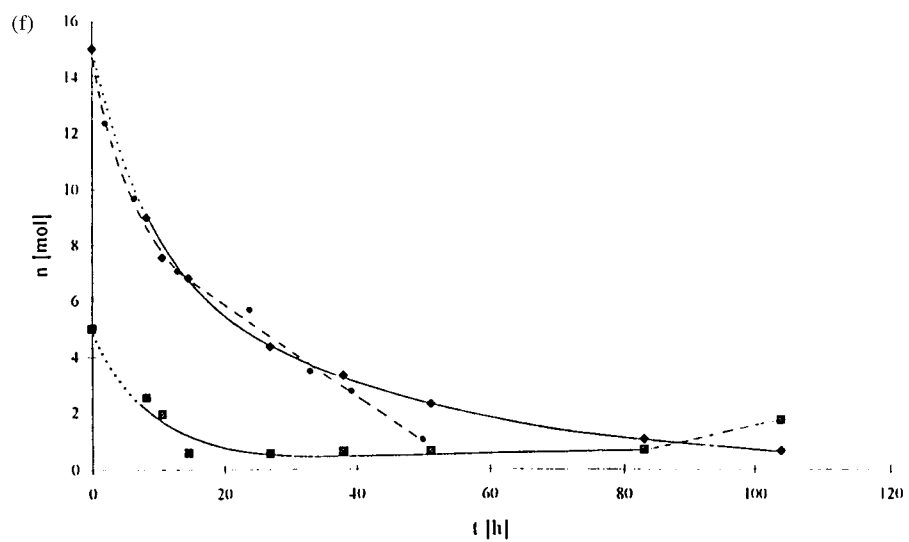
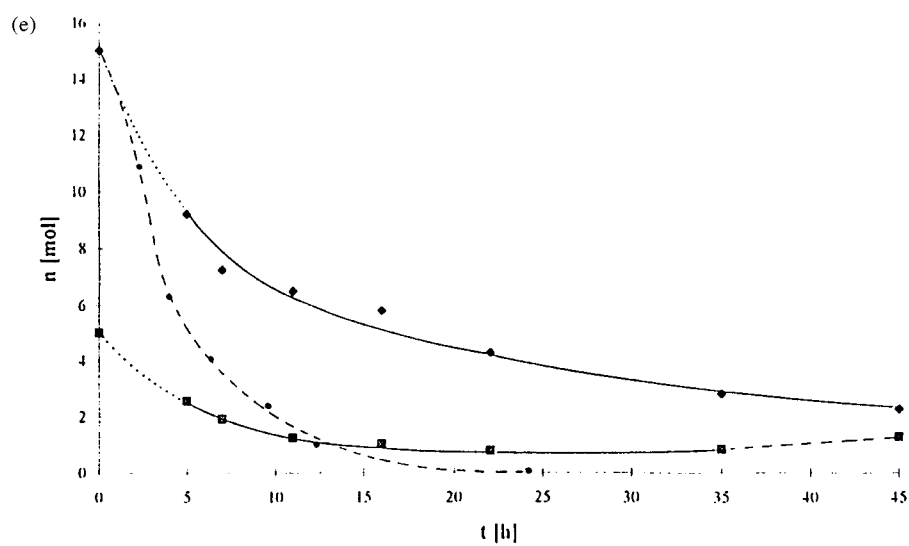
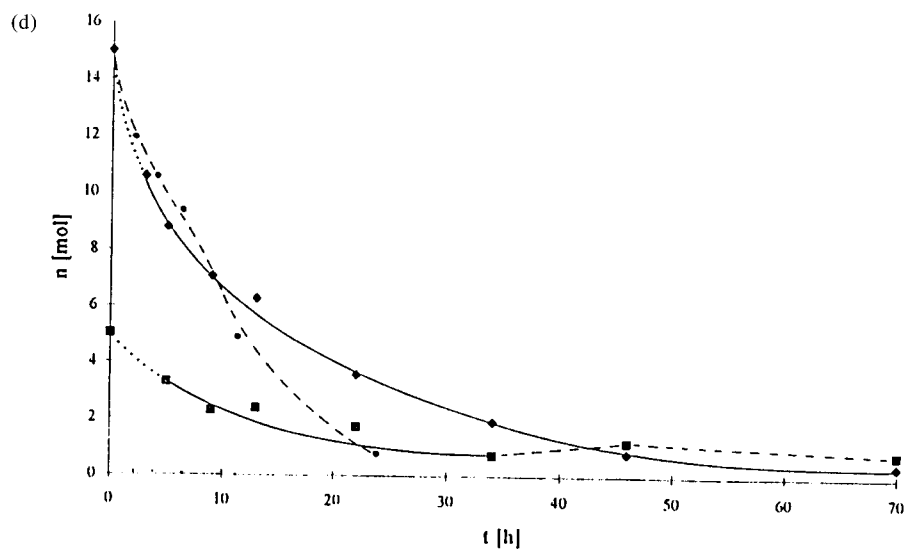


