Polyetherols from Isocyanuric Acid and Ethylene Carbonate

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ABSTRACT: A new method of preparation of poly-etherols containing perhydro-1,3,5-triazine rings from iso-cyanuric acid and an excess of ethylene carbonate was developed. The course of reaction was studied at various molar ratios of reagents. The structure of the products was estab-lished, and some physical properties were measured. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 91: 2750–2755, 2004

Key words: isocyanuric acid; ethylene carbonate; subsequent hydroxyalkylation; product analysis; polyetherol properties

INTRODUCTION

In reactions of isocyanuric acid (IA) with an excess of oxirane, such as ethylene oxide, propylene oxide, or glycerin epichlorohydrin, one obtains trifunctional polyetherols containing heterocyclic perhydro-1,3,5-triazine rings (Scheme 1),[1,2] with R = —H, —CH$_3$, or —CH$_2$Cl and $n = x + y + z$.

Compounds **I** are suitable reagents for isocyanates in preparation of polyurethane foams, and the presence of s-triazine rings substantially improves thermal stability of the resulting products.[3,4]

The main complication in the synthesis of polyetherols **I** is the lack of feasible solvents providing sufficient solubility of cyanuric acid. The latter is insoluble in most solvents except dimethyl sulfoxide and water, where it dissolves only slightly. For practical reasons, the reactions of isocyanuric acid with oxiranes are carried out in dimethyl sulfoxide, since oxiranes readily react with water, yielding the respective glycols and polyglycols. Furthermore, the solvent has to be removed from the final products by distillation. Distillation usually leads to partial decomposition of the high-boiling solvent and hence contamination of polyetherols with products of the decomposition that have an unpleasant aroma.

An alternative method of preparing polyetherols from isocyanuric acid was described some time ago.[5,6] The method consists of reacting the acid with formal-dehyde to obtain N,N',N''- tris(hydroxymethyl) isocya-nurate (THMI). The latter dissolves well in oxiranes in the presence of a small amount of water, and hence no additional solvents are needed. The reaction is shown in Scheme 2,[5] with $3n + 2w = 3$, $x + y + z = r$.

The main disadvantage of the method is that hy-droxymethyl groups, blocked by just one hydroxyal-kyl unit of oxirane, tend to release formaldehyde. The latter then migrates to the end of etherol chain. There-fore, in order to prevent formaldehyde release, one has to use a higher excess of oxirane (or methyl ox-irane) than in the direct reaction with unmodified isocyanuric acid.

While seeking a simple method of synthesis of polyetherols with thermostable heterocyclic rings, preferably a non-solvent one, we turned our atten-tion to alternative hydroxyalkylating agents, namely alkylene carbonates, such as ethylene car-bonate (EC) or propylene carbonate. These com-pounds were expected to react directly with isocya-nuric acid yielding the same or similar products as in the direct oxyalkylation with oxiranes as shown in Scheme 3.

We have not found in the literature any data on the second reaction in Scheme 3. The only exceptions were patent descriptions published in 1990[7] and 2000,[8] where a reaction of isocyanuric acid with up to a fourfold molar excess of EC was described. The prod-uct was 1,3,5-tris(2-hydroxyethyl) isocyanurate.

Back in 1993, one of the present authors also sug-gested the use alkylene carbonates in reactions with melamine, another s-triazine.[9] Indeed, Kucharski and Kijowska[10] have recently confirmed the feasibility of this method. Their results urged present authors to try to use ethylene carbonate and isocyanuric acid as raw materials in the synthesis of similar triazine-ring-con-taining polyetherols. The increasing interest in indus-trial applications of alkylene carbonates has been re-cently reviewed by Clements.[11]
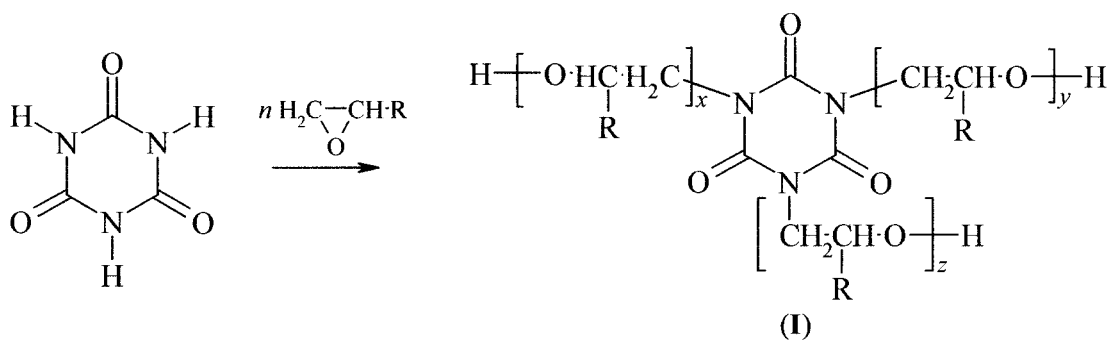
Scheme 1

EXPERIMENTAL

Synthetic procedures

Reactions of isocyanuric acid with EC used in molar excess < 4

Isocyanuric acid (pure, Fluka, Buchs, Switzerland), 12.9 g (0.1 mol), was placed together with 10.6 g (0.12 mol), 19.4 g (0.22 mol), or 28.2 g (0.32 mol) of ethylene carbonate (pure, Fluka) and 0.4 g of potassium carbonate catalyst, in a three-necked 250-mL flask equipped with mechanical stirrer, thermometer, and reflux condenser. The content was heated to 155–160°C and kept at this temperature until all EC reacted (3–6 h). The solid content of the flask was dissolved in 25 cm^3 of DMSO at 60°C and filtered hot. The solid remaining on the filter was washed with acetone and dried at 40°C to constant weight. Its acid number and melting point (see notes under Table I) were measured. The
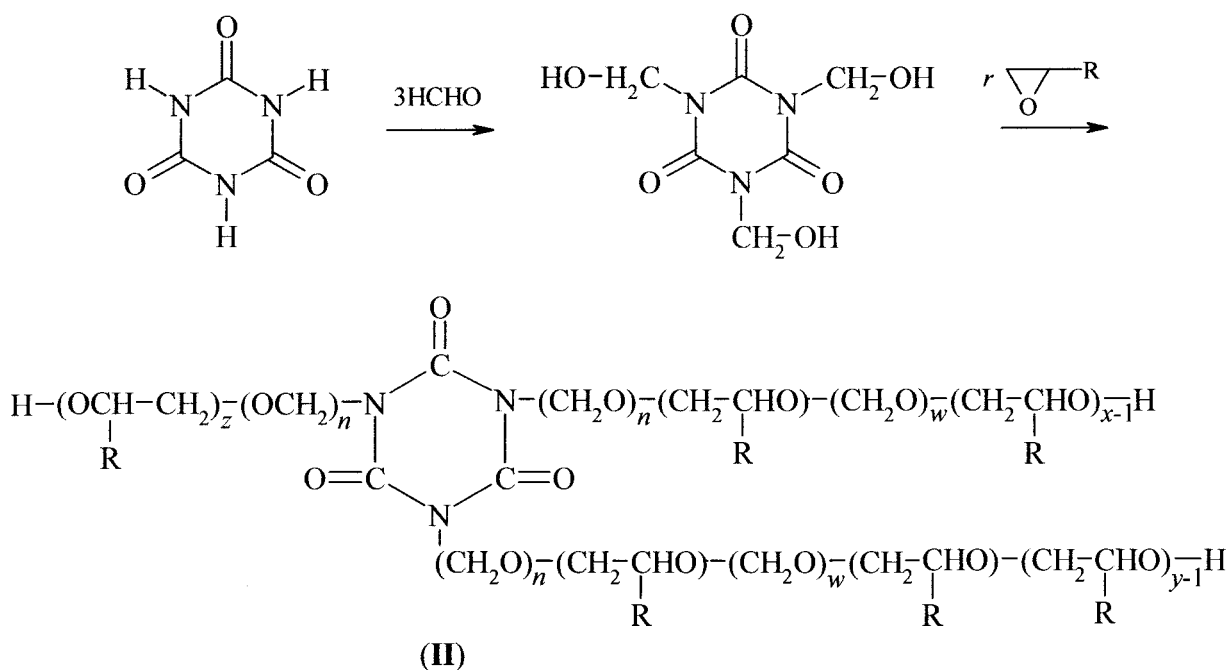
filtrate was freed from DMSO by distillation under reduced pressure to obtain a resinous product.

Reactions of isocyanuric acid with EC used in molar excess ≥ 4

The reactions were carried out as described in previous paragraph at 140–145 or 155–160°C, with the molar excess of EC ranging from 4 to 12 using various amounts of catalyst (0–0.4 g of K$_2$CO$_3$). The products were light-yellow resins.

Analytical methods

The course of reaction between IA and EC was followed by measuring the content of unreacted ethylene carbonate. A small amount of reacting mixture (0.1–0.2 g) was withdrawn from the reactor, quickly cooled

Scheme 2

$\diagdown$N—H $+$ x H₂C—CH·R $\longrightarrow$ (over O)

$\diagdown$N$\left[\text{CH}_2\text{CH·O}\right]_x$H
|
R

$\diagdown$N—H $+$ x H₂C—CH·R (O O, C=O)

$\diagdown$N$\left[\text{CH}_2\text{CH·O}\right]_x$H $+$ x CO₂
|
R
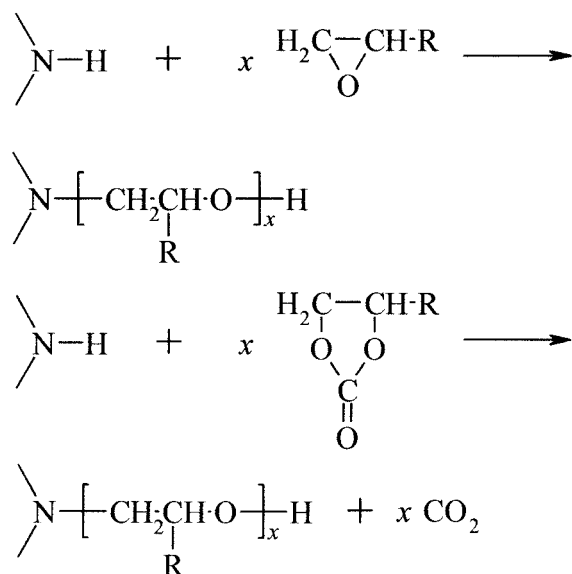
Scheme 3

down, carefully weighed, and diluted with 10 cm³ of water. If necessary, the sample was acidified with hydrochloric acid solution against thymolphthalein. The sample was then treated with 2.5 cm³ of 0.15M barium hydroxide and vigorously shaken, and the excess of barium hydroxide was titrated off with 0.1M HCl solution.

The acid and hydroxyl numbers were determined by titration with a standard potassium hydroxide solution and by applying the methods of Glinka and Majewska,[12] respectively. The uncorrected melting points were measured on a Boëtius apparatus. Refraction index, density, viscosity, and surface tension of polyetherols were determined with an Abbe refractometer, pycnometer, Höppler viscometer, and by the detaching ring method, respectively.

GLC analysis was made on a Hewlett-Packard 5890 chromatograph [capillary column HP-FFAP, 10-m length and 0.53-mm diameter; layer thickness, 0.1 μm; temperature, 20–220°C (20°C/min) and 5 min at 240°C; injector and detector temperature, 220°C; carrier gas (He) rate, 18.3 cm³/min; sample size, 0.2 μL]. Calibration curves were used as described in the literature.[10]

^{1}H-NMR spectra of the reaction products dissolved in d_6-DMSO were recorded in the range 0–15 ppm on a BS-587A 80-MHz spectrometer (Tesla, Czechoslovakia) with a trimethyldisilane internal standard. IR spectra of capillary films or Nujol suspensions were recorded on a Carl Zeiss Specord 71 IR spectrometer (Carl Zeiss, Jena, Germany). Thermal analysis of the polyetherols was made using a Paulik-Paulik-Erdey derivatograph (MOM, Budapest, Hungary) under the following conditions: sample mass, 100 mg; temperature range, 20–1000°C; nitrogen atmosphere; registra-

TABLE I
Reactions of Isocyanuric Acid (IA) with Ethylene Carbonate (EC) in the Presence of Potassium Carbonate Catalyst

Run no.	Initial EC molar excess per mole of IA	Catalyst conc. [g/mol of IA]	Reaction condition Temperature (°C)	Time (h)	Time to IA dissoln. (min)	Post-reaction mixture [wt %] Solid residue	Resinous product	Oxyethylene units per IA molecule	Decomposed EC per IA molecule
						(I) 11.5^c			
1	1.2	0.4	155–160	6^a	—^{b}	(II) 6.0^d	82.5	–	–
2	2.2	0.4	155–160	5^a	—^{b}	2.0^e	98.0^f	1.7	0.5
3	3.2	0.4	155–160	3	3	—^{g}	100^g	2.6	0.6
4	4.2	0.4	155–160	2.5	60	–	100	3.8	0.4
5	5.2	0.4	155–160	2.5	70	–	100	5.0	0.2
6	6.2	0.0	140–145	3.0	No dissolution	–	100	–	–
7	6.2	0.2	140–145	27.0	180	–	100	6.0	0.2
8	6.2	0.4	140–145	17.0	180	–	100	6.0	0.2
9	6.2	0.2	155–160	5.0	60	–	100	6.0	0.2
10	6.2	0.4	155–160	3.0	80	–	100	6.1	0.1
11	9.2	0.4	155–160	6.0	75	–	100	9.0	0.2
12	10.0	0.4	160–165	11.0	ca. 50	–	100	9.9	0.1
13	12.2	0.4	155–160	15.0	40	–	100	12.0	0.2
14	13.0	0.4	160–165	17.3	ca. 40	–	100	12.3	0.7

^{a} Reaction time was longer then in runs further than in runs 3–5 due to heterogenic conditions in runs 1,2 caused by limited solubility of IA in EC.

^{b} Only partial dissolution of IA in EC was observed.

^{c} Solid I precipitated from filtrate; it melts with decomposition in the range of 363–380°C; Acid Number (AN) = 215 mg KOH/g; soluble in hot water; N [wt. %] = 30.7.

^{d} Melts with decomposition in the range of 330–340°C: AN = 251.7 mg KOH/g, (for disubstituted IA: AN = 258.5 mg KOH/g); soluble in hot water.

^{e} Melts with decomposition in the range 376–380°C; AN not measured due to insolubility in water.

^{f} After removal DMSO: AN = 71.2 mg KOH/g.

^{g} Solid 1,3,5-tris(2-hydroxyethyl) isocyanurate precipitated from resinous product after a month.
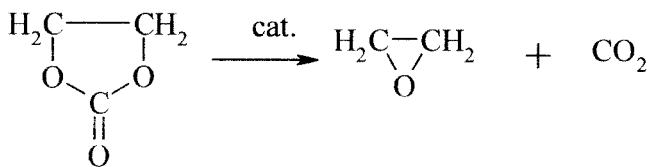
Scheme 4

tion time, 100 min; amplifications, DTA 1/10 and DTG 1/15.

RESULTS AND DISCUSSION

Synthesis and properties of polyetherols

Preliminary attempts at preparing polyetherols from IA and EC were started at the molar ratio of the reagents 1:6.2. The reason was that, as shown in ref. 5, the desired resinous products, not containing the low-molecular solid *N*-2-hydroxyethyl derivatives of IA, can be obtained at an IA/oxirane molar ratio of 1:> 5. In these attempts, hydroxyethylation was carried out at 140–145°C without any catalyst. It was found that IA did not dissolve in EC even after 3 h of heating. A catalyst that was typical for reactions involving alkylene carbonate was then added, namely, potassium carbonate.[13] Initially 0.2 g of K_2CO_3 was used per mole of IA. With this amount of catalyst, IA dissolved in EC within 3 h, and the reaction was completed after 27 h. With 0.4 g/mol of catalyst, the reaction time was reduced to 17 h. Further reaction time reduction, down to 3 h, was observed when temperature was raised to 155–160°C (Table I).

The simplest method of following the course of reaction was to measure the amount of carbon dioxide discharging from the reaction pot. This amount, together with the concentration of unreacted EC, was the basis of calculating the reaction mass balance and helped to determine the end of reaction. As follows from data shown in Table I, the number of oxyethylene groups in the products was smaller than calculated from the initial reagent ratio. This confirms that some amount of EC decomposed to volatile ethylene oxide and carbon dioxide (Scheme 4).[14]

In order to introduce a predetermined number of oxyethylene groups into the product (*n*), one should use a small excess of EC (about *n* + 0.2 mol per mole of IA). The reaction temperature should not exceed 170°C, because above that temperature some decomposition takes place and darkening of products is observed.

The optimal conditions for the reaction of isocyanuric acid and ethylene carbonate seem to be as follows: temperature 155–160°C and catalyst concentration 0.4 g per mole of IA. Under these conditions, polyetherols were obtained with the molar excess of oxyethylene groups ranging from 6 to 12 (Table I).

Some physical properties of polyetherols, such as density, viscosity, refraction index, and surface tension, were measured (Table II). It was found that reaction conditions and amount of catalyst did not influence their physical properties. As the average number of oxyethylene groups in the molecules was increased from 6 to 12, slight reductions of refraction index, density, and surface tension were observed. The properties depended on temperature in the typical way. The physical properties of these products seem to be typical for most commonly used polyetherols used in manufacturing of polyurethane foams.[15]

In order to find the smallest excess of EC that still provides useful polyetherols, we carried out reactions of IA with EC using molar ratios of IA/EC ranging from 1:1 to 1:5 (Table I). Resinous products were obtained only if the excess of EC exceeded 4. At the molar ratio 1:3, a desired, resinous product was obtained at first, but within a month, a crystalline solid precipitated within the product. By recrystallization from benzene, it was identified as 1,3,5-tris(2-hydroxyethyl) isocyanurate (m.p. 134°C). At a still smaller excess of EC, products containing solid substance were obtained. The solid melted at 360–380°C with decomposition. Its acid number was high (71–252 mg KOH/g), and nitrogen content reached 31 wt %. These

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

Run no. (as in Table I)	Surface tension τ [N/m] $\cdot$ 10^3		Refraction index n_{20}^D		Viscosity η [N $\cdot$ s/m^2] $\cdot$ 10^3		Density d [g/cm^3]	
	$\tau = aT + b$		$n_{20}^D = aT + b$		$\eta = AT^{-a}$		$d = aT + b$	
	$a \cdot 10^2$	b	$a \cdot 10^4$	b	$A \cdot 10^{-5}$	a	$a \cdot 10^4$	b
7	−7.821	39.2536	−3.1679	1.4932	1.1059	1.9172	−8.8321	1.2850
8	−8.771	40.1929	−2.9893	1.4938	1.5562	1.9964	−9.6071	1.2956
9	−10.714	41.4929	−3.0429	1.4933	1.0596	1.9278	−9.7571	1.2904
10	−9.161	39.2604	−3.0214	1.4951	1.1684	1.9095	−9.3071	1.2944
11	−9.943	38.1186	−2.9964	1.4899	1.1450	1.9028	−8.4964	1.2554
13	−8.254	34.2668	−3.1179	1.4820	1.1772	1.9213	−8.7464	1.2303

TABLE III
Structure of Products Determined by ^{1}H NMR

| Run no. (as in Table I) | >NH groups | | —OH groups in product | —OCH$_2$CH$_2$—OH terminal groups* | Distribution of EC among | |
	Reacted	Left			>NH groups	Reacted in subsequent reactions
2	1.7	1.3	1.7	Trace	1.7	Trace
3	1.6	1.4	1.6	1.0	1.6	1.0
4	2.0	1.0	2.0	1.8	2.0	1.8
10	2.4	0.6	2.4	2.4	2.4	3.7
12	3.0	0.0	3.0	3.0	3.0	6.9
14	3.0	0.0	3.0	3.0	3.0	9.3

i.e., hydroxyethyl groups in the chains consisting of at least two oxyethylene units attached to nitrogen

findings suggest the presence in the product of a high proportion of unreacted cyanuric acid. The isolated solids were insoluble in DMSO but dissolved in hot water (Table I).

Reaction course

The analysis of the reaction of isocyanuric acid with various amounts of ethylene carbonate, and the structure of the resulting polyetherols, was based on ^{1}H-NMR and IR spectra of post-reaction mixtures and isolated products. The presence of unreacted EC is easy to see in ^{1}H-NMR spectra of reaction products because of the characteristic signals from methylene group protons at 4.45 ppm.[10] In the spectrum of isocyanuric acid there appears a signal from all imides groups at 10.6 ppm. The signal slowly vanishes in the spectra of the products with increasing amount of ethylene carbonate. It is absent in the spectra of products obtained with a 9-fold molar excess of EC. Instead, signals appear from methylene group protons in oxyethylene units at 3.9 and 3.45 ppm from >N—CH$_2$— and —CH$_2$—O—, respectively.[5] The signal from terminal methylene groups in the oxyethylene chains —CH$_2$OH was found to appear at 4.3 ppm.

The compositions of some polyetherols prepared in this work, as calculated from ^{1}H-NMR spectra, are presented in Table III.

The structures of polyetherols, represented by Scheme 1, are further confirmed by IR spectra, where characteristic bands are present, such as those due to valency at ca. 3400 cm^{-1} and deformational vibrations

at 1043 cm^{-1} due to OH groups and those due to perhydro-1,3,5-triazine ring vibrations at 780 cm^{-1}. Furthermore, the carbonyl group band is present at ca. 1720 cm^{-1} due to s-triazine ring as well as valency (2918 and 2877 cm^{-1}) and deformational bands (1441 and 1435 cm^{-1}) of methylene groups. The band due to deformational vibrations of >NH groups at 534 cm^{-1} vanishes as the excess of EC increases confirming successive hydrogens to be replaced with 2-hydroxyethyl groups. At the same time, the intensity of the band at ca. 1043 cm^{-1} increases, as does the concentration of ether links.

The products, obtained from reactions of isocyanuric with ethylene carbonate used in molar excess exceeding 6, were analyzed by gas chromatography in order to determine the amount of diols and their substitution products resulting from side reactions of ethylene carbonate with water. The latter is introduced to the system with raw chemicals and from thermal dehydration of semi products during the synthesis. The analysis was carried out after removing catalyst from the product. In order to identify all signals in chromatograms coming from the presence of products of reaction of ethylene carbonate with water, we made use of the retention times published by Kucharski and Kijowska.[10] The chromatograms recorded in the present work contained peaks due to glycol and products of its subsequent oxyethylation (Table IV). The higher the excess of EC, the smaller the proportion of side products found. At an IA/EC molar ratio of 1:13, the content of side products was smaller than 15 wt %,

TABLE IV
Contents of Side Products in Reactions of Isocyanuric Acid with Ethylene Carbonate by GLC

| Run no. (as in Table I) | IA/EC molar ratio | Side products [wt %] | | | | | Polyetherol content [wt %] |
		ED	OPD	DOOD	TOUD	Σ %	
10	1:6.2	10.5	17.1	1.45	0.50	29.55	70.45
12	1:10	5.87	13.4	2.77	1.96	24.00	76.00
14	1:13	0	4.70	5.60	4.00	14.30	85.70

Products of reaction of EC with water: ED: ethane-1,2-diol; OPD: 3-oxapentane-1,5-diol; DOOD: 3,6-dioxaoctane-1,8-diol; TOUD: 3,6,9-trioxaundecane-1,11-diol
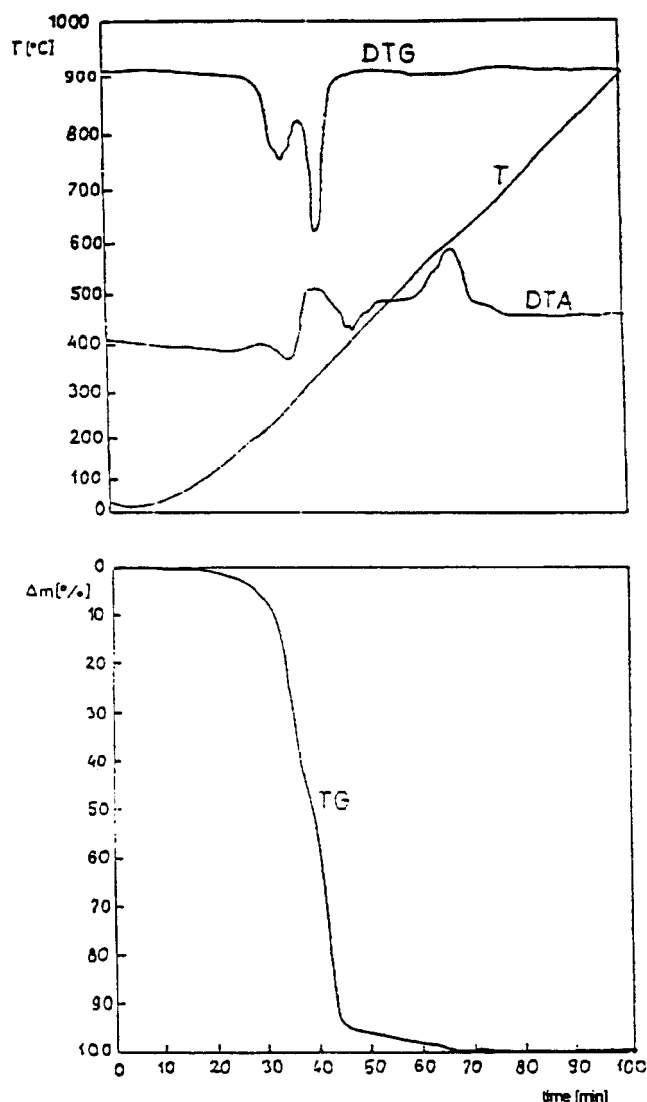
Figure 1 Results of thermal decomposition of reaction product of 1 mol of isocyanuric acid with 10 mol of ethylene carbonate

and it was similar to that found among the products of reaction of melamine with ethylene carbonate.[10]

The thermal stabilities of polyetherols were evaluated by using thermal analysis performed on a Paulik-Paulik-Erdey derivatograph. Decomposition of pure isocyanuric acid started at ca. 400°C with a rate maximum at about 420°C. The thermal stabilities of polyetherols was found not to depend on the initial molar ratio of reagents. In the DTA, DTG, and TG curves

recorded for polyetherols, obtained with six- to 12-fold molar excess of EC, three endothermic peaks were present. The first, at ca. 140°C, was due to evaporation of glycol formed as a side product. The second, at 260°C, was ascribed to evaporation of polyglycols formed by oxyethylation of ethylene glycol. The third peak was due to decomposition of s-triazine ring and appeared at ca. 400°C (Fig. 1). The size of the first peak decreased, and that of the second increased as the excess of EC increased. These findings were also consistent with the results of GLC analysis presented earlier (26 and 15 wt % of glycol and polyglycols were present in the products of reaction of IA with 10- and 13-fold molar excess of EC, respectively).

CONCLUSIONS

In the reactions of isocyanuric acid with an excess of ethylene carbonate one obtains polyetherols containing perhydro-1,3,5-triazine rings in their structure, that were also obtained in reactions of this acid with ethylene oxide. The advantage of the present method is that ethylene carbonate acts in this reaction as both solvent and reagent and hence need not be removed from the product. The structure of the product is very similar to that obtained directly from isocyanuric acid and ethylene oxide.

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