

Synthesis of Polyetherols from Melamine and Propylene Carbonate. II

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ABSTRACT: Results of the reaction of melamine with propylene carbonate in the synthesis of polyetherols with 1,3,5-triazine rings are presented. Optimal conditions of synthesis of the polyetherols are presented and the products characterized by determining selected physical properties and by using spectral methods [$^1\text{H-NMR}$, IR, mass spectroscopy (MS) electrospray ionization (ESI)]. The content of side prod-

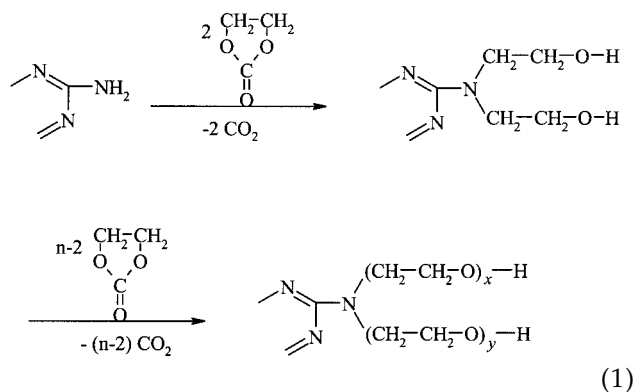
ucts was established by GLC. The resulting polyetherols have been found suitable for preparation of polyurethane foams of improved thermal stability. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 104–115, 2003

Key words: mass spectrometry; oligomers; structure-property relations

INTRODUCTION

From the studies conducted by us so far,¹ it follows that polyetherols containing *s*-triazine rings can be obtained in reactions of melamine with an appropriate excess of ethylene carbonate. The catalysts in these reactions are potassium carbonate or hydroxide or diazabicyclo[2.2.2]octane (DABCO). Similar polyetherols have so far been obtained in reaction of melamine² or its derivatives^{3,4} with an excess of oxiranes, such as ethylene oxide, propylene oxide, or glycerin epichlorohydrin. The reactions were carried out in dimethylsulfoxide (DMSO) or dimethylformamide solutions and the solvent had to be distilled off after the reaction under reduced pressure. The resulting polyetherols were often contaminated with the products of the solvent decomposition. The other disadvantage was the use of oxiranes that were highly flammable and toxic. The reactions had to be carried out in autoclaves.

It turned out that replacing ethylene oxide with ethylene carbonate yielded reactions with melamine products of exactly the same structure that were formally the adducts of melamine with ethylene oxide:



No solvent was needed in these reactions because melamine not only reacted, but also dissolved well, in this reagent at elevated temperatures.

We expected similar reactions to be possible between melamine and propylene carbonate. Results of the study on this reaction are presented in this article.

EXPERIMENTAL

Syntheses

In a 250-cm³ three-necked flask equipped with a mechanical stirrer reflux condenser and thermometer, 3.2 g (0.025 mol) melamine (Kędzierzyn Koźle, Chemical Plant, Poland) and a predetermined amount of propylene carbonate (Avocado, Chemicals for Research and Development, Germany) (the molar excess of propylene carbonate over melamine was 6, 12, 18, 20, and 22) and catalyst [the following catalysts were used: potassium carbonate (Polish Chemical Reagents, POCH, Gliwice, Poland) (8 g/mol of melamine); po-

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TABLE I
Diols Used as Calibration Standards in GLC Analysis of Side Products Formed in the Reactions of Melamine with Propylene Carbonate (PC)

Reaction	Formula	Name	Calibration line coefficients		Correlation coefficient	Retention time, R_t
			a	b		
PC + H ₂ O	$\begin{array}{c} \text{CH}_2-\text{CH}-\text{CH}_3 \\ \quad \\ \text{OH} \quad \text{OH} \end{array}$	Propane-1,2-diol (PD)	0.283	0.488	0.997	2.92
PD + PC	$\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}-\text{CH}_3 \\ \qquad \qquad \\ \text{OH} \qquad \qquad \text{OH} \\ \text{CH}_3-\text{CH}-\text{CH}_2-\text{O}-\text{CH}-\text{CH}_3 \\ \qquad \qquad \\ \text{OH} \qquad \qquad \text{CH}_2\text{OH} \end{array}$	4-Oxaheptane-1,6-diol (OHD) 2-Methyl-3-oxaheksane-1,5-diol (MOHD)	0.165	0.192	0.995	4.23

tassium hydroxide (Polish Chemical Reagents) (8.16 or 32 g/mol of melamine); DABCO (Avocado) (4, 8, 16, 24, or 32 g/mol of melamine)] were placed. The contents of the flask were heated to 175–180°C (reactions were also carried out in the temperature ranges 170–175 and 180–185°C) and kept in this range until carbon dioxide stopped to be released and then for another hour. The end of the reaction was established by determining the amount of unreacted propylene carbonate. The reaction was carried out under nitrogen.

Analytical methods

The conversion was established by carefully controlling the mass balance and by determining the amount of propylene carbonate by titrating it with barium hydroxide. Other properties of polyetherols that have been determined were the hydroxyl number,⁵ pycnometric density,⁶ Höppler viscosity, ring-detach surface tension, and refractive index. The content of melamine in precipitating solids was determined by using the Swann and Esposito method.⁷

¹H-NMR (80 MHz, BS-586A spectrometer, Tesla Czechoslovakia, *d*₆-DMSO solution, HMDS internal standard), IR (Paragon 1000 FTIR spectrometer, Perkin-Elmer, UK), and MS ESI (Fennigan MAT 95S spectrometer, Germany, reversed geometry, methanol solutions) spectra were recorded.

GLC analysis [Hewlett Packard 5890 chromatograph, USA, 10 m capillary column HP-FFAP, temperature profile 50–180°C at 20 deg/min, 180°C (5 min) 180–220°C at 30 deg/min, He inert gas at 18.3 cm³/min; sample 0.2 μdm³] was performed to analyze the composition of side products (mono- and dipropylene glycols). The calibration parameters and retention times of the glycols are listed in Table I.

The thermal properties of the products were determined by using a Paulik-Paulik system derivatograph (MOM, Hungary, sample 0.5 g, temperature range

20–1000°C, nitrogen atmosphere, registration time 100 min, amplification DTA 1/15, DTG 1/10).

RESULTS AND DISCUSSION

Synthesis of polyetherols

In our previous article,¹ we found that melamine dissolves well in ethylene carbonate at an elevated temperature. The dissolution was accompanied by a chemical reaction. The resulting solutions were polyetherols with *s*-triazine rings. The same procedure can be applied to the pair, melamine-propylene carbonate. The reagents were initially mixed in a ratio of 1 : 6 in the presence of potassium carbonate, previously found to be a good catalyst of melamine oxyethylation with ethylene carbonate.¹ The reaction was carried out at 175–185°C (Table II, rows 1–3). Under these conditions, however, melamine did not fully dissolve and some unreacted melamine (as verified by ¹H-NMR) was present in the flask even after all propylene carbonate had fully reacted. More solid precipitated upon cooling. The solid was a mixture of hydroxypropyl derivatives of melamine and melamine itself (again as verified by ¹H-NMR, cf. Fig. 1). The amount of unreacted melamine was determined in the solid and the results are listed in Table II. Similar results were obtained in reactions carried out with a larger excess of propylene carbonate, and in the presence of potassium hydroxide catalyst (Table II, rows 4–8).