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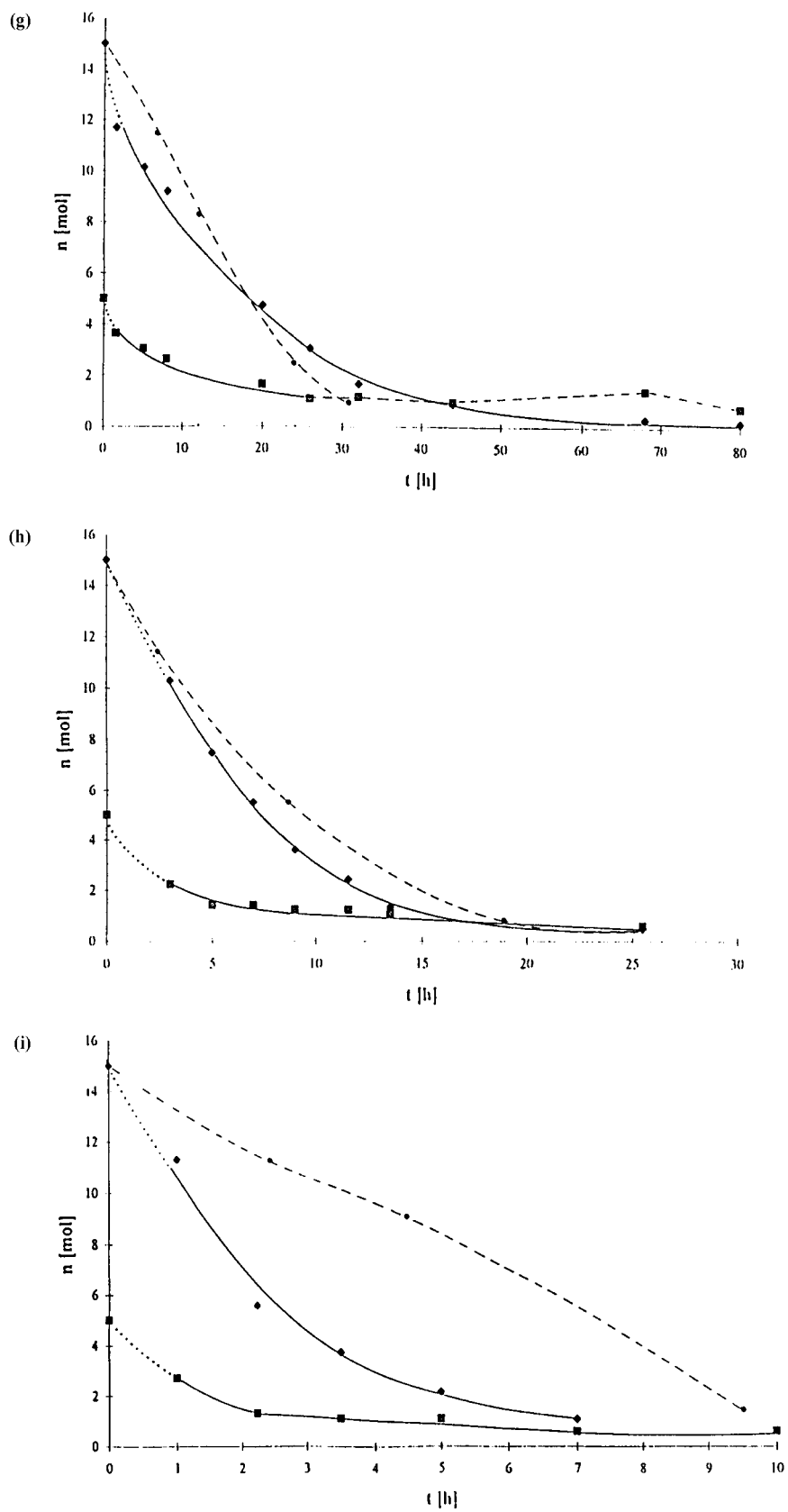


