Polyetherols from Melamine and Alkylene Carbonates: Properties and Application of Foamed Polyurethanes

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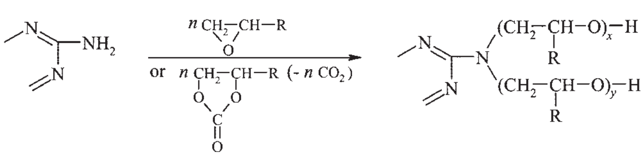
ABSTRACT: Some results are presented on the applications of polyetherols obtained in reactions of melamine with alkylene carbonates for preparation of foamed polyurethanes. Physical properties of the polyetherols and the parameters of their use are evaluated. Selected properties of polyurethane foams obtained by using the polyetherols, such as apparent density, uptake volume, linear shrinkage, and flammability, are presented. Thermal properties of the products have been found to be much better than those of traditional polyurethane foams. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 2302–2308, 2004

INTRODUCTION

Polyurethane foams are more and more widely used in automobile industry, civil engineering, and for domestic appliances. Despite many advantages, the traditional polyurethane foams have too poor thermal stability to be used in many applications. The temperature limit of safe application of these polymers is around 90–120°. By applying polyetherols containing in their structure *s*-triazine rings, this limit can be raised. Several methods have been developed thus far to prepare such polyetherols. Among them are reactions of melamine or derivatives thereof with oxiranes[1–4] as well as with ethylene carbonate or propylene carbonate[5,6]:



where R = -H, $-CH_3$.

This work deals with polyurethane foams obtained using polyetherols prepared by reactions of melamine with alkylene carbonates.

EXPERIMENTAL

Polyetherols from melamine and alkylene carbonates

In a three-necked 500 cm^3 flask equipped with mechanical stirrer, reflux condenser, and thermometer, 32 g (0.25 mol) of melamine (MEL) (reagent grade, a product of KêŸdzierzyn-Kole Nitrogen Plant, Poland) and a predetermined amount of alkylene carbonate (AC) were placed. Two AC were used: ethylene carbonate (EC) (pure, Avocado, Germany) in the amount of 264 g (3 mol), 396 g (4.5 mol), or 484 g (5.5 mol), or propylene carbonate (PC) (pure, Avocado, Germany) in the amount of 561 g (5.5 mol). The catalysts were potassium carbonate (8 or 16 g per mole of MEL) in reactions with EC or 1,4-diazabicyclo[2.2.2]octane (DABCO) (p.a. grade, Avocado, Germany) in the amount of 8, 16, 24, or 32 g per mole of MEL in reaction with both EC and PC. The flask content was kept at the temperature of reaction until all AC introduced had reacted. The reactions with EC were carried out at 170–175°C, while those with PC were at 175–185°C. The conversion was also calculated from mass balance. Some of the reactions were carried out under nitrogen.

Physical properties of polyetherols

The density was determined pycnometrically,[7] viscosity, η [Pa s], in Höppler viscometer,[8] the surface tension γ [N/m] in a torsion balance by the ring detachment method,[9] and the refractive index in an Abbe refractometer. The measurements were carried out at 20–80°C.

Polyurethane foams

The polyurethane foams were prepared in a small scale in polyethylene 250 cm^3 cups at room temperature. To 5 g of polyetherol weighed into the cup, 0.1 g of Silikon 5340 (Houdry Hülls, USA) surfactant, 1–3 wt % of catalyst, that is, triethylamine (p.a., Fluka,

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TABLE I
Physical Properties of Polyetherols Obtained from Melamine and Alkylene Carbonates (AC); Temperature 20–80°C