Positive results were obtained in the presence of DABCO and KOH (used at the weight ratio 8 : 1). Melamine had fully dissolved NMRHH, but after some time, a solid precipitated from reaction mixture, again. The use of DABCO catalyst alone provided full dissolution of melamine. With this catalyst, the amount of precipitated solid decreased with increasing excess of propylene carbonate. In fact, no solid appeared after the reaction at 20-fold molar excess of

TABLE II
The Conditions of Reaction of Propylene Carbonate (PC) with Melamine (MEL)

Run	Initial molar ratio MEL : PC	Catalyst	Catalyst concentration (g/mol MEL)	Temperature (°C)	Reaction time (h)	Number of moles of PC per mole of MEL that		Remarks
						Reacted with MEL	Decomposed and left reactor	
1	2	3	4	5	6	7	8	9
1	1 : 6		8	175–185	3	5.5	0.5	Melamine did not solubilize completely
2	1 : 12		8	175–185	10	10.6	1.4	As above, from liquid part a solid precipitates containing with 48% wt MEL
3	1 : 18	K ₂ CO	8	175–185	12	17.7	0.3	As above, from liquid part a solid precipitates containing with 50 wt % MEL
4	1 : 6		16	175–185	4	5.4	0.6	Melamine not dissolved completely
5	1 : 12		8	175–185	5	11.33	0.67	As above, from liquid part a solid precipitates containing with 44 wt % MEL
6	1 : 18	KOH	8	175–185	7	17.18	0.82	As above, from liquid part a solid precipitates containing with 53 wt % MEL
7	1 : 20		16	175–185	8	17.96	2.04	As above, from liquid part a solid precipitates containing with 48 wt % MEL
8	1 : 22		32	175–185	8	19.65	2.35	As above
9	1 : 22	DABCO + KOH	32 + 4	170	8	19.65	2.35	Melamine solubilizes completely, solid precipitates from liquid part
10	1 : 16	DABCO	32	170	12	14.8	1.2	As above
11	1 : 18		4	170	12	16.44	1.56	As above
12	1 : 18		8	170	6.5	16.55	1.45	As above
13	1 : 18		24	170	4.5	16.28	1.72	As above
14	1 : 18		32	170	4	16.32	1.68	As above
15	1 : 20		16	170	10	18.14	1.86	As above
16	1 : 20	DABCO	24	170	8	18.31	1.69	Melamine solubilizes completely, solid did not precipitate
17	1 : 20		32	170	6	18.43	1.57	As above
18	1 : 22		32	175–185	5	19.27	2.73	As above

melamine and at a catalyst concentration of 24 g/mol of melamine (Table II, row 6).

The reaction was monitored by following the amount of carbon dioxide released from the system. The end of the reaction was established by checking the amount of unreacted propylene carbonate.

As follows from the data in Table II, the total weight of the postreaction mixture is somewhat smaller than that calculated from the initial content of reagents. It is caused by partial decomposition of propylene carbonate to propylene oxide at the initial stages of the process when the system is still heterogenic.

Decomposition is promoted by the structure of reagent, high temperature, and basic medium.⁸ In the case of ethylene carbonate, no such decomposition was observed.¹

Thus, to obtain a product of desired molar ratio of melamine-to-propylene carbonate, a somewhat higher excess of the latter has to be used than follows from stoichiometry. Besides, one has to take into account the presence of a small amount of water in this hygroscopic system. Water reacts with propylene carbonate to propan-1,2-diol, and the latter further reacts to yield dipropylene glycol, and so on. This problem will be discussed later on in this article.

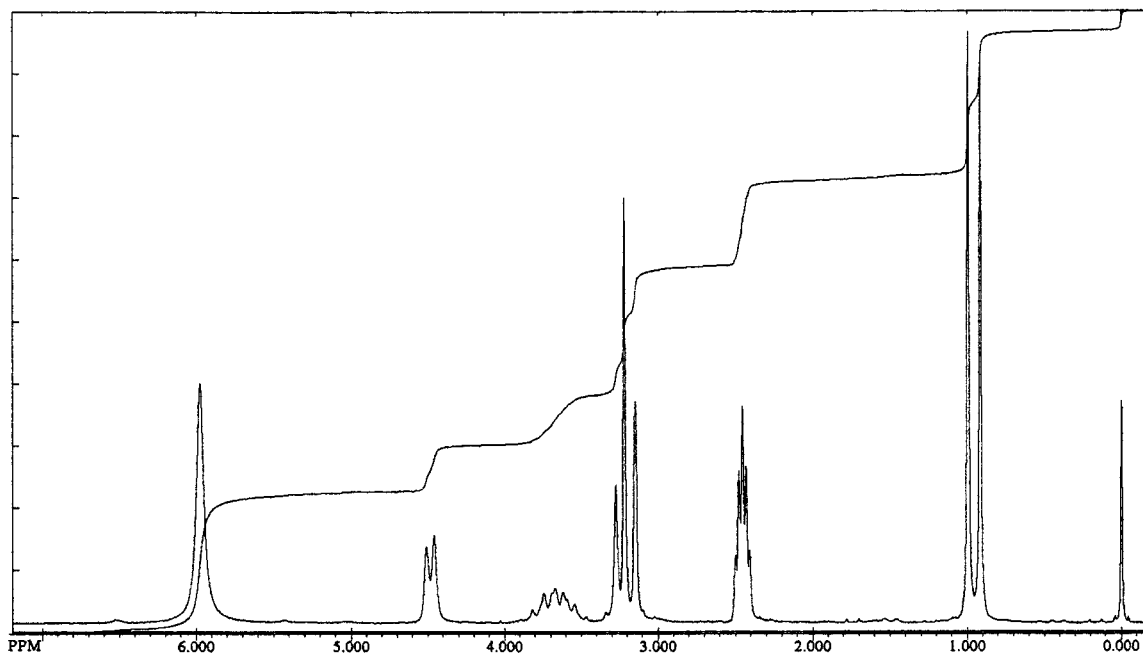


Figure 1 $^1\text{H-NMR}$ spectrum of the solid which precipitates after reaction of 1 mol melamine (MEL) with 19.5 mol of propylene carbonate (PC).

Spectral analysis of products

The course of reaction was followed by $^1\text{H-NMR}$ analysis of its products. In the spectrum of propylene carbonate, the signals are observed at 1.2–1.4 ppm doublet of methyl group, 4–4.5 ppm multiplet due to methylene group (isomers R and S), and 4.7–5 ppm multiplet due to the methine group (isomers R and S) in Figure 2. Because the signal from methyl protons in propylene carbonate has a different chemical shift

than that of methyl groups in the products, the lack of signal at 1.2–1.4 ppm indicates a full conversion of propylene carbonate.