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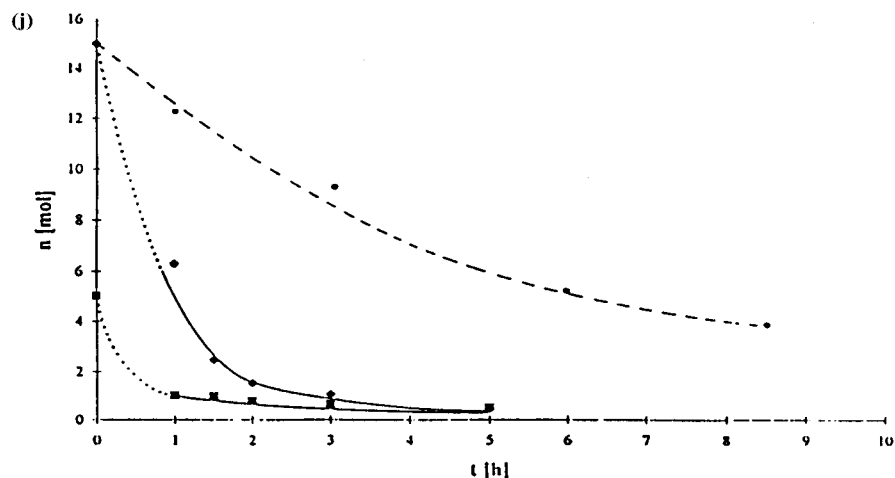
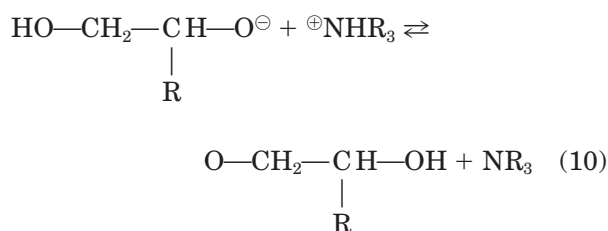
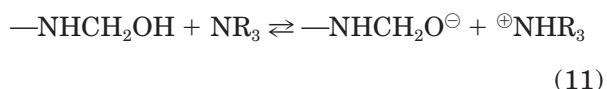


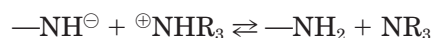
Figure 1 (Continued from the previous page)



and subsequent reactions favoring formation of glycols and polyglycols. The large amount of subsequent products (Tables III and IV) confirmed that glycols, once formed, reacted more readily with oxiranes than N-hydroxymethyl groups. It seemed that anions formed from hydroxymethyl groups according to:



more readily released formaldehyde:



than they were able to accept oxirane molecules to become blocked. Because of being stabilized by the aromatic *s*-triazine ring, the anion $\text{:}\ddot{\text{N}}\text{H}^\ominus$ formed by dissociation of hydroxymethyl group was in reactions with oxiranes much less reactive than $\text{NHCH}_2\text{O}^\ominus$ anion. An increase of content of these latter anions could be affected by increasing catalyst content. Only then, they could compete with hydroxy groups in reactions with oxiranes.

The content of side products in the reactions of oxiranes with water was determined by GLC after water/catalyst had been removed. The chromatograms of the postreaction mixtures obtained without PHMM contained, beside the low-molecular glycols, also peaks due to polyglycols. These polyglycols have not been found in the products obtained with PHMM present (Table II).

The effect of the following factors on the composition of reaction mixtures in the synthesis of polyetherols based on PHMM have been verified:

- initial PHMM : PO molar ratio,
- water content,
- temperature, and
- catalyst (TEA) content.

An increase of PO content resulted in a larger amount of diol and subsequent reaction products of oxirane with water in reaction mixture. Although at the molar ratio of PHMM : PO = 1 : 12, ca. 8 mol of PO was found reacted with PHMM, further increase of oxirane excess yielded only a moderate increase in bounded PO to at most ca. 9 mol (Table IV). This was the reason why we did not go beyond the ratio of 1 : 15 for both EO and PO.

