

# Products of Polyaddition of 4',4-Diphenylmethane Diisocyanate with Triethylene Glycol Glycolate, Thioglycolate, Lactate, and *p*-Hydroxybenzoate

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## Synopsis

Investigations on the suitability of triethylene glycol glycolate, thioglycolate, lactate, and *p*-hydroxybenzoate for the synthesis of new polyurethanes from 4,4'-diphenylmethane diisocyanate were carried out. The products obtained were subjected to physicochemical, thermal, dielectric, and analytical tests. IR, DTA, and TG analyses were also done.

Polyurethanes belong to the group of polymers which have gained the growing appreciation of a great number of research workers as well as of many users of their products. The interest these polymers attract is due to the wide range of their advantageous properties. They have proven to be especially suitable for the production of expanded plastics, highly elastic fibers, elastomers, glues, varnishes, water emulsions, and constructional materials.<sup>1-3</sup>

Pursuing tests on the synthesis of new polyurethanes,<sup>4,5</sup> the reactions of polyaddition of 4,4'-diphenylmethane diisocyanate (MDI) with, respectively, triethylene glycol glycolate, thioglycolate, lactate, and *p*-hydroxybenzoate were carried out.

The enumerated esters were synthesized in our laboratory by a standard method of esterification.<sup>6</sup> Their yields varied between 98.8% and 99.5% of the theoretical yield. The percentage composition, saponification number, acid number, and hydroxyl group content of the esters were determined. The results are given in Table I.

The esters obtained constituted the components for the synthesis of polyurethanes. The polyaddition reaction of the enumerated esters with MDI was conducted in a three-necked flask provided with a reflux condenser and electrical stirrer with a special seal.

In order to determine the most favorable reaction conditions, the process was carried out with or without a catalyst in the following solvents: toluene, dioxane, and ethyl acetate. Anhydrous lead acetate was used as catalyst. Preliminary tests proved that most favorable results were obtained when conducting the reaction in toluene without catalyst. The presence of catalyst accelerates the reaction to such an extent that at the boiling point of the mixture the reaction takes place almost immediately and the products obtained have unwanted physicochemical properties.

The synthesis of the polymer from triethylene glycol alone and MDI was done

TABLE I  
Results of Ester Tests

No.	Ester	C, %		H, %		S, %		Saponification number, mg KOH	Acid number, mg KOH	Hydroxyl group content, %
		Calcd	Found	Calcd	Found	Calcd	Found			
1	Triethylene glycol glycolate	45.1	44.7	6.7	6.7	—	—	439.3	0.55	11.9
2	Triethylene glycol thioglycolate	40.2	39.6	6.0	6.2	21.4	20.8	380.5	2.8	—
3	Triethylene glycol lactate	48.9	49.2	7.4	7.2	—	—	414.7	4.1	11.1
4	Triethylene glycol p-hydroxybenzoate	60.5	60.1	5.6	5.6	—	—	580.3	295.0	8.1

TABLE II  
Results of Elemental Analysis

Resin	C, %		H, %		N, %		S, %	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
Resin 1	58.1	59.0	5.4	5.8	5.4	5.2	—	—
Resin 2	54.7	55.6	5.1	5.4	5.1	5.8	11.6	10.8
Resin 3	59.5	60.2	5.8	5.5	5.1	5.8	—	—
Resin 4	65.6	66.7	5.0	5.2	4.3	4.2	—	—
Resin 5	63.0	62.1	6.0	5.7	7.0	7.2	—	—

under analogous conditions, thus allowing a comparison of the properties of the obtained products and a test of the possible influence of ester groups introduced into macromolecules on the change of these properties.