In the spectra of the products, one can distinguish signals in Figure 3 at 0.9–1.1 ppm from methylene groups of both normal and abnormal products [(cf. eq. (7)), 2.9–4.0 ppm from protons of groups $-\text{CH}_2$ and $-\text{CH}$ in the normal and abnormal products, 4.55 ppm multiplet from protons of methine group in the grouping⁹:

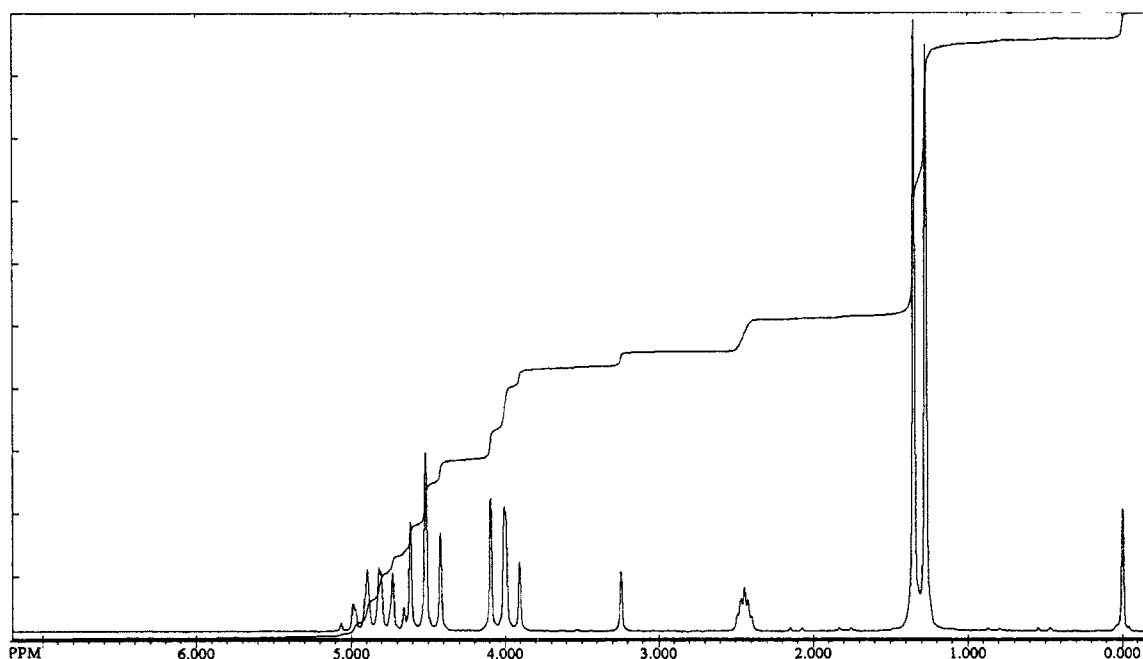
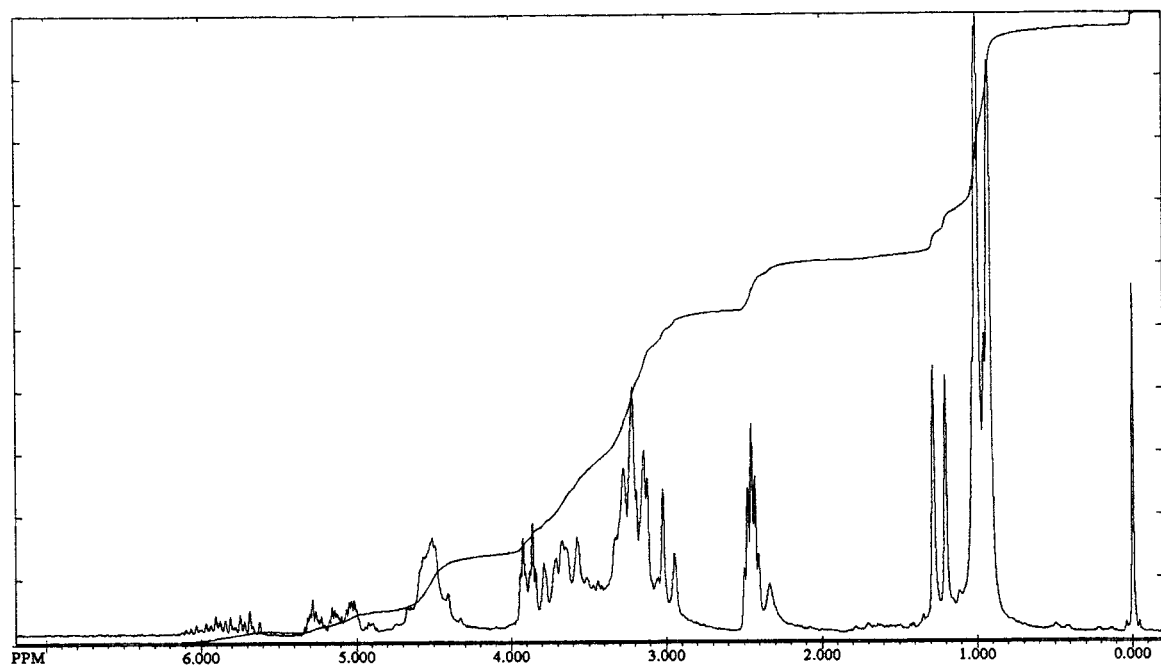
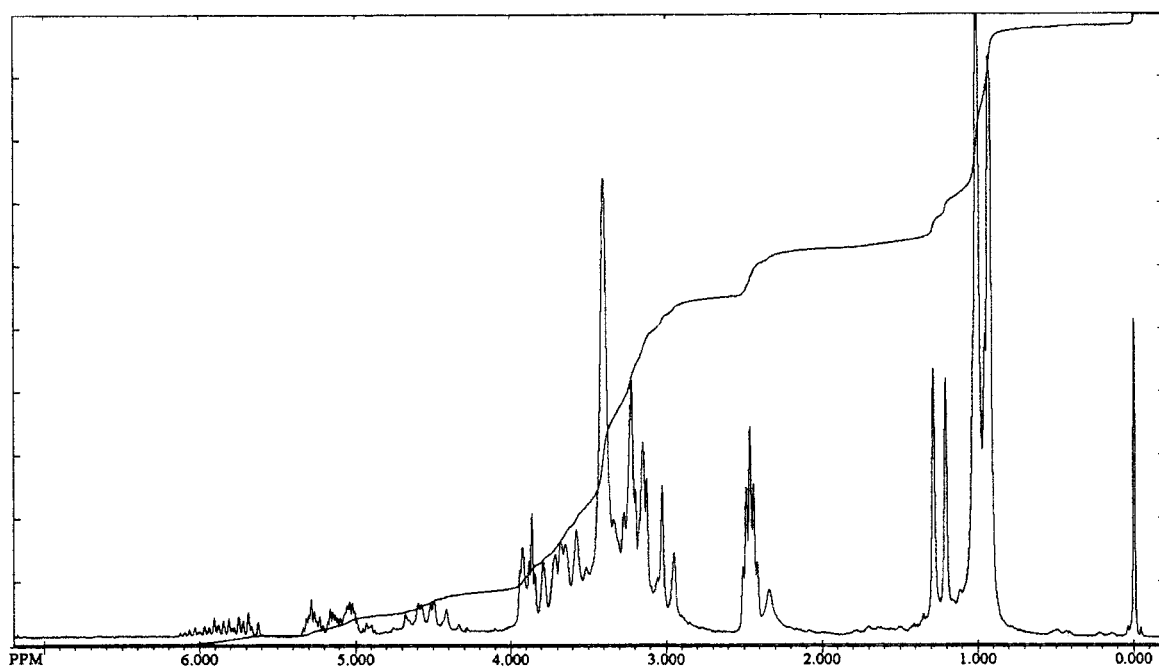


Figure 2 $^1\text{H-NMR}$ spectrum of propylene carbonate.