The amount of water had the key effect on the efficiency of the synthesis. Water excess favored PO hydration, whereas a decrease of its content led to an increase of proportion of higher glycols among side products (see Tables III and IV, runs 2, 4, and 5). On the other hand, a drop of water concentration below 11 mol per mol of PHMM was disadvantageous because of difficulties in dissolu-

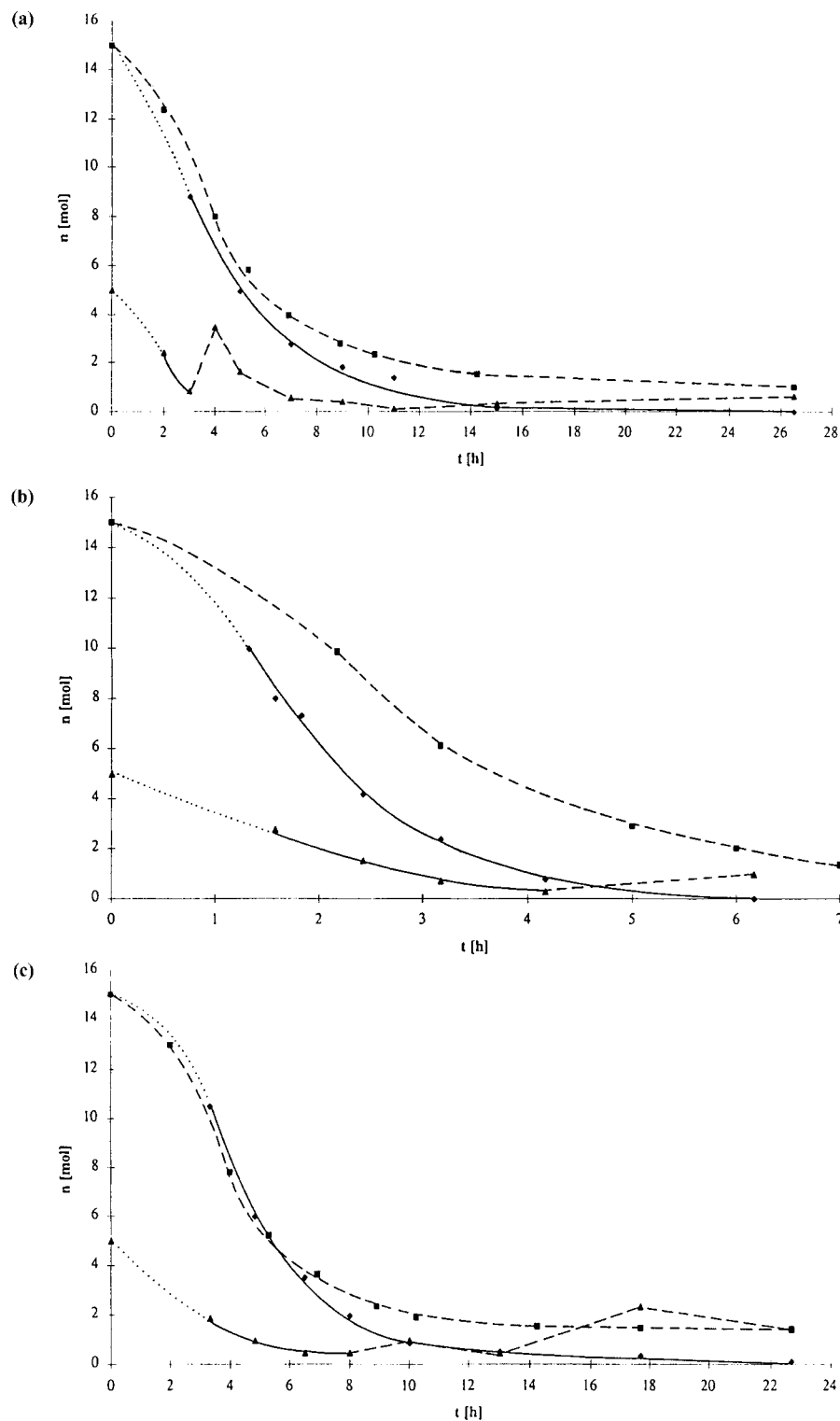


Figure 2 The course of reaction between 1 mol of PHMM and 15 mol EO with (a) 400 cm³ H₂O and 13 cm³ TEA; (b) 200 cm³ H₂O and 20 cm³ TEA; (c) 200 cm³ H₂O and 13 cm³ TEA; (d) 200 cm³ H₂O and 6 cm³ TEA; all carried out at 40°C.

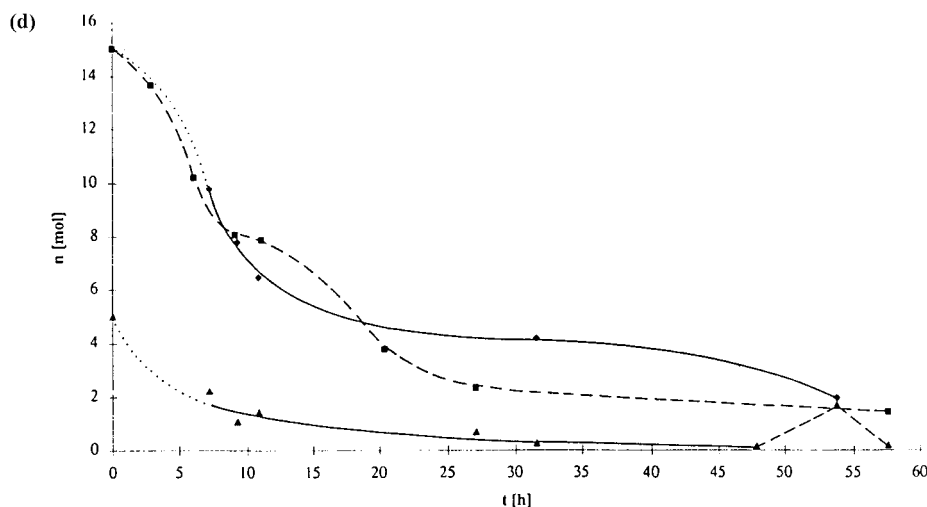


Figure 2 (Continued from the previous page)

tion of the latter and hence better conditions for PO hydration.

Similar effects of the synthesis conditions on the composition of products were observed for EO-PHMM systems (see Table IV, runs 11–16).

The best temperature of synthesis with respect to the yield of polyetherol was 40°C for EO and 50°C for PO. At temperatures lower than the optimal ones, more side products were formed, whereas at higher temperature than optimal, the condensation reactions started to take over.⁵

The catalyst concentration had also a significant effect on the course of reaction. Too large catalyst concentration shifted the equilibria in reactions 11 and 12 towards the poorly reactive amino groups, thus favoring oxirane hydration (Tables III and IV, run 10). At the same time, hydroxy ion formed in reaction 8 catalyzed condensation of hydroxymethyl groups with amino ones. This was the reason why signals of amino protons were absent in ¹H NMR spectra (Table IV, runs 9 and 10). A small amount of catalyst did not prevent formation of amino groups according to reaction 7, and the condensation of this reaction was poorly catalyzed with hydroxymethyl groups. Therefore, the amino groups could be found in the products of PO polyetherol synthesis, particularly in those obtained with a small catalyst concentration.

As mentioned previously, the increasing amount of TEA made the reaction 11 of hydroxymethyl groups with catalyst, which in effect led to formation of polyetherols, to compete with formation of propylene glycol and its subsequent products. At the same time, the extent of condensation

reaction increased. These conclusions could be drawn basing on ¹H NMR spectra where signals at 4.5 and 4.6 ppm appeared from dimethylether (>N—CH₂—O—CH₂—N<) and methylene (>N—CH₂—N<) bridges, respectively. The latter had not been present in the spectra of analogous products obtained in DMSO.¹

Similar effect of catalyst concentration was observed in the system PHMM-EO. The amount of 20 cm³ of TEA per mol of PHMM, however, suitable in the reaction with PO, was too large for the system involving EO. Unfortunately, a reduction of catalyst concentration did not result in a reduction of side products, which remained disappointingly large.

By optimizing the catalyst concentration, a reduction of the extent of PO hydration could be reduced from 50 to a mere 20 wt % without affecting the condensation reaction. The polyetherol obtained at these optimal conditions (Tables III and IV, run 9) could be used as a raw material for manufacturing heat-resistant polyurethane foams without additional treatment.

CONCLUSIONS

The chromatographic analysis of the products of reaction between PHMM and oxiranes carried out in aqueous solutions revealed that the synthesis of *s*-triazine containing polyetherols is accompanied by oxirane hydration leading to formation of glycols and polyglycols in the amount reaching as much as 50 wt %.

The fraction of side products in the polyetherols obtained from PHMM and PO can be reduced to 20 wt % by adjusting TEA catalyst concentration and carrying the synthesis at 50°C in an autoclave.

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