

# Polyetherols from Isocyanuric Acid and Propylene Carbonate

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**ABSTRACT:** A new method for the synthesis of polyetherols containing perhydro-1,3,5-triazine rings by the reaction of isocyanuric acid and an excess of propylene carbonate is described. The reaction was studied in the presence of various catalysts and with varying substrate molar ratios. The structures and physical properties of the prod-

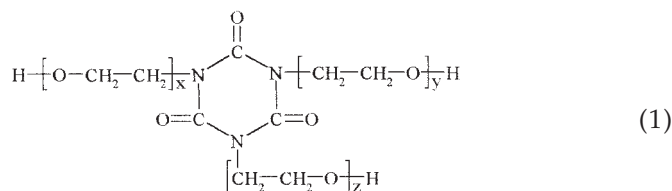
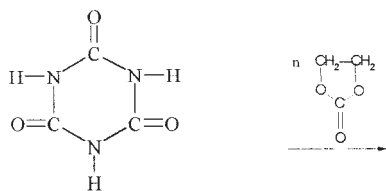
ucts were also studied. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 2130–2138, 2005

**Key words:** heteroatom-containing polymers; ring-opening polymerization; structure-property relations

## INTRODUCTION

Polyetherols with perhydro-1,3,5-triazine rings can be obtained from isocyanuric acid (IA)<sup>1,2</sup> or its hydroxymethyl derivatives<sup>3,4</sup> and an excess of oxiranes such ethylene oxide (EO) and propylene oxide or from epichlorohydrine or glycerin. The resulting polyetherols can be used as components of polyurethane foams with high thermal resistances.<sup>5,6</sup> Because of the low solubility of IA in organic solvents, the syntheses

of polyetherols are difficult to perform. The solvents that have been used in synthetic protocols were dimethyl sulfoxide (DMSO) and water.<sup>3</sup> The solvent was then removed by distillation, which resulted in partial decomposition with a product of unpleasant aroma. One can avoid this disadvantage by using alkylene carbonates, as demonstrated in ref. 7 by the one-step synthesis of polyetherols from IA and ethylene carbonate (EC) according to the following equation:



where  $n$  is the number of oxyalkylene groups in the product. EC played the roles of both reagent and solvent. The structure of the product was analogous to those obtained from IA and EO. Other advantages of alkylene carbonates in comparison with corresponding oxides include their lack of toxicity and inflammability. The reaction does not require the use of high-pressure reactors (EO bp = 14°C; EC bp = 248°C).

Here, the results of our studies on the reaction between IA and propylene carbonate (PC) are presented.

## EXPERIMENTAL

### Syntheses

Reaction of IA with PC at 1 : 1 to 1 : 3 molar ratios

To a 250-cm<sup>3</sup> three-necked flask equipped with a mechanical stirrer, thermometer, and reflux condenser, we added 12.9 g (0.1 mol) of IA (pure, Fluka, St. Gallen, Switzerland); 24.8 g (0.24 mol), 30.8 g (0.30 mol), or 40.8 g (0.40 mol) of PC (Avocado, Heysham-Lacashire, GB, Germany); and 2 g of a 55% aqueous solution of tetrabutylammonium hydroxide (TBAH; pure, Fluka) catalyst. The mixture was heated to 175–

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180°C, and this temperature was maintained until the PC disappeared (usually after 3–5 h). After that time, 25 cm<sup>3</sup> of DMSO was added to the mixture, which was heated up to 60°C to dissolve solid, low-molecular-weight hydroxyalkyl derivatives of IA and unreacted IA. The solution was filtered off while hot, and the solid residue was washed with acetone and dried at 90°C. The solid was analyzed by the determination of the acid number and melting point. The resin-like products were recovered from the filtrates after the removal of DMSO and were analyzed by means of <sup>1</sup>H-NMR spectroscopy.

Reaction of IA with PC at a ratio of 1 to greater than 3

The reaction was performed as described in the previous section, except variable catalysts were used: potassium hydroxide (KOH), a mixture of KOH and TBAH, a mixture of K<sub>2</sub>CO<sub>3</sub> and TBAH, 1,4-diazobicyclo[2.2.2]octane (DABCO), or TBAH itself. The reactions were conducted at 175–190°C at variable starting molar ratio of the reagents (IA–PC = 1 : 5 to 1 : 28.7) and various amounts of catalyst (0.2–2.4 g). The products obtained were pale yellow resins.

### Analytical methods

The analytical methods used here were the same as described in a previous article.<sup>7</sup> The percentage of unreacted propylene carbonate (*p*<sub>PC</sub>) was calculated from the following equation:

$$p_{PC}(\%) = \frac{0.51(V_0 - V_1)}{m} \quad (2)$$

where *V*<sub>0</sub> is the volume of a 0.1M solution of HCl consumed in the blank (cm<sup>3</sup>), *V*<sub>1</sub> is the volume of a 0.1M solution of HCl consumed in the studied sample (cm<sup>3</sup>), and *m* is the mass of the sample (g).