Alkyl carbonate 1	Molar ratio MEL:AC in product 2	Temperature [°C] 3	Density ρ [g/cm^3] 4	Viscosity $\eta \cdot 10^3$ [Pa · s] 5	Surface tension $\gamma \cdot 10^3$ [N/m] 6	Refractive index n_D 7
EC	1 : 12	20	1.21475	3763	49.84	1.5115
		30	1.20630	1577	47.88	1.5072
		40	1.19834	653	46.48	1.5043
		50	1.19090	324	44.94	1.5013
		60	1.18409	181	38.36	1.4987
		70	1.17627	104	33.88	1.4945
		80	1.16882	62	30.52	1.4918
	1 : 18	20	1.19976	1348	52.64	1.4980
		30	1.18985	591	40.88	1.4952
		40	1.18459	302	42.56	1.4916
		50	1.17666	167	40.32	1.4877
		60	1.16885	96	31.92	1.4845
		70	1.16054	61	31.92	1.4808
		80	1.15255	41	31.92	1.4780
	1 : 22	20	1.18837	1110	46.66	1.4982
		30	1.18061	536	44.87	1.4948
		40	1.17257	269	44.52	1.4917
		50	1.16516	157	43.96	1.4879
		60	1.15797	94	43.40	1.4842
		70	1.15022	60	41.44	1.4814
		80	1.14287	41	41.16	1.4781
PC	1 : 18,31	20	1.06306	240	37.66	1.4726
		30	1.05527	111	34.02	1.4688
		40	1.0474	59	32.90	1.4655
		50	1.03928	34	31.78	1.4623
		60	1.03082	21	30.38	1.4604
		70	1.02252	13	29.54	1.4581
		80	1.01400	10	28.42	1.4565
	1 : 19,22*	20	1.10434	2344	37.94	1.4831
		30	1.09726	782	33.69	1.4801
		40	1.09037	327	28.51	1.4770
		50	1.08182	145	24.64	1.4741
		60	1.07443	78	21.89	1.4700
		70	1.06556	47	21.00	1.4670
		80	1.05677	28	20.55	1.4639

* Synthesis under nitrogen with simultaneous by-product removal.

Switzerland), and 1–3 wt % of water were added with respect to polyetherol weight. The components were thoroughly mixed, and a calculated amount of 4,4′-diphenylmetane diisocyanate (pure, Merck, Germany) was added. The components were vigorously mixed until the compositions started to cream. The times of creaming, growth, and drying of the foams were measured. Test samples were cut out from the foams thus obtained.

Thermal properties

The thermal properties of polyetherols and polyurethane foams were measured in ceramic cups in a derivatograph MOM, Hungary. The measurement conditions were: sample mass 500 mg, temperature range 20–1000°C, recording time 100 min, amplification of DTA: 1/15, amplification of DTG: 1/10.

Foam properties

The following foam properties were measured: apparent density,[10] volume uptake,[11] linear shrinkage,[12] and thermal stability. The last was determined as the percentage of the loss of mass upon heating at 150, 175, or 200°C for several days.

RESULTS AND DISCUSSION

As a result of synthetic works, liquid polyetherols were obtained of dark-brown color (products of reaction of MEL with EC) or brown-yellow (products of reaction of MEL with PC). Some properties of the polyetherols, such as density, viscosity, surface tension, and refractive index, were measured for the products (see Table I). Typical dependence of these properties on temperature was observed. As the excess of alkylene carbonate in the reacting mixtures increased, the smaller was the product viscosity.

The thermal stability of polyetherols was determined by using differential thermal analysis. In the DTA plot of pure melamine, one observes just one peak at 360°C due to thermal decomposition of the *s*-triazine ring. In the case of polyetherols, one also has one peak in the range 280–400°C with maximum at ~ 360°C (Fig. 1). From the TG curve it follows that the decomposition practically starts at 180°C and ends at 600°C. Up to 100°C one observes a kink on the DTA curve not accompanied by a loss of mass. Evidently, a phase transition takes place here, a melting of a small amount of hydroxyethyl or hydroxypropyl derivatives of melamine (Figs. 1 and 2).

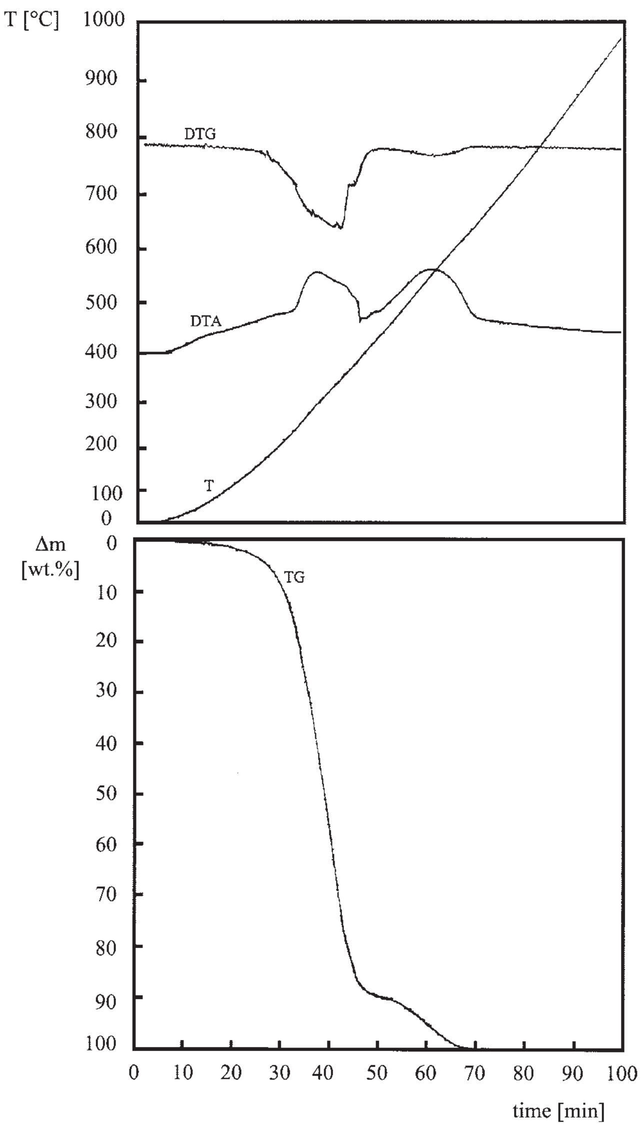

Figure 1 Thermal analysis of polyetherols obtained in reaction of 1 mol MEL with 22 mol EC (synthesis carried out in temperature 175°C under nitrogen).

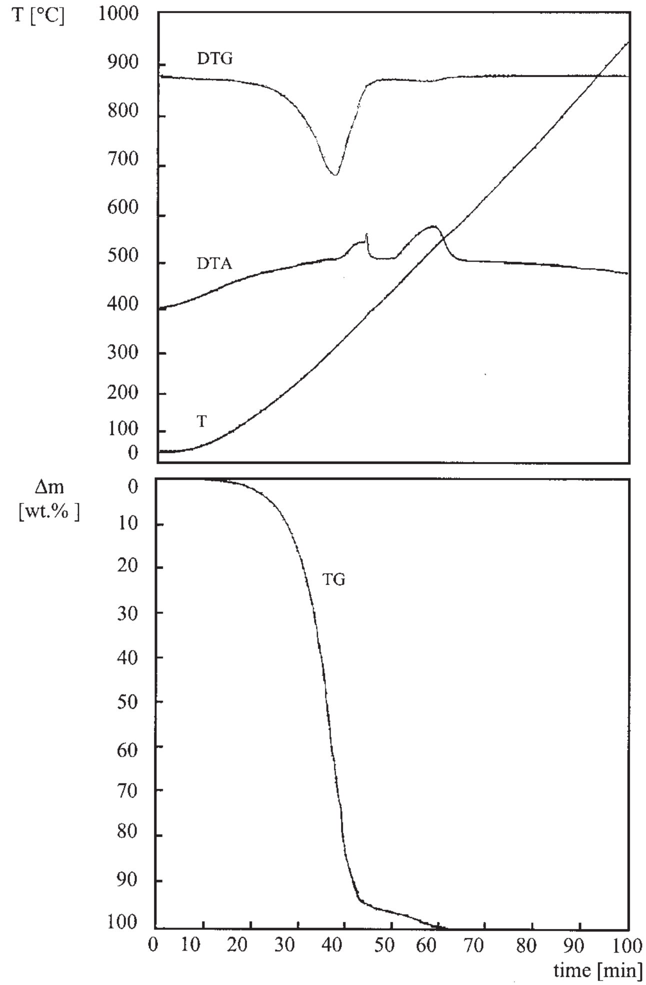

Figure 2 Thermal analysis of polyetherols obtained in reaction of 1 mol MEL with 22 mol PC (synthesis carried out in temperature 175–185°C under nitrogen).

Hence, one concludes that polyetherols are suitable products for preparation of polyurethanes of improved thermal stability.

The foaming of polyetherols was carried out in laboratory scale with 4,4′-diphenylmethane diisocyanate. The polyetherols were used as polyol components. Both the products prepared with potassium carbonate or DABCO catalyst were used. The study aimed at determining the effects of diisocyanate proportion, amount of foaming agent (water), catalyst, and the length of etherol chains on the foaming process. It was found that the amount of diisocyanate should be higher than the stoichiometric one. Otherwise the samples were not fully cured. Too large an amount of diisocyanate, on the other hand, caused significant polymerization shrinkage. The optimal amount of water was 2 g per 100 g of polyetherol in the case of polyetherols obtained from MEL and EC, and 2 or 3 g per 100 g of polyetherols prepared from MEL and PC.

The optimal amount of catalyst was 0.24–0.76 g per 100 g of polyetherol, and the presence of catalyst was

TABLE II
Influence of Composition on the Foaming Process

Molar ratio MEL : AC in product 1	Comp. no. 2	Composition [g/100g of polyetherol] Isocyanate 3	Catalyst 4	Water 5	Foaming process Time of creaming [s] 6	Time of expanding [s] 7	Time of drying [s] 8	Characteristic of foams just prepared 9
MEL : EC = 1 : 11,7	1	322	-	2	15	60	20	R, significant shrinkage, sample not fully cured
	2	322	0.24	2	10	50	30	very small degree of expansion, sample not fully cured
	3	255	0.47	2	10	75	20	R, irregular cells, very expanded
	4	255	0.24	2	10	80	20	R, small shrinkage
	5	220	0.24	2	15	70	15	as above
MEL : EC = 1 : 17,7	6	108	0.48	2	8	10	30	SR, shrinkage, irregular cells
	7	108	-	2	10	30	40	SR, very small degree of expansion, irregular cells
	8	140	-	2	12	40	45	very small degree of expansion, shrinkage
	9	180	-	2	8	40	30	SR, expanded cells
	10	242	-	2	8	33	40	SR, small shrinkage, regular cells
	11	300	-	2	20	80	50	as above
MEL : EC : PC = 1 : 7 : 7	12	208	0.484	1	10	15	45	irregular cells
	13	208	0.484	2	10	20	35	irregular cells, small shrinkage after polymerization
	14	208	0.726	2	10	20	20	as above
MEL : EC = 1 : 12*	15	220	0.242	2	15	40	40	sample not fully cured, bad homogenization of components
	16	220	0.726	2	15	28	50	as above
	17	266	0.726	2	26	28	50	as above
MEL : EC = 1 : 12*	18	220	0.726	1	20	28	60	as above
	19	220	0.968	2	20	25	50	as above
MEL : EC = 1 : 18*	20	242	0.484	2	10	28	65	shrinkage after polymerization
	21	184	0.242	2	8	10	40	shrinkage after polymerization, brittle
	22	140	0.242	2	8	10	35	sample not fully cured
	23	150	-	2	7	5	25	as above
	24	162	0.242	2	7	5	25	irregular cells
	25	174	0.242	2	7	5	30	sample fully cured
	26	160	0.242	2	7	5	30	sample not fully cured
MEL : EC = 1 : 22*	27	110	-	2	8	Very quick growth of composition	-	-
	28	84	-	2	10	as above	-	-
	29	120	-	2	8	as above	-	-
	30	100	-	2	12	as above	-	-
MEL : PC = 1 : 19,22	31	242	0.726	3	15	35	25	brittle
	32	240	0.726	2	15	25	20	regular cells
	33	218	0.726	2	10	27	20	heterogenous cells
MEL : PC = 1 : 18,3*	34	220	0.484	2	5	18	30	R, regular cells
	35	196	0.484	2	8	23	27	R, regular cells
	36	260	0.484	2	5	30	40	R, regular cells
	37	222	0.726	2	8	18	24	R, regular cells
	38	242	0.726	3	8	23	35	R, regular cells

* Synthesis of polyetherols carried out under nitrogen.
R - rigid foam, SR - semi-rigid foam.

TABLE III
Some Properties of Polyurethane Foams

Comp. no.	Density [kg/m^3]	Absorb. of water [wt %]	Linear post-shrinkage [%]
3	81	1.32	0.41
4	201	0.93	0.35
5	114	2.18	0.00
9	105	2.24	0.00
10	96	2.34	0.30
11	84	1.82	0.60
14	91	4.43	9.42
25	78	7.90	0.00
32	54	10.2	0.00
34	89	1.4	0.00
38	80	1.3	0.00

not necessary for MEL/EC polyetherols, or its amount could be smaller than that specified above (see Table II, comparison of composition no. 3–5 with 9–11) because of the high reactivity of primary hydroxyl groups. In the case of polyetherol obtained at the molar ratio MEL : EC = 1 : 22, the compositions were too reactive and the foam grew even before it started to cream (see Table II, comparisons 27–30).

To obtain foams from MEL/PC polyetherols, it was necessary to use threefold excess of catalyst as compared to those from MEL and EC.

The creaming times were longer in the tests with MEL/EC polyetherols obtained at the molar ratio 1 : 12.

For polyetherols prepared with DABCO catalysts, the creaming was difficult because of too high viscosity of the components. MEL/EC polyetherols obtained at the ratio MEL : EC = 1 : 18 and those prepared from PC creamed the most easily.

The times of foam growth were short. They ranged from 5 to 30 s and did not differ from those observed for polyetherols prepared by oxyalkylation of hydroxymethyl melamines.[13]

The samples obtained from MEL/EC polyetherols prepared at molar ratio 1 : 12 were stiff, but those from polyetherols prepared at molar ratio 1 : 18 were semistiff at room temperature. Only after being exposed to thermal treatment did they became stiff. All foams prepared from MEL/PC polyetherols were stiff.

Some physical properties of selected foams were measured: apparent density, linear shrinkage ratio, volume uptake, and the thermal properties as a mass loss upon heating. The results are presented in Table III. The apparent density of all samples was in the range 50–100 kg/m^3 and classifies the foams among the semistiff and stiff products.[14] The water uptake by the foams was rather small; it was in the range of 0.9–10.2 wt %, that is, smaller than that of the foams obtained from 1,3,5-tris(hydroxymethyl)isocyanurate and oxiranes.[13] The linear shrinkage was comparable with that for other products of the type. Somewhat higher shrinkage was observed for MEL/PC polyetherols. This might have been caused by decomposition of ester links present in the polyetherol structure during prolonged heating that degraded also the physical structure.

The foams were all found flammable.

The thermal stability of the foams was assessed by heating them at 150, 175, and 200°C and measuring the loss of mass. For all samples, a reduction of weight was observed, the highest reduction taking place during the first day of treatment. Comparing thermal stability of the present foams with the stability of those obtained using polyetherols prepared from hydroxy-

TABLE IV
Comparison of Thermal Stability of Polyurethane Foams Obtained from Various Polyetherols

No.	Polyetherol	T [°C]	Mass loss [wt %] after time of heating [days]					References
			1	2	3	4	5	
1	MEL : PO = 1 : 9	200	16.7	20.5	23.0	24.0	24.8	[3]
2	PHMM : EO = 1 : 6	175	26.2	29.3	30.2	30.3	30.4	[3]
3	PMMM : PO = 1 : 7	175	5.7	6.4	7.2	9.0	11.4	[3]
		200	17.2	20.3	21.8	23.0	23.8	
4	MEL : EC = 1 : 18*	175	16.7	18.9	20.0	21.9	22.1	
		200	19.6	22.5	24.6	26.4	27.4	
5	MEL : EC : PC = 1 : 7 : 7	175	15.1	16.5	17.8	18.9	19.2	
		200	17.9	20.8	22.4	23.9	24.8	
6	MEL : PC = 1 : 18,3*	175	5.4	6.9	7.3	8.1	8.8	
		200	11.8	13.8	16.1	17.3	18.4	
7	MEL : PC = 1 : 19,2	175	6.6	8.6	9.4	10.4	11.4	
		200	11.6	14.3	15.4	16.4	16.9	
8	MEL : EC = 1 : 9	175	6.9	8.2	11.3	12.4	13.7	
9	MEL : EC = 1 : 14	175	11.63	13.9	16.8	18.6	19.7	

* Synthesis of polyetherols carried out under nitrogen.

PO - propylene oxide, EO - ethylene oxide, PHMM - pentakis(hydroxymethyl)melamine, PMMM - pentakis(metoxymethyl)melamine.

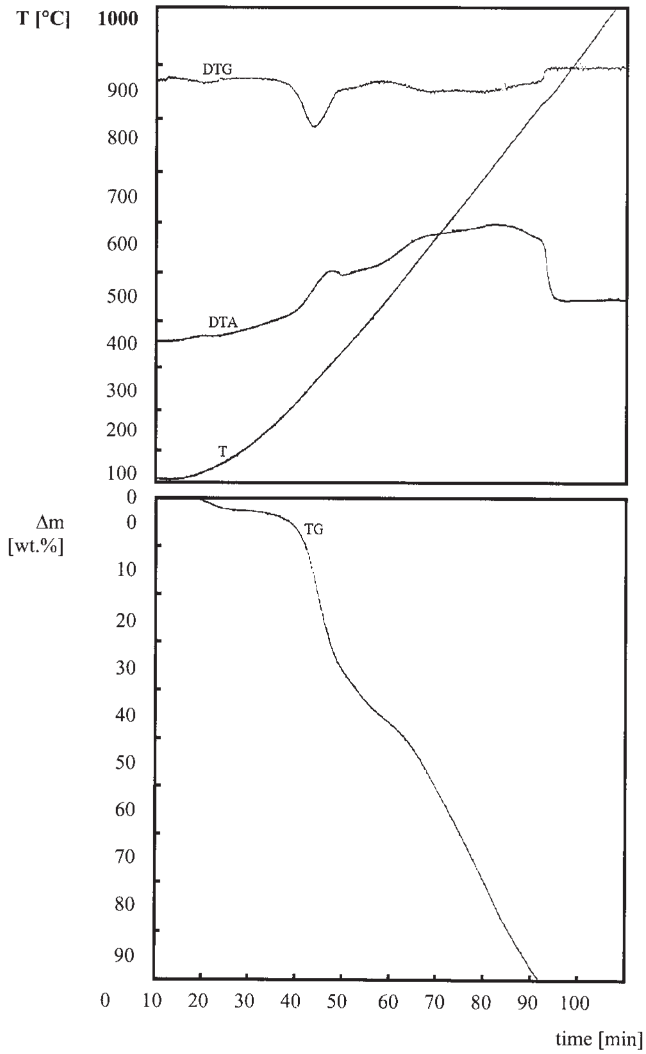

Figure 3 Thermal analysis of polyurethane foam obtained from polyetherol prepared in reaction of 1 mol MEL with 18 mol EC.

methyl derivatives of melamine and oxiranes, one can state that the former, prepared directly from melamine and carbonates, are much more stable (see Table IV, rows 2 and 8). An excellent stability was found in the foams obtained from melamine and propylene carbonate, for example, as compared with that of foams prepared using polyetherols prepared from pentakis(hydroxymethyl)melamine and propylene oxide. This is despite that the former contained some carbonate links. The reason might be that the foams basing on hydroxymethyl melamines contain oxymethylene groupings (–O–CH_2–O–) that are even less stable than carbonate links. On the thermal analysis plots of the foams prepared from melamine and propylene carbonate, the 10 wt % mass loss occurs at 200°C and the 50 wt % loss at as high temperature as ~ 500°C (Figs. 3 and 4). These figures confirm the high thermal stability of foams.

To summarize, one should point out that the new polyurethane foams prepared in this work are similar to classical stiff foams in their physical properties, but have superior thermal properties. Their thermal stability is also better than that of the foams obtained using polyetherols prepared from melamine or some of its derivatives and oxiranes.

CONCLUSION

1. Polyetherols obtained in reactions of melamine with alkylene carbonates have an improved thermal stability and can be used for preparation of rigid or semirigid polyurethane foams.

2. The polyurethane foams obtained in this work have much better thermal stability than the traditional products. Their thermal stability is also better than the

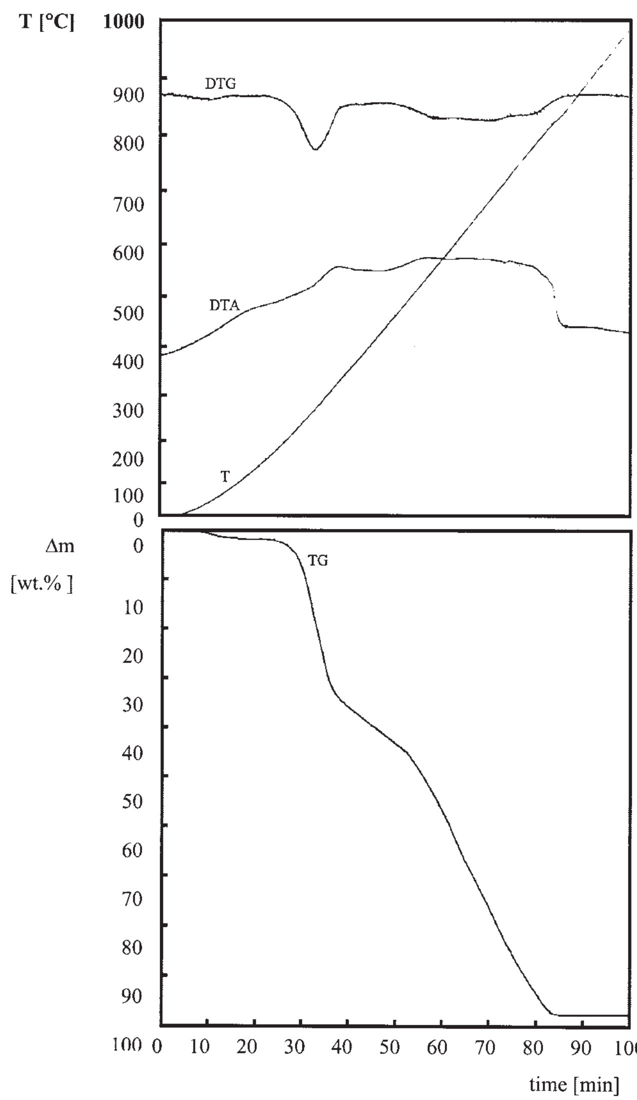

Figure 4 Thermal analysis of polyurethane foam obtained from polyetherol prepared in reaction of 1 mol MEL with 22 mol PC.

stability of those obtained from polyetherols prepared in reactions of hydroxymethyl derivatives of melamine with oxiranes.

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