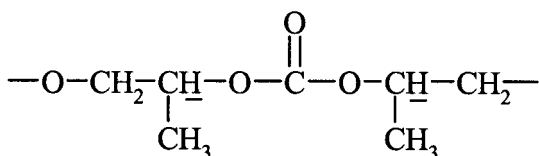


(a)



(b)

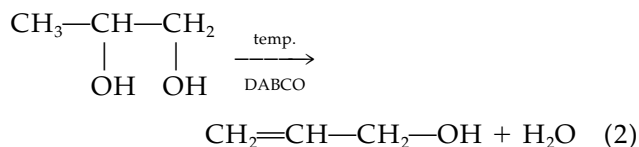
Figure 3 (a) $^1\text{H-NMR}$ spectrum of the reaction product MEL : PC = 1 : 22, 32 g DABCO/mol MEL, temperature 175°C . (b) $^1\text{H-NMR}$ spectrum of the reaction product MEL : PC = 1 : 22, 32 g DABCO/mol MEL, temperature 175°C , D_2O .



The last signal is overlapped by that from the hydroxyl groups; the intensity of the latter reduces in the presence of heavy water [Fig. 3(a)].

In the spectra reaction products of melamine with propylene carbonate, a multiplet at 5–6 ppm is also

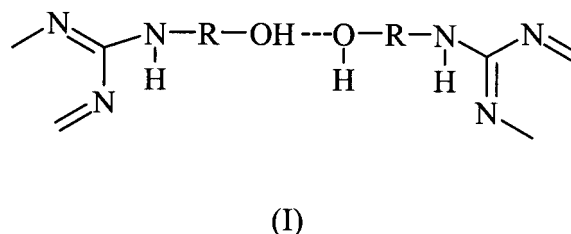
present because of the protons at the double bonds of allyl groups formed from α -hydroxyl groups:



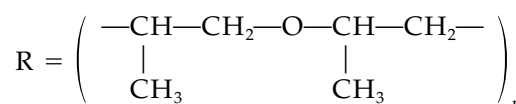
The presence of this compound is also found in the spectra of the distillate removed after completion the reaction. The presence of signals from propylene glycol [compare Fig. 4(a), with Fig. 4(b and c)] was also seen in the same spectra. The relevant multiplet is absent in the distillate obtained at reduced pressure ($p = 22$ mmHg, temp. = 160°C , Fig. 5). No glycol was found in the products obtained under nitrogen and with continuous removal of low-molecular-weight products (Fig. 6).

In the spectrum of the product purified under reduced pressure, a signal at 6.1 ppm from unreacted protons of amino group can be seen (Fig. 5). This means that hydroxyl groups react with propylene carbonate more readily than amino groups. Furthermore, the etherol chains hinder the access of the reagent to amino groups. As, however, the reaction is carried out with simultaneous removal of low-molecular-weight compounds, all amino protons in melamine become blocked (compare Fig. 5 with Fig. 6). The reason seems to be that water formed in reaction 2 is readily removed and does not react with propylene carbonate to propane-1,2-diol or a product of its further oxypropylation. Hence, less propylene carbonate reacts in side reactions and more propylene carbonate reacts with melamine.

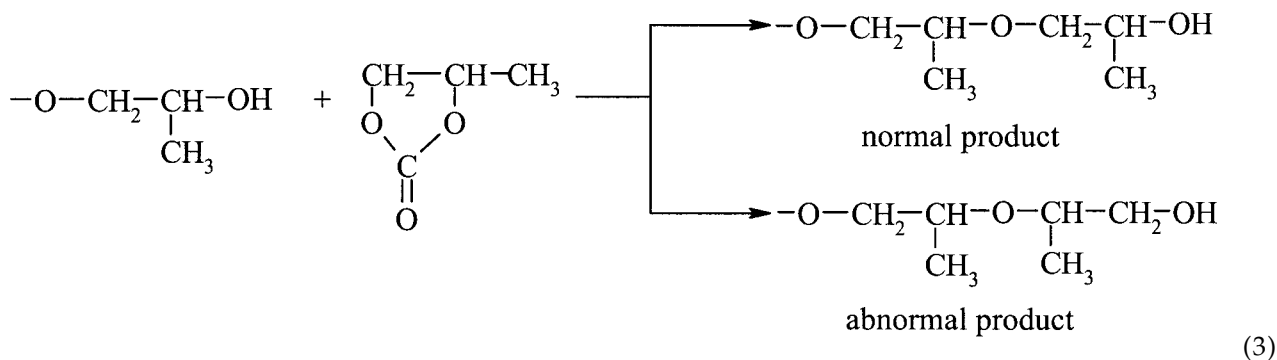
The structure of products was also analyzed by examining IR spectra. In the spectra of the products of reaction of melamine with propylene carbonate, no bands at 3330 and 3130 cm^{-1} are present because of stretching symmetric and antisymmetric vibrations of $-\text{NH}_2$ group. A band at 3400 cm^{-1} appears instead because of stretching vibrations of $-\text{OH}$ groups. The band is intense and wide (cf. Fig. 7), suggesting the existence associates of the structure:



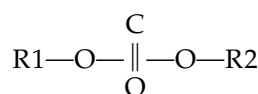
with



In IR spectra, the following band can also be distinguished: at 1052 cm^{-1} from stretching vibrations of $-\text{C}-\text{O}$ in primary alcohols; at 1088 cm^{-1} from stretching vibrations of $-\text{C}-\text{O}$ in secondary alcohols, thus indicating that both normal and abnormal products are formed in the reaction. The same conclusion has been drawn from $^1\text{H-NMR}$ spectra where the signal from protons of methyl group of the normal and abnormal products appears at 0.9 and 1.2 ppm, respectively, and(3)



Further bands in IR spectra are those at ~ 1130 cm^{-1} related to asymmetric stretching vibrations typical for ether links (slightly hidden under the slope of the band at 1088 cm^{-1}); 1730 cm^{-1} due to carbonyl group in the ester groups:



These groups are formed in the reaction(4)

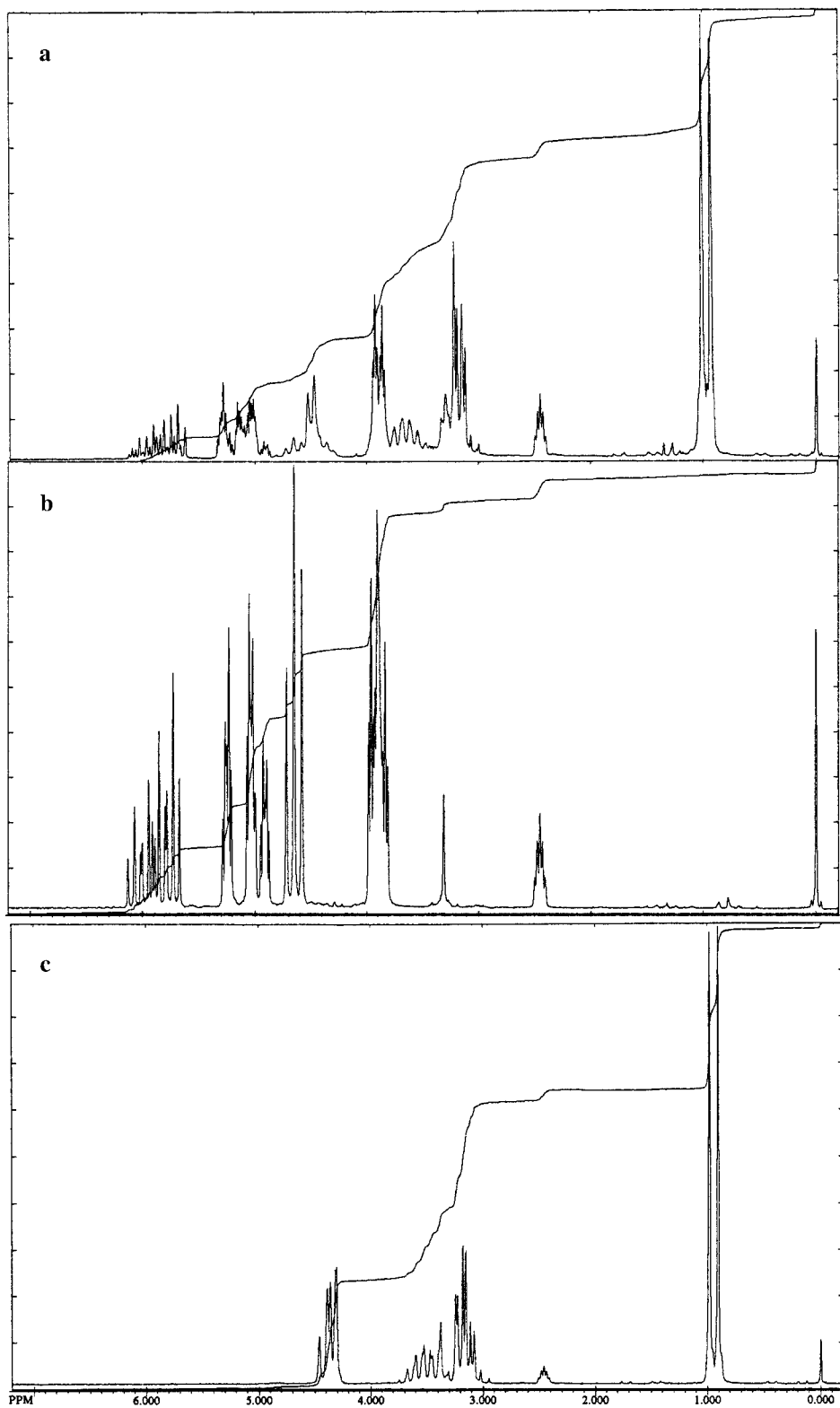


Figure 4 $^1\text{H-NMR}$ spectrum of distillate obtained after vacuum distillation of reaction product of 1 mol melamine with 22 mol PC 32 g DABCO/mol MEL 175–185°C (a), allyl alcohol (b), propane-1,2-diol (c).

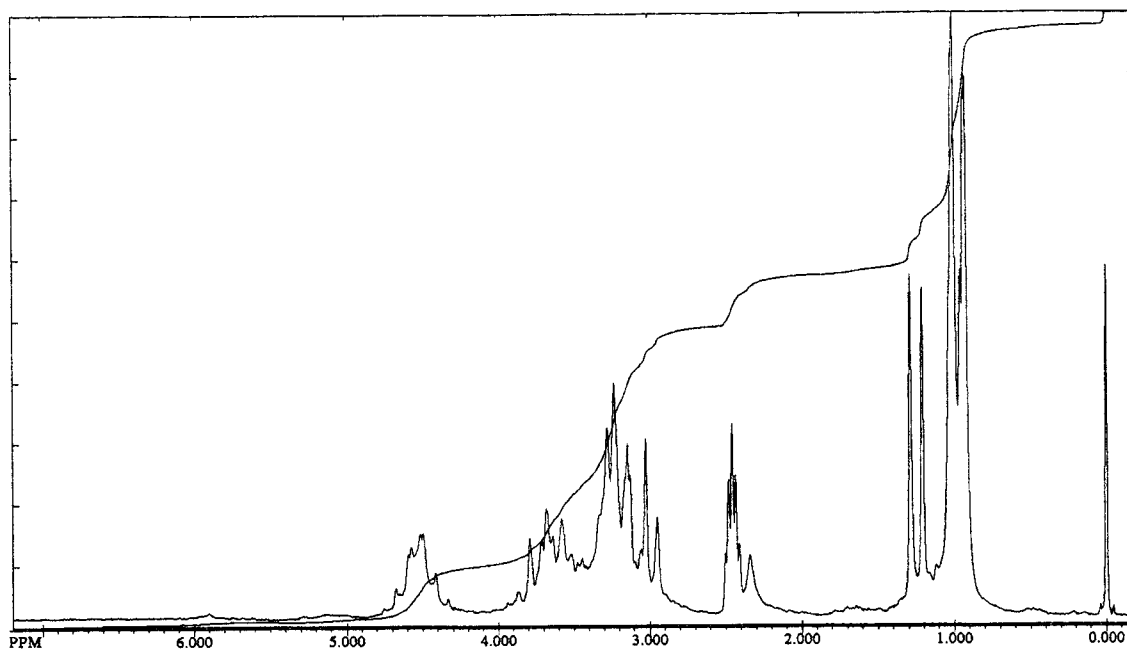
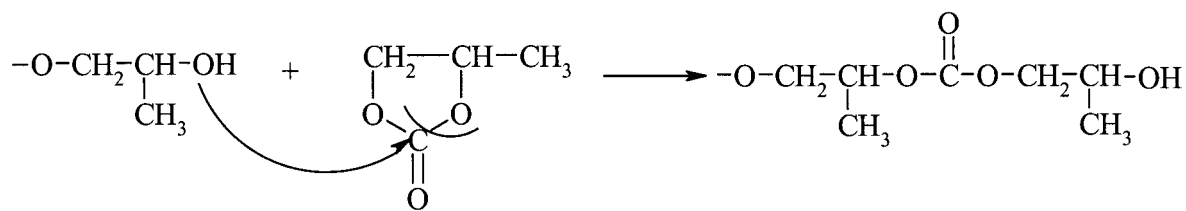


Figure 5 $^1\text{H-NMR}$ spectrum of the reaction product MEL : PC = 1 : 22, 32 g DABCO/mol MEL, temperature 175°C , after vacuum distillation.



(4)

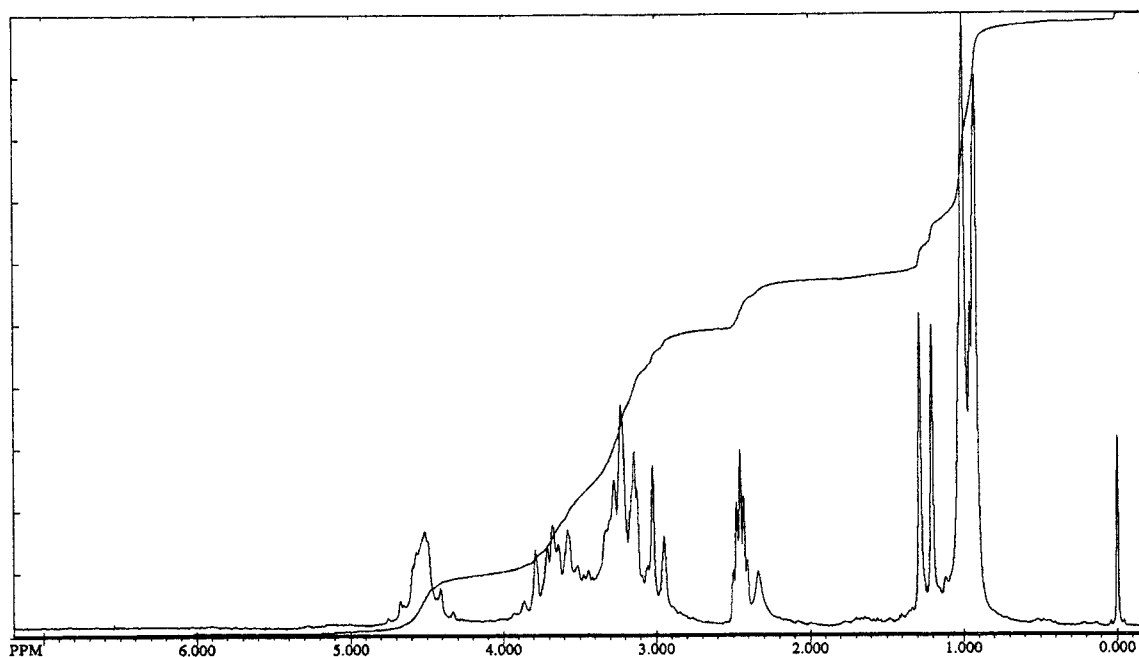


Figure 6 $^1\text{H-NMR}$ spectrum of reaction product of 1 mol melamine with 22 mol propylene carbonate, 32 g DABCO/mol MEL $175\text{--}185^\circ\text{C}$, under nitrogen with simultaneous distilling off of by-products.

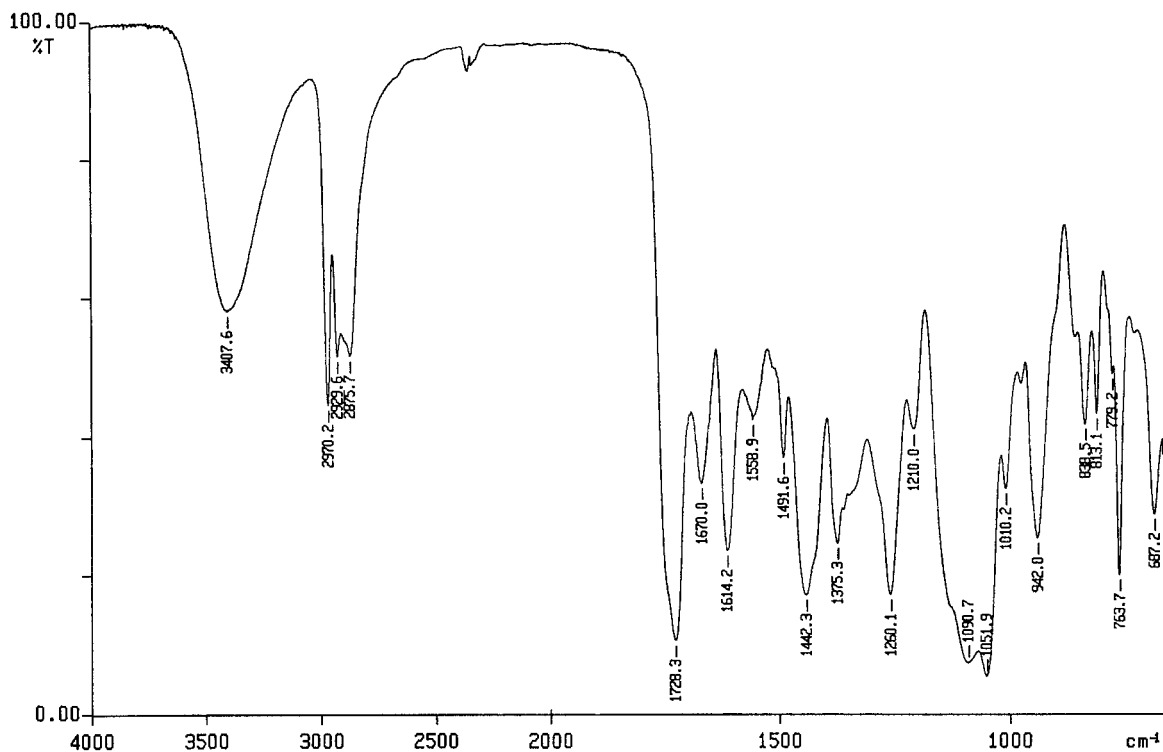


Figure 7 IR spectrum of reaction product of 1 mol melamine with 22 mol propylene carbonate, 32 g DABCO/mol MEL 175–185°C, under nitrogen with simultaneous distilling off of by-products.

that takes place at low temperature at the beginning of synthesis. Low temperature favors ester formation.¹⁰ Hence, two reactions compete in the system: that of

polyetherol formation and that of linear carbonate formation. Consequently, besides the ether groups, some carbonate links are present in the products.

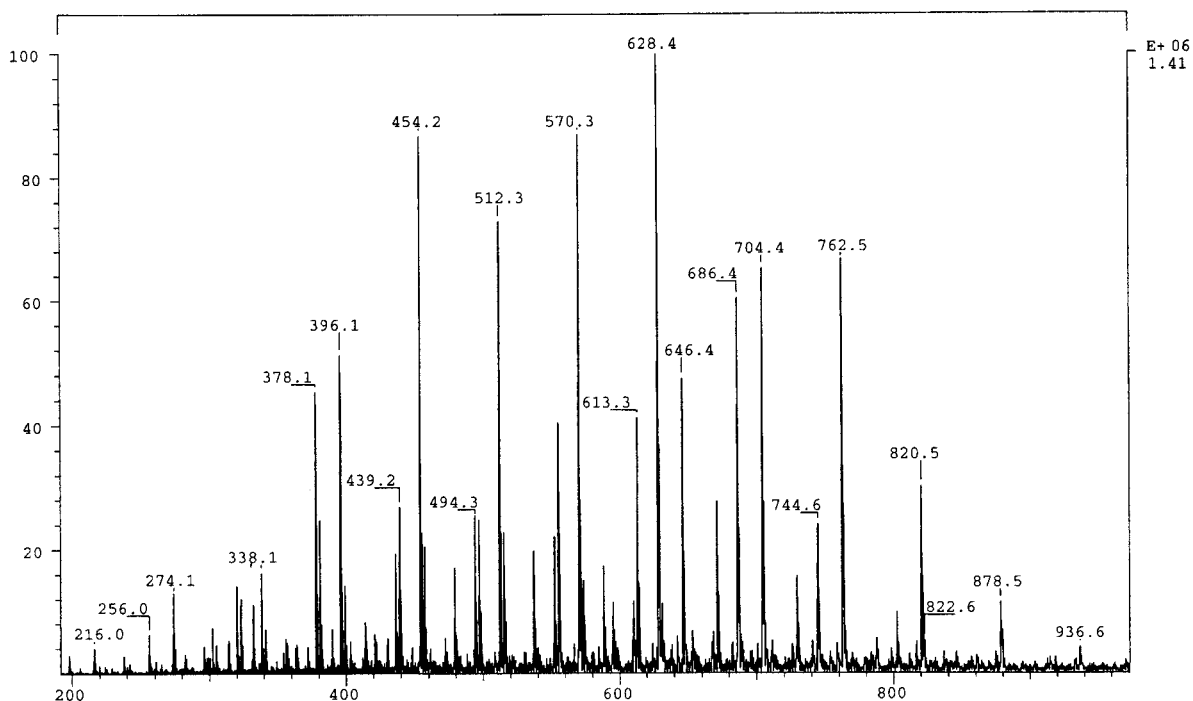


Figure 8 MS (ESI) spectrum of reaction product of 1 mol melamine with 22 mol propylene carbonate, 32 g DABCO/mol MEL 175–185°C, under nitrogen with simultaneous distilling off of by-products.

TABLE III
The Composition of the Products of Addition of Propylene Carbonate (PC) to Melamine (MEL)
as Determined from Mass Balance and by GLC.

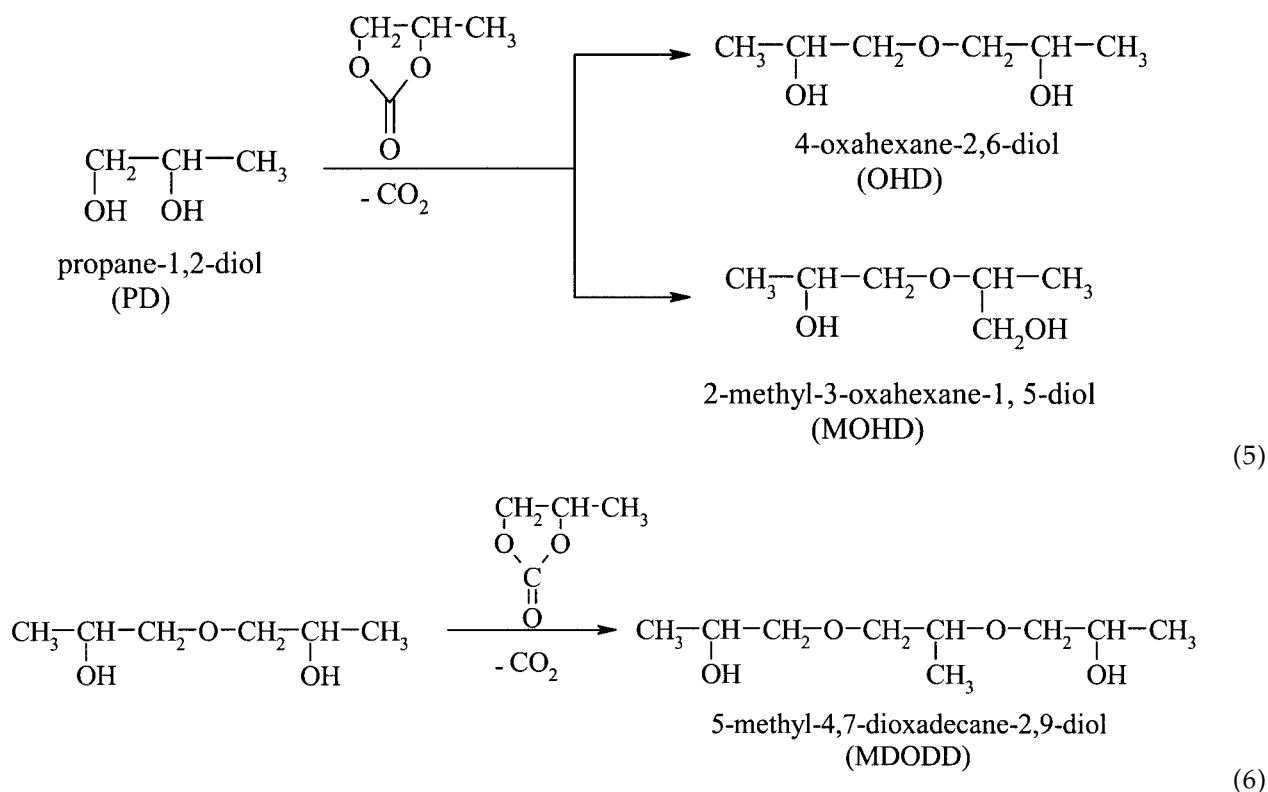
Run ^a	Moles of PC per mole of MEL	Moles of PC per mole of MEL that decomposed	Catalyst (g/mole MEL)	Temperature (°C)	Contents of side products (wt %)		Moles of PC per mole of MEL converted into		Moles of EC per mole of MEL that reacted directly with MEL
					PD	OHD	PD	OHD MOHD	
			DABCO + KOH						
9	22	2.35	32 + 4	170	0.79	12.50	0.13	2.36	17.2
11	18	1.56	4	170	0.90	14.44	0.13	2.33	14.0
12	18	1.45	8	170	1.78	9.78	0.25	1.58	14.7
15	20	1.86	16	170	1.11	14.02	0.17	2.46	15.5
16	20	1.65	24	170	—	7.74	—	1.37	17.0
17	20	1.57	32	170	2.57	9.59	0.4	1.71	16.3

^a Conditions as in Table II.

The structure has further been confirmed by mass spectroscopy (MS) (ESI) spectra. The peaks are separated by 58 M/z units, exactly equal to the mass of oxypropylene unit. Peaks separated by 44 M/z units of carbon dioxide are also present in the spectra (Fig. 8).

Chromatographic analysis

The products of reaction of melamine with propylene carbonate were analyzed by GLC. The aim was to establish the kind and amount of side products. The main side products were propane-1,2-diol and the products of its reactions with further molecules of propylene carbonate:



The results are presented in Table III. As follows from its content, the content of side products depends first of all on the amount of catalyst used. The more catalyst is used, the less side products are present in the reaction mixture (Table III, runs 15, 16). The reason is that with less catalyst, the alco-

holate anions of propane-1,2-diol formed at the early stages of reaction react easier with propylene carbonate than melamine, especially because the latter reaction proceeds in heterogeneous system. Hence, the following reactions are favored (reactions for abnormal products are omitted):

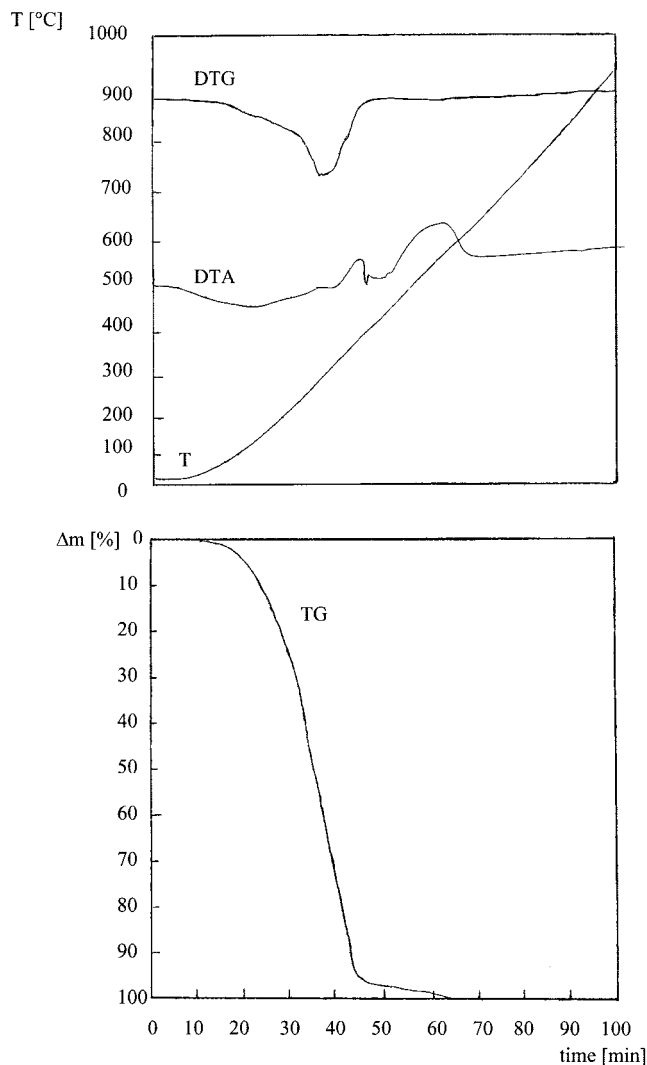


Figure 9 Thermal analysis of the reaction product of 1 mol melamine with 22 mol of propylene carbonate, 32 g DABCO/mol MEL 175–185°C, before vacuum distillation.

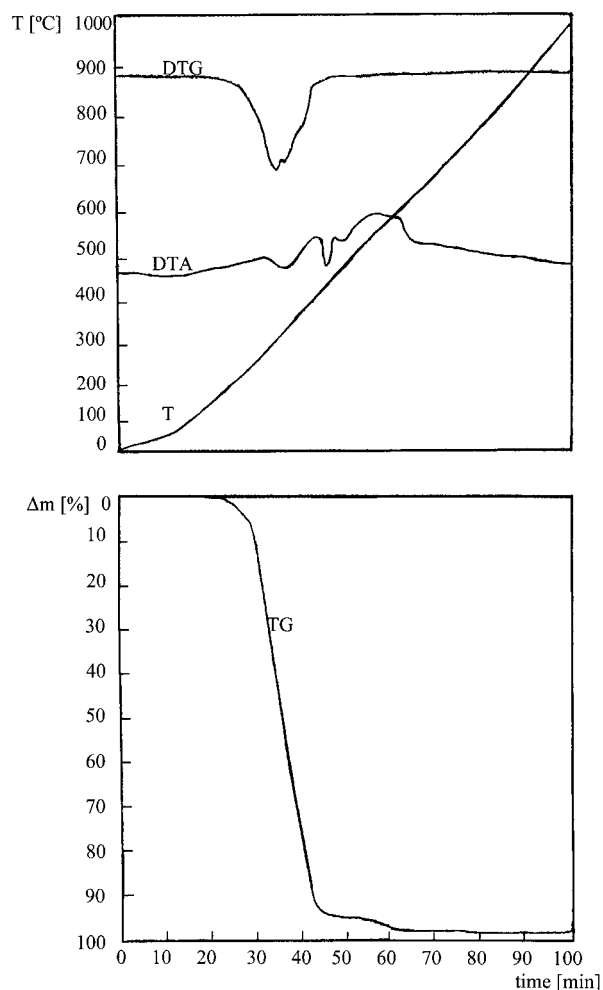
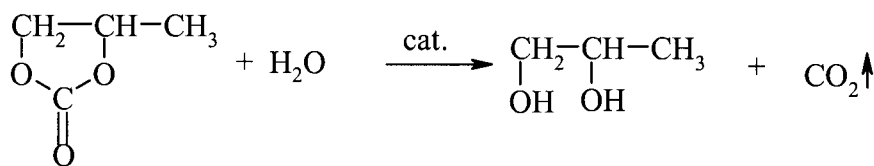
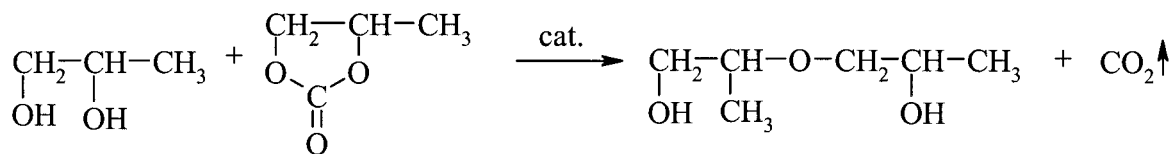


Figure 10 Thermal analysis of the reaction product of 1 mol melamine with 22 mol of propylene carbonate, 32 g DABCO/mol MEL 175–185°C, after vacuum distillation.



(7)



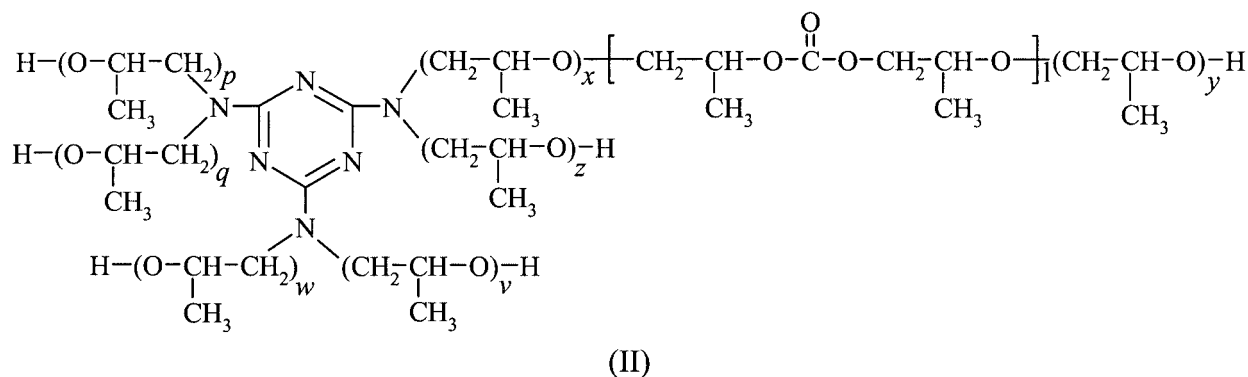
(8)

In the chromatograms of the products of reaction of melamine with propylene carbonate, one does not observe any presence of a propane-1,2-diol peak (or at most a very small one). This is because the diol takes

part in subsequent reactions to yield OHD, MOHD, or MDODD. Even at a longer reaction time, the amount of polyglycol does not substantially increase (Table III, runs 15 and 16). As follows from calculations pre-

sented in Table III, to obtain a polyetherol of a desired molar ratio of components, one should use some excess of propylene carbonate with respect to the stoi-

chiometric ratio. Hence, the general formula of the product of addition of propylene carbonate to melamine reads



The thermal analysis suggests that polyetherols obtained from melamine and propylene carbonate have an improved thermal stability (Figs. 9 and 10) and can be used in manufacturing thermostable polyurethanes. Only one endothermic peak essentially can be seen in derivatograms at 360°C that corresponds to decomposition of *s*-triazine ring. The polyetherols purified by distillation under reduced pressure start to decompose at 180°C. Up to that temperature, only a small kink is observed on DTA curve not related to any weight loss. The kink can be attributed to phase transitions taking place in hydroxypropyl derivatives of melamine. The samples not purified by distillation start to decompose already at 50°C. The properties of polyurethane foams obtained from polyetherols prepared in this work will be the subject of a forthcoming article.

CONCLUSION

1. In reactions of melamine with an excess of propylene carbonate, one obtains polyetherols containing 1,3,5-triazine rings.
2. The known methods of preparation of *s*-triazine containing polyetherols involving propylene oxide can be replaced by a reaction with propylene carbonate which acts as both the reagent and the solvent of melamine. The resulting products contain both ether and ester (carbonate) groupings.
3. The advantage of propylene carbonate over propylene oxide is that the former reduces certain problems met in industry, including flammabil-

ity, toxicity, and explosivity of the oxirane, and eliminates the need for using autoclaves when operating with propylene oxide having a low boiling point. No extra solvents are needed because melamine dissolves in propylene carbonate at elevated temperature.

4. The reaction leading to polyetherols is accompanied by some unwanted side reactions, mainly the reactions of propylene carbonate with water that lead to the formation of a small amount of propane-1,2-diol and products of its reactions with propylene carbonate.

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