Calibration curves for the chromatographic determinations (glycols and polyglycols) were used as described in the literature.<sup>8</sup> The reference substances were propane-1,2-diol, 4-oxaheptane-2,6-diol (OHD), 2-methyl-3-oxahexane-1,5-diol (MOHD), and 5-methyl-4,7-dioxadecane-2,9-diol (MDODD).

### Properties of the polyetherols

The refractive index was studied with an Abbe refractometer (A. Kruss Optronic, GmbH, Hamburg, Germany), the viscosity was determined with a Höppler viscosimeter (type BHZ, Ottendorf-Okrilla, Germany), and the surface tension was also measured.

## RESULTS AND DISCUSSION

### Synthesis of the polyetherols and their properties

Initially, the synthesis of the polyetherols was performed with IA and an excess of PC to maintain the IA

TABLE I  
Reaction Conditions and Mass Balance in the IA + PC System in the Presence of Various Catalysts

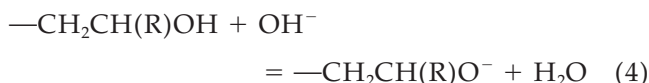
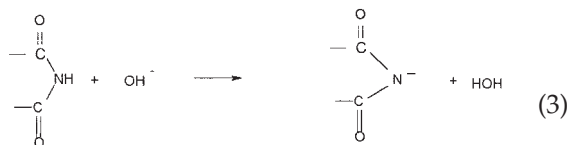
Run no.	Initial PC molar excess per mole of IA	Catalyst	Catalyst concentration (g/mol of IA)	Reaction conditions			Post reaction mixture (wt %)			Oxyalkylene units per IA molecule	Decomposed PC per IA molecule
				Temperature (°C)	Time (h)	IA dissolving time (min)	Solid residue	Resinous product			
1	28.7	KOH	4.0	180–195	35	No dissolution	<1	<100	17.1	11.6	
2	21.5	KOH	4.0	180–190	55	no dissolution	<1	<100	13.6	7.9	
3	21.7	KOH	4.0	175–185	18	no dissolution	0.48	99.52	15.7	5.9	
4	13.3	KOH	4.0	180–190	14	no dissolution	0.72	99.28	9.6	3.7	
5	14.3	TBAH + KOH	20 + 4.0	180–190	10.5	90	0.24	99.76	9.7	4.7	
6	14.3	First TBAH, then KOH	20	175–180	5	30	0.20	99.72	11.6	2.7	
7	14.3	TBAH + K <sub>2</sub> CO <sub>3</sub>	20 + 4.0	175–180	5	7	0.60	99.40	11.5	2.0	
8	14.3	DABCO	8.0	175–180	52	15	—	100	10.2	4.1	
9	14.3	DABCO	16	155–160	26	15	—	100	10.8	3.6	

TABLE II  
Reaction Conditions and Mass Balance for the IA + PC System in the Presence of TBAH (Added as 20 g of a 55% Aqueous Solution per Mole of IA) at 175–180°C

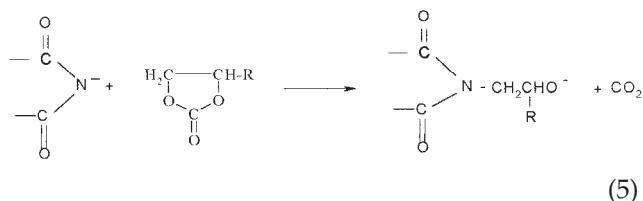
Run no.	Initial PC molar excess per mole of IA	Reaction conditions		Oxyalkylene units per IA molecule	Decomposed PC per IA molecule
		IA dissolving time (min)	Time (h)		
10	2.4	150	3.5	1.3 <sup>a</sup>	1.1
11	3.0	25	3.5	1.7	1.3
12	4.0	25	5.0	3.0	1.0
13	5.0	25	5.0	4.1	0.9
14	5.5	20	5.0	4.5	0.9
15	6.5	25	5.5	6.1	0.4
16	7.3	25	5.0	6.9	0.4
17	10.0	20	8.5	8.8	1.2
18	12.0	20	9.5	9.7	2.3
19	14.3	35	10.5	11.3	3.0

<sup>a</sup> 1% solid residue remained in the postreaction mixture.

dissolved in the presence of different catalysts. As first, the typical catalyst for alkylene carbonates was used, that is, KOH.<sup>9</sup> However, a solid admixture of potassium isocyanurate in the reaction product (<1%, identified via elemental analysis and flame color) resulting a turbid resin (Table I, syntheses 1–4) was noticed. Also, IA slowly dissolved in PC within 35 h. The solid admixture was also present when mixtures of catalysts were used. Therefore, other catalysts were eventually chosen, including DABCO and TBAH (Table I, syntheses 5–9), which were successfully used before for the reactions of alkylene carbonates with melamine<sup>8</sup> and uric acid.<sup>10</sup> These catalysts allowed us to avoid the formation of solid admixtures, resulted in shorter procedures, and last, but not least, were cheaper. Finally, TBAH was chosen for further studies (Table II). The role of the catalysts can be briefly described as follows. KOH catalyzes both the formation of imide  $\text{—N}^-$  and alcoholate  $\text{—CH}_2\text{CH(R)O}^-$  anions

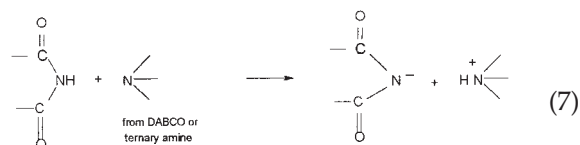


which reacts consecutively with alkylene carbonates:

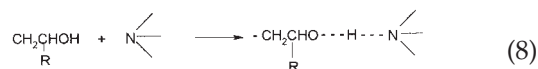


$\text{K}_2\text{CO}_3$  plays a similar role: it hydrolyzes to KOH in water (from a 50% solution of TBAH).

DABCO and other ternary amines catalyze mostly the formation of imide anions<sup>11–14</sup>



and alcoholates to a lesser extent:



TBAH plays an ambivalent role: (1) it enables the formation of imide anions due to the presence of OH groups [eq. (3)], and (2) it facilitates the formation of alcoholates because of the decomposition of TBAH at elevated temperatures to tributylamine, which plays the same role as DABCO shown in eq. (8). These observations will be the subject of a separate report.

The reactions were considered complete on the basis of the mass balance and the determination of unreacted PC. The percentage of oxyalkylene groups was determined in the products on the basis of the mass balance (Table I) and turned out to be lower than that based exclusively on the starting molar ratio of the reagents. It was also lower than that found previously in analogous systems with IA and EC. We concluded that PC was partially decomposed at temperatures

TABLE III  
Some Physical Properties of the Polyetherols and Equations Describing Their Dependence on Temperature in the Range 20–80°C

Run no.	$\tau$ (N/m) $\times 10^{3a}$				$n_{20}^{Db}$			$\eta$ (N s/m <sup>2</sup> ) $\times 10^{3c}$				$d$ (g/cm <sup>3</sup> ) <sup>d</sup>		
	$a \times 10^2$	$b$	$c$	$r$	$a \times 10^4$	$b$	$r$	$a \times 10^{-5}$	$b$	$c$	$r$	$a \times 10^4$	$b$	$r$
3	9.1249	9.5654	40.01	0.9949	-3.6714	1.4599	0.9980	2.61	91.10	14.56	0.9996	-8.2857	1.0138	0.9999
4	-5.954	25.6635		0.9971	-3.6321	1.4657	0.9970	4.374	305.32	14.37	0.9996	-7.9586	1.0389	0.9996
5	-6.230	26.0483		0.9928	-3.7214	1.4605	0.9995	6.1135	558.13	13.41	0.9995	-9.1143	1.0626	0.9994
6	19.3392	9.0028	38.06	0.9980	-3.6429	1.4638	0.9997	4.192	226.25	15.54	0.9997	-8.0714	1.0509	0.9991
7	-10.104	29.0232		0.9987	-3.5071	1.4642	0.9990	4.560	311.45	14.83	0.9999	-8.4714	1.0628	0.9962
8	17.3825	17.1664	35.61	0.9964	-3.5000	1.4660	1.0000	4.600	552.05	14.98	0.9992	-8.6658	1.1159	0.9994
9	-7.129	24.2793		0.9996	-3.9500	1.4707	0.9933	7.306	602.98	13.33	0.9996	-8.6571	1.1112	0.9992
16	-5.439	24.7970		0.9960	-3.6071	1.4724	0.9960	0.0000	569.10	15.72	0.9971	-8.2360	1.1276	0.9996
17	-5.636	23.7993		0.9993	-3.5286	1.4653	0.9993	5.2017	361.36	14.23	0.9996	-7.9740	1.1053	0.9990
18	-6.607	24.4721		0.9920	-3.4036	1.4663	0.9994	4.1352	325.81	15.44	0.9998	-8.1036	1.0961	0.9993
19	-7.664	34.0638		0.9990	-3.5643	1.4654	0.9988	5.6740	455.55	14.01	0.9996	-8.0357	1.0714	0.9998

$\tau$ , surface tension;  $n_{20}^D$ , refractive index;  $\eta$ , viscosity;  $d$ , density;  $a, b, c$ , parameters of equation;  $T$ , temperature;  $r$ , correlation coefficient. The equations describing dependence of surface tension ( $\tau$ ) on temperature, including the  $c$  parameter, are represented by  $\tau = a + be^{-T/c}$ .

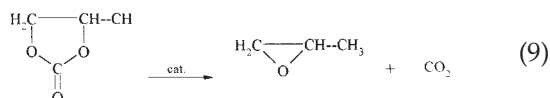
$$^a \tau = aT + b.$$

$$^b n_{20}^D = aT + b.$$

$$^c \eta = a + be^{-T/c}.$$

$$^d d = aT + b.$$

higher than 180°C with the formation of propylene oxide and CO<sub>2</sub><sup>15</sup> according to the following reaction:



Thus, to keep  $n$  under control, it was necessary to use excess of PC (cf. Tables I and II). We also found that the formation of polyetherols at temperatures above 180°C was accompanied by darkening of product.

On the basis of the previously mentioned observations, the optimal conditions for polyetherol synthesis from IA and PC were established (Table II) as temperatures of 175–180°C and TBAH as the catalyst (20 g of a 55% aqueous solution per mole of IA). Under these conditions, we obtained polyetherols in which the molar ratios of IA to oxyalkylene groups were about 1 : 6, 1 : 7, 1 : 8, 1 : 9, and 1 : 11.

The physical properties of the polyetherols (density, viscosity, refractive index, and surface tension) were studied (Table III). The kind of catalyst and its concentration had no relevant influence on the properties of the products. On the other hand, we determined that the oxyalkylene chain elongation within the 6–11 groups per mole of IA range resulted in a slight decrease in the refractive index, surface tension, and typical thermal characteristics of those properties. Those properties fell into value regions typical for polyetherols used for the formation of polyurethane foams.<sup>16</sup>

To follow the reaction of IA with PC, we used a smaller excess of PC (Table II, runs 10–12). We found that resin products were formed when the initial IA–PC ratio was 1 to 2.4 or greater. For instance, resin products were formed at IA–PC = 1 : 3, whereas the use of EC instead of PC led to solid 1,3,5-tris(2-hydroxyethyl isocyanurate).<sup>7</sup> For the system IA–PC = 1 : 2.4, a mixture of solid (0.12% w/w) and resin products was obtained. The acid number of the latter was 26 mg of KOH/g, which pointed to the presence of unreacted imide groups, which was confirmed by the <sup>1</sup>H-NMR spectrum. The solid was insoluble in DMSO, and elemental analysis indicated that the main product was unreacted IA (28.9% N).

### Analysis of the IA–PC reaction

The reaction was monitored for the systems with IA–PC ratios of 1 : 2.4 to 1 : 28.7 by means of the <sup>1</sup>H-NMR and IR spectra of the postreaction mixtures and isolated products. Unreacted PC was detected in the <sup>1</sup>H-NMR spectra by characteristic methyl group resonances at 1.35 ppm. The disappearance of imide proton resonances of IA at 10.6 ppm allowed us to monitor the progress of the reaction. This resonance disappeared completely in products for which  $n \geq 6$  mol/mol of IA (Fig. 1). Intermediates showed the imide proton resonances in the region 7.3–7.4 ppm, which were quenched by the addition of D<sub>2</sub>O.

Simultaneously, the resonances from methine and methylene groups in oxyalkylene chains appeared at 4.2 and 2.9 ppm, respectively.<sup>3</sup>

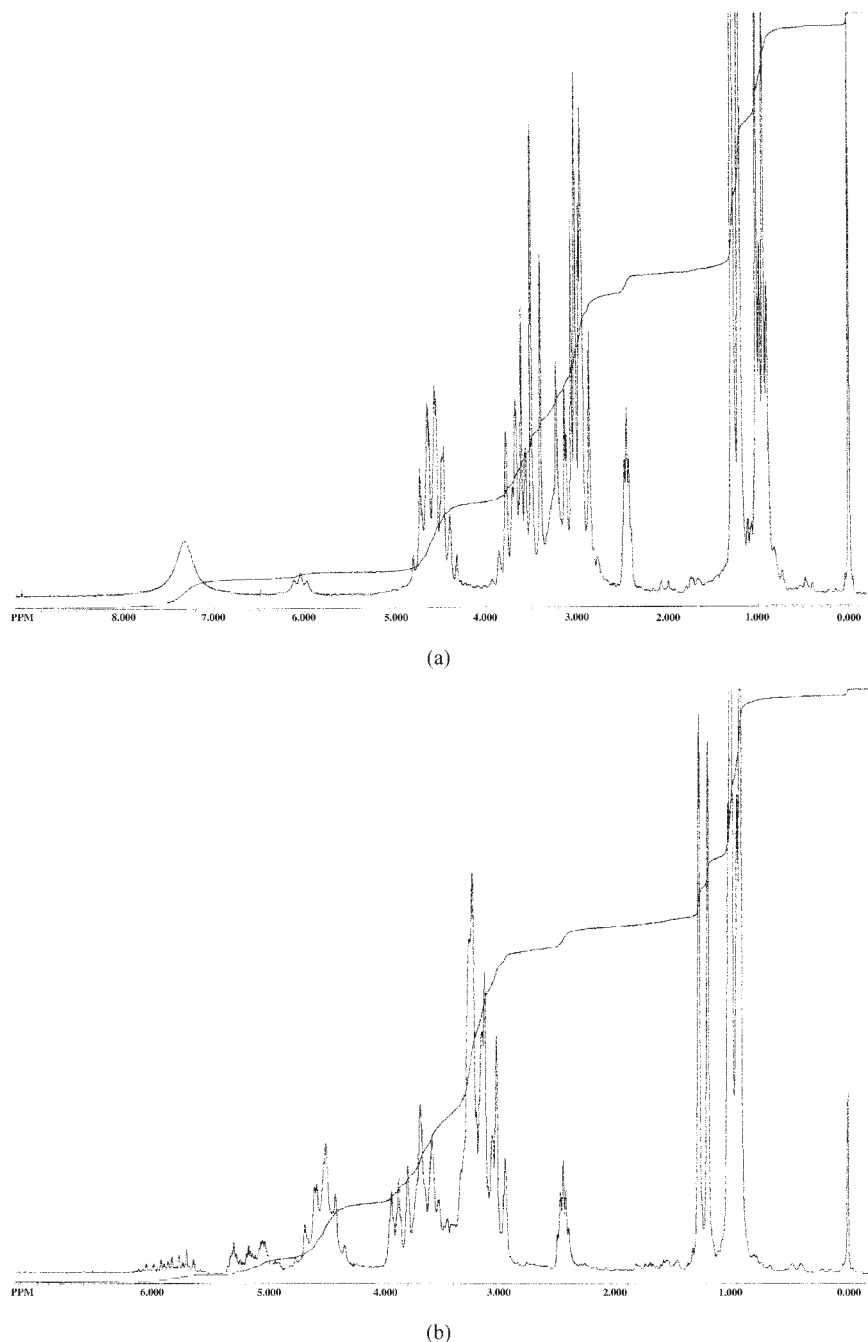
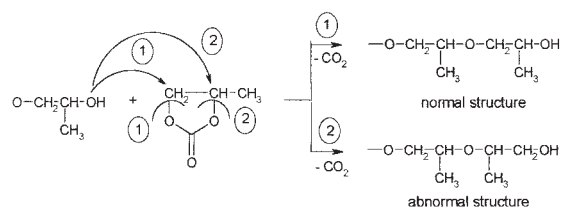


Figure 1  $^1\text{H-NMR}$  spectra of the product of the reaction of 1 mol of IA with (a) 4 and (b) 14.3 mol of PC.

Having determined the number of moles of oxyalkylene units in polyetherol (from mass balance), we were able to estimate the number of moles of PC per mole IA being reacted with  $\text{—NH—}$  groups and the number of moles of PC involved in consecutive reactions with hydroxy groups (from  $^1\text{H-NMR}$  spectra). The results of the estimation are collected in Table IV. Moreover, on the basis of the  $^1\text{H-NMR}$  spectrum, we were able to predict the direction of ring opening, depending on the pH of solution. According to lowered symmetry, the PC ring can open in two different ways with formation of normal or abnormal structures:<sup>17,18</sup>



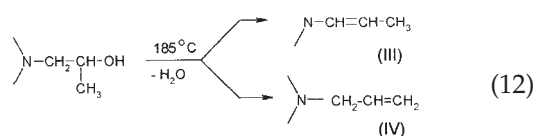
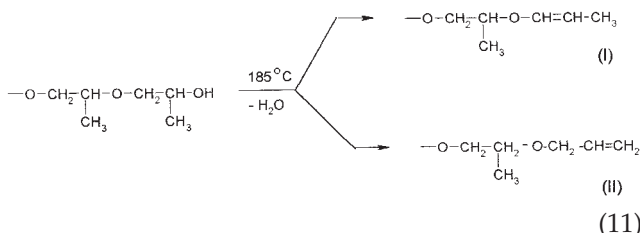
(10)

The methyl protons of the normal products have different chemical shifts than those in the abnormal products;<sup>19</sup> thus, it was possible to calculate the per-

TABLE IV  
Product Analysis by <sup>1</sup>H-NMR

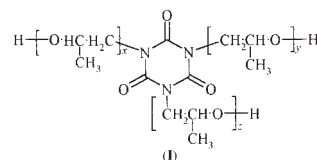
Run no.	>NH groups		—OH groups in the product	Distribution of PC		Mol % of structure		Note
	Reacted	Left		Among >NH groups	Reacted in subsequent reactions	Normal	Abnormal	
11	1.65	1.35	1.65	1.65	0.05	32	68	C=C bonds absent
12	2.0	1.0	2.0	2.0	1.0	39	61	
13	2.3	0.7	2.3	2.3	1.8	50	50	
15	3.0	0	3	3	3.1	67	43	C=C bonds present
4	3.0	0	3	3	8.3	73	27	
19	3.0	0	3	3	8.6	73	27	
6	3.0	0	3	3	6.7	73	27	
5	3.0	0	3	3	6.6	77	23	
2	3.0	0	3	3	10.6	90	10	
1	3.0	0	3	3	14.1	93	7	

centages of the products in the postreaction mixtures (Table II). As shown by these data, for the reaction performed in acidic conditions, where the acidic protons of imide groups were present, the product was mostly abnormal [cf. Fig. 1(a,b)]. The resonances from methylene protons at 3.5 ppm and triplets from the primary hydroxyl protons at 6 ppm, which could be quenched with the addition of D<sub>2</sub>O, were attributed to abnormal product. This situation prevailed when PC was present in slight excess. However, the imide groups were blocked in the presence of further PC; the acidity diminished, partly because of the basic character of the introduced catalyst; and eventually, the percentage of normal product increased up to 90% or greater in the presence of a large excess of PC. This feature was analogous to that found for the reaction of propylene oxide, depending on pH.<sup>17</sup> Moreover, at higher temperatures and prolonged reaction times, which needed to be maintained in the presence of a large excess of PC, group of resonances at 4.8–5.3 ppm (—CH=CH— and —CH=CH<sub>2</sub>) and 5.7–6.1 ppm (—CH=CH— and —CH=CH<sub>2</sub>) attributed to unsaturated hydrocarbon protons were observed in the <sup>1</sup>H-NMR spectra [Fig. 1(b)]. The unsaturated groups formed at the termini of hydroxyalkyl chains due to the elimination of water in the reaction:



By the integral integration of the resonances at 4.8–5.3 and 5.7–6.1 ppm regions, we concluded that the percentage of terminal vinyl groups in **II** and **IV** in relation to the other unsaturated groups in **I** and **III** was considerably larger and reached 90 mol %.

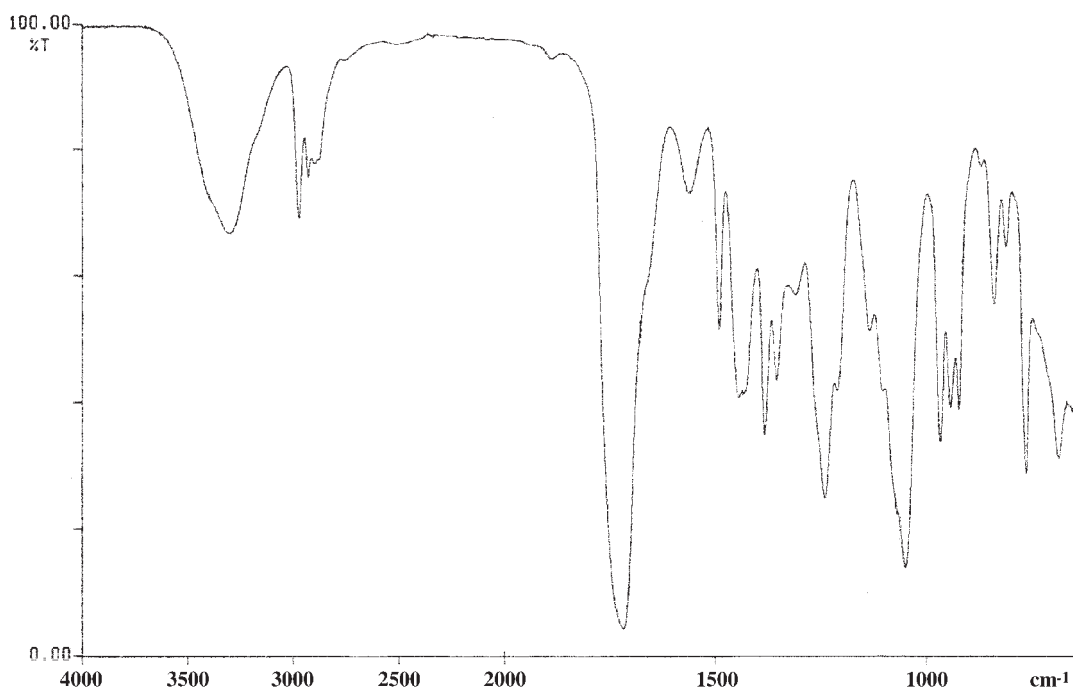
They became detectable during the reaction of 1 mol of IA with 6 mol of PC, that is, in conditions of prolonged reaction time and high temperature. Thus, the structure of polyetherols corresponded to the putative formula:



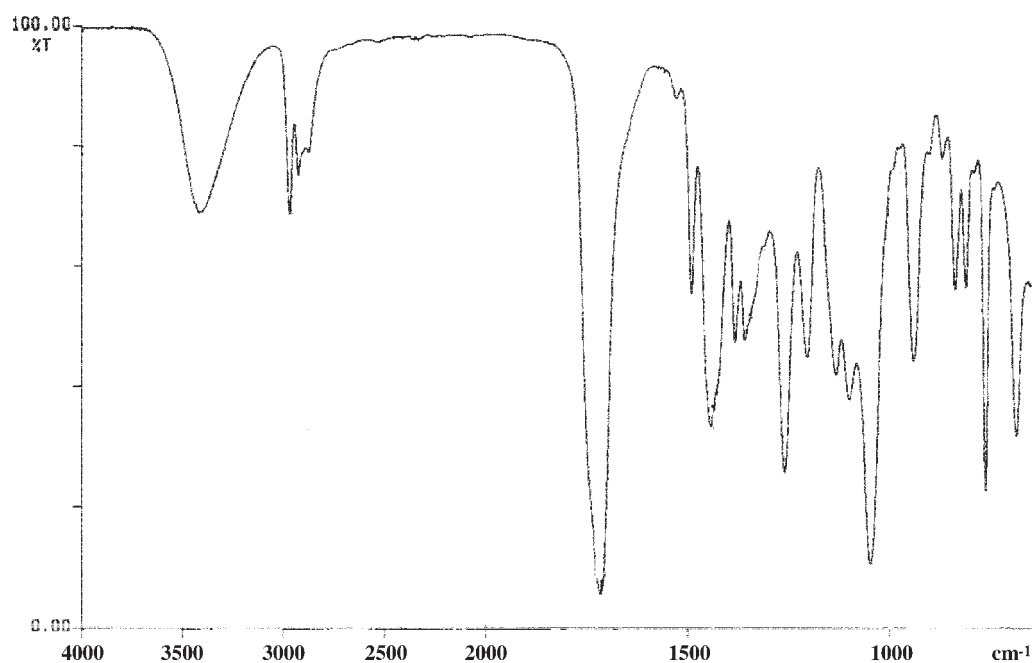
where  $x + y + z = n$ .

This formula was consistent with the IR spectra of the products (Fig. 2), in which the following changes during the reaction of IA with an increasing number of equivalents of PC were observed:

- In the region 3400–3000  $\text{cm}^{-1}$ , a broad, diffused band of associates or coassociates of hydroxyl groups appeared in place of a series of narrower bands from  $\nu(\text{OH})$ .
- In the spectra of the lower products of hydroxyalkylation, apparently the deformation mode band of NH at 1561  $\text{cm}^{-1}$  diminished and finally disappeared in the product in which the number of hydroxyalkylene groups per IA was 6.
- In the spectra of the lower products of the deformation mode, the band of OH at 1065  $\text{cm}^{-1}$  increased; this band in the progress of the reaction was overlapped with the valence mode band of C—O—C at 1050  $\text{cm}^{-1}$ . This evidenced the growing of oxyalkylene chains along with the increas-



(a)



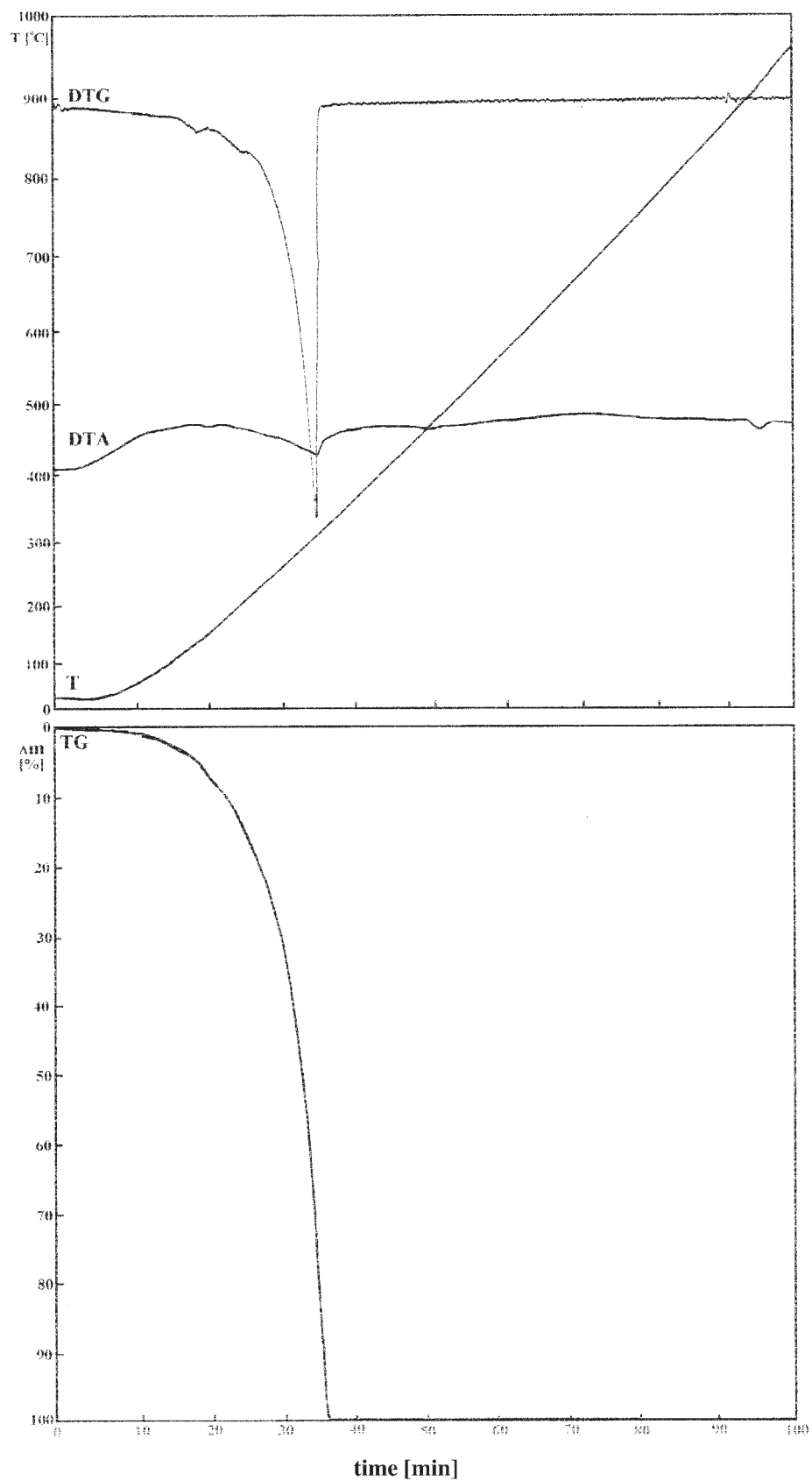
(b)

Figure 2 IR spectra of the product of the reaction of 1 mol of IA with (a) 4 and (b) 6.5 mol of PC.

TABLE V  
GC Analysis of the Side Products Obtained During the Reaction of IA with PC

Run no.	Initial IA : EC molar ratio	Side products (wt %)				Polyetherol content (wt. %)
		OHD	MDODD	MDODD + PC	Σ%	
1	1 : 28.7	2.7	4.6	4.9	12.2	87.8
2	1 : 21.5	3.0	3.7	2.8	9.5	90.5
19	1 : 15.6	2.6	2.9	0.7	6.2	93.8

Σ%, content amount of polyglycols. The side products formed in the reaction of water with propylene carbonate were: OHD-4-oxaheptane-2,6-diol; MDODD-5-methyl-4,7-dioxadecane-2,9-diol.



**Figure 3** Results of the thermal decomposition of the product of the reaction of 1 mol of IA with 6.5 mol of PC (DTG = dynamic thermogravimetry). T is the temperature in °C and  $\Delta m\%$  is the mass loss in %.



ing amount of PC. Similarly, the intensity of the valence band of  $\text{—O—C}$  at  $941\text{ cm}^{-1}$  increased.

- Deformation mode bands of NH in the region of  $1600\text{--}1750\text{ cm}^{-1}$  disappeared, whereas the carbonyl stretching vibration remained unchanged at  $1720\text{--}1725\text{ cm}^{-1}$ .
- In the spectra of all of the products, the characteristic band attributed to the perhydro-1,3,5-triazine ring was present at  $760\text{--}775\text{ cm}^{-1}$ .
- In the spectra of the higher products of hydroxyalkylation, the bands at  $1668$  and  $1645\text{ cm}^{-1}$  appeared and belonged to valence  $\text{C=C}$  bands, which evidenced the dehydration of the chain.

The products of the reaction of IA with PC at molar excesses of PC higher than 15 : 1 were analyzed by gas chromatography (GC). To determine the percentage of glycols and the products of consecutive reactions, that is, the reactions of PC with  $\text{H}_2\text{O}$  (water formed in the dehydration of hydroxyalkylene chains and trace water), determinations were carried out after the removal of catalyst from the products. The results were analyzed on the basis of our earlier research.<sup>8</sup> The percentage of glycols and consecutive products depended on the starting ratio of the substrates (Table V). The less PC there was in the reaction mixture, the less side products were present in the postreaction mixture. For the IA–PC system with a molar ratio of 1 : 15.6, the percentage of side products was less than 7%, whereas in some cases, when a larger amount of PC was used, this number reached 13%. This was, however, a lower value than for the reaction between melamine and EC.<sup>8</sup>

We found by dynamic thermal analysis (DTA) and thermogravimetry (TG) that the thermal stability of the polyetherols did not depend on the starting molar ratio of IA to PC within the studied system. For the 1 : 6 to 1 : 11 systems, one endothermic peak at  $300\text{--}310^\circ\text{C}$  was observed, corresponding to 1,3,5-triazine ring cleavage (Fig. 3). A slight 10% mass loss was also

observed at  $150\text{--}170^\circ\text{C}$ . This was attributed to a small amount of propane-1,3-diol and consecutive products of its reaction with PC, which in this temperature, evaporated from the polyetherol sample.

## CONCLUSIONS

Polyetherols containing perhydro-1,3,5-triazine rings were formed in the reaction between IA and an excess of PC. These polyetherols were previously obtained from propylene oxide. The studied reaction was analogous to that of EC and needed the TBAH catalyst. A small number of vinyl structures were formed when an extensive reaction with a large excess and high temperatures were maintained in the system. These high-molecular-weight admixtures were due to the thermal dehydration of oxyalkylene chains.

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