On the basis of the results of the elemental analysis (Table II) and IR spectra (Figs. 1-5), the following general reaction can be assumed:

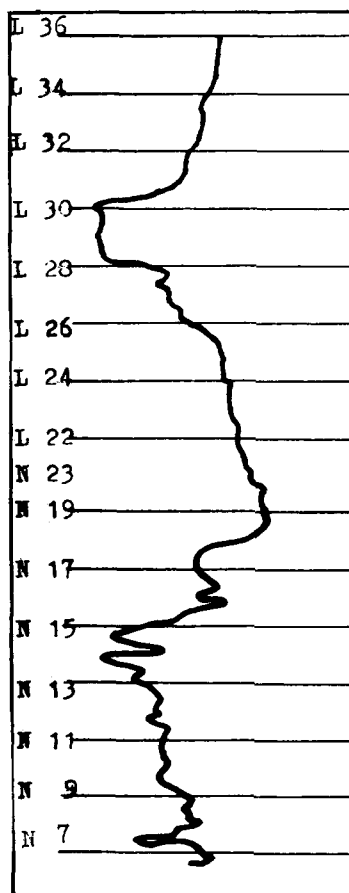


Fig. 1. Infrared spectrum of resin 1.

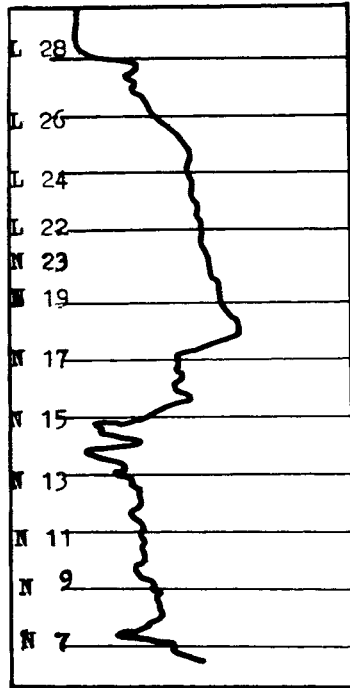


Fig. 2. Infrared spectrum of resin 2.

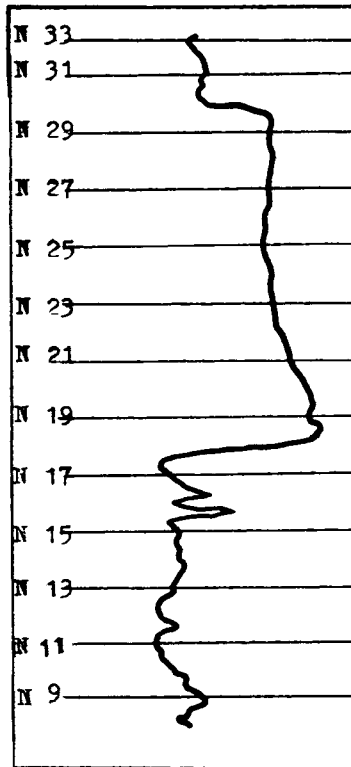


Fig. 3. Infrared spectrum of resin 3.

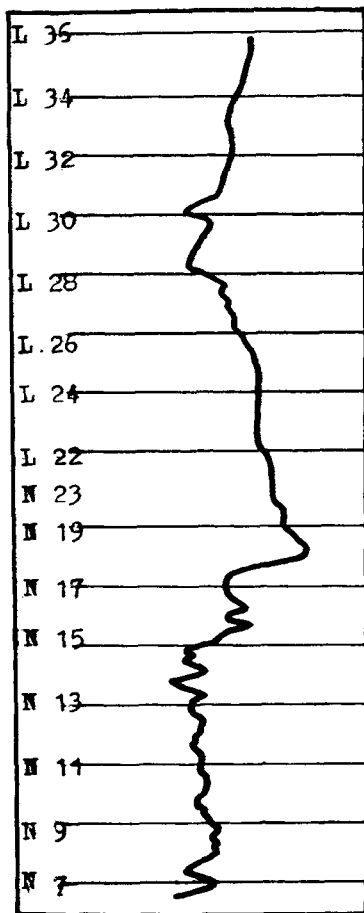
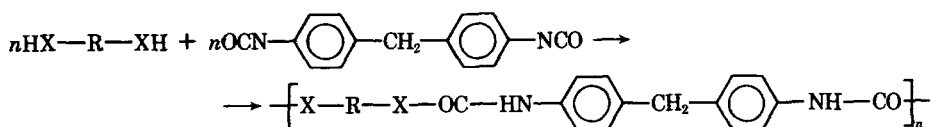
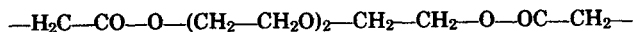


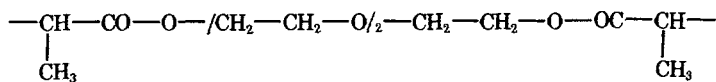
Fig. 4. Infrared spectrum of resin 4.



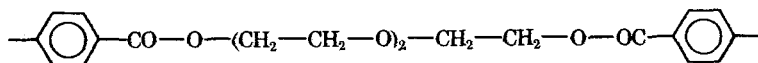
where X is O or S; and R is



when triethylene glycol glycolate (resin 1) or triethylene glycol thioglycolate (resin 2) is used,



when triethylene glycol lactate (resin 3) is used,



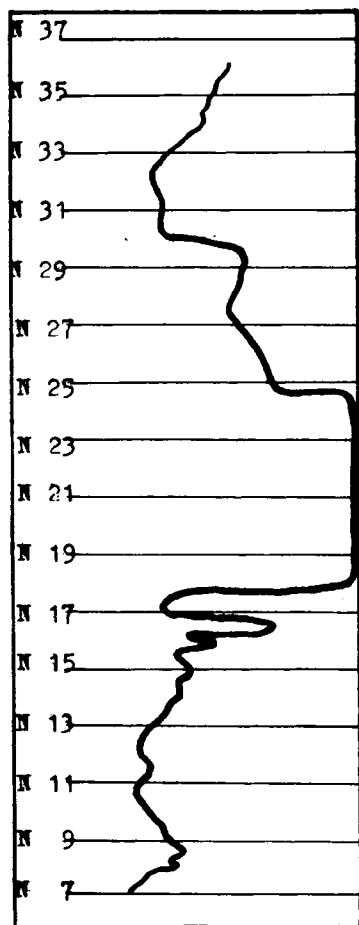
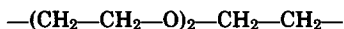


Fig. 5. Infrared spectrum of resin 5.

when triethylene glycol *p*-hydroxybenzoate (resin 4) is used,



when triethylene glycol (resin 5) is used.

Absorption bands in the  $1740\text{ cm}^{-1}$  zone indicate that presence of urethane groups,  $(-\text{O}-\text{OC}-\text{NH}-)$ . Bands in the  $1370\text{ cm}^{-1}$  zone confirm the presence of branched chains, and those in the  $730\text{ cm}^{-1}$  and  $750\text{ cm}^{-1}$  zones confirm the presence of three substituted aromatic rings.<sup>7</sup>

The products obtained during the synthesis after filtration, breaking up, and drying had the form of brown solids. Their yield varied between 92.5% (resin 5) and 99.7% (resin 4) of theoretical yield.

The polymers obtained were subjected to analytical, physicomechanical, thermal, and dielectric tests (Table III). The tensile strength and the relative extension were measured using an Instron strength tester Type TT-C. The range of tensile strength of the polymers tested was  $1.25 \times 10^7\text{ N/m}^2$  (resin 2) to  $5.15 \times 10^7\text{ N/m}^2$  (resin 3).

The impact strength of the polymers was determined by means of a Dynstat

TABLE III  
Results of Certain Physicochemical, Thermal, and Dielectric Tests for Resins 1-5

Test	Resin 1	Resin 2	Resin 3	Resin 4	Resin 5
Tensile strength, N/m <sup>2</sup>	1.26 × 10 <sup>7</sup>	0.35 × 10 <sup>7</sup>	3.04 × 10 <sup>7</sup>	2.16 × 10 <sup>7</sup>	1.0 × 10 <sup>7</sup>
Bending strength, N/m <sup>2</sup>	1.50 × 10 <sup>7</sup>	1.25 × 10 <sup>7</sup>	5.15 × 10 <sup>7</sup>	1.76 × 10 <sup>7</sup>	1.49 × 10 <sup>7</sup>
Impact strength, J/m <sup>2</sup>	2.50 × 10 <sup>3</sup>	0.66 × 10 <sup>3</sup>	5.30 × 10 <sup>3</sup>	3.41 × 10 <sup>3</sup>	1.08 × 10 <sup>3</sup>
Relative extension, %	2	0.8	6	3	2
Hardness, N/m <sup>2</sup>	1.40 × 10 <sup>8</sup>	3.53 × 10 <sup>8</sup>	1.52 × 10 <sup>8</sup>	2.09 × 10 <sup>8</sup>	1.03 × 10 <sup>8</sup>
Thermal resistance, °K	321	356	340	346	306
Melting-point, °K	498-528	531-568	538-565	477-501	538-583
Water absorption after 42 days, wt-%	2.3	1.0	1.8	1.4	7.8
Relative dielectric permeability	2.0	2.1	2.6	1.9	2.8
Dielectric loss coefficient	8.3 × 10 <sup>-2</sup>	1.3 × 10 <sup>-2</sup>	8.8 × 10 <sup>-2</sup>	1.5 × 10 <sup>-2</sup>	3.8 × 10 <sup>-2</sup>

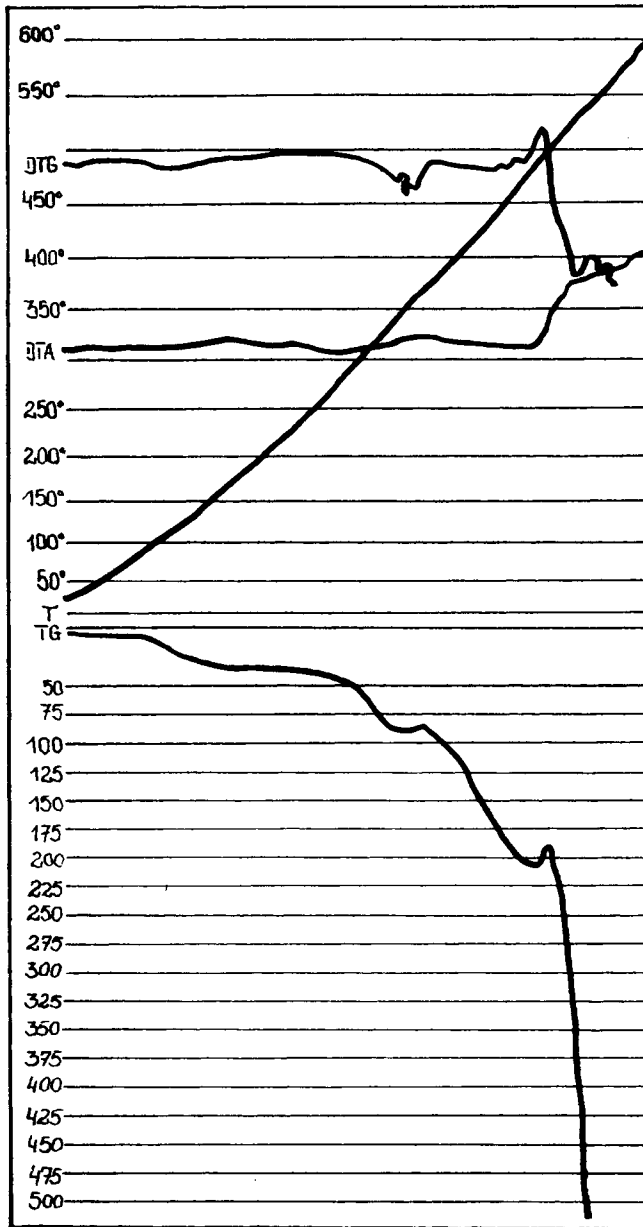


Fig. 6. DTA and TG curves for resin 1.

apparatus made by Falmechamic Company. The impact strength varied between  $1.08 \times 10^3 \text{ J/m}^2$  (resin 5) and  $5.30 \times 10^3 \text{ J/m}^2$  (resin 3).

The hardness was measured using a Brinell hardness tester Type HP-250 produced by Werkstoffprurmaschinen. The hardness values of the polymers varied between  $1.03 \times 10^8 \text{ N/m}^2$  (resin 1) and  $3.53 \times 10^8 \text{ N/m}^2$  (resin 2).

Subsequently, tests by differential thermal analysis (DTA) and thermogravimetric (TG) analysis were carried out under the following conditions: initial



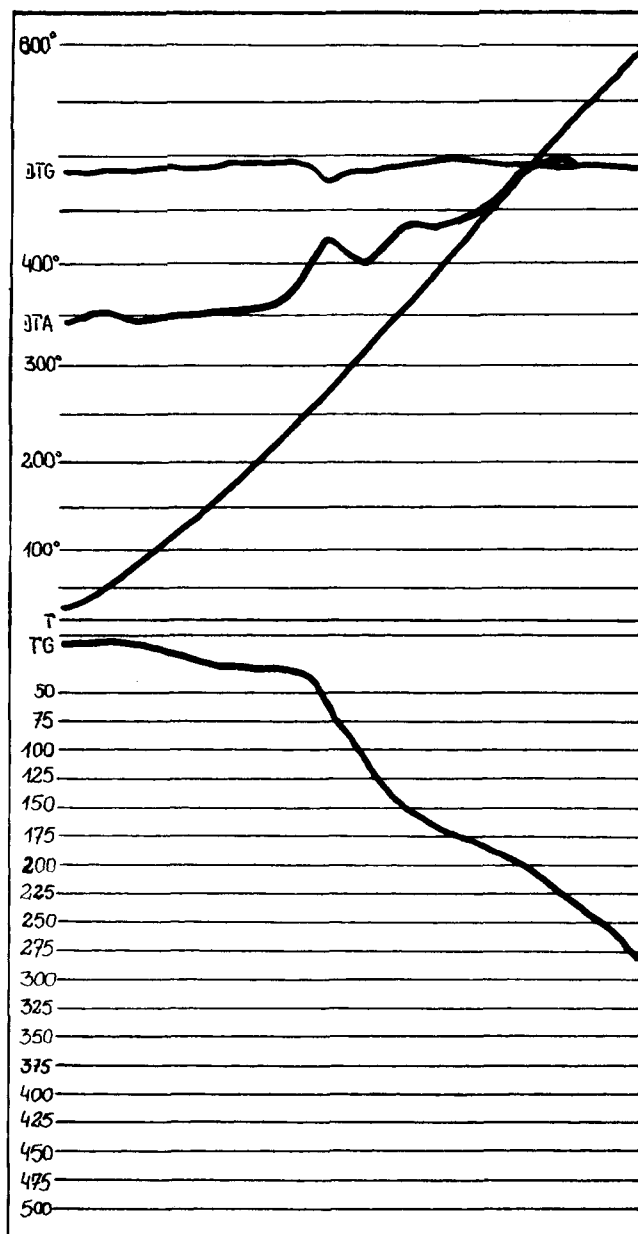


Fig. 7. DTA and TG curves for resin 2.

voltage, 50 V; heating rate, 3°C/min; TG sensitivity, 500; DTA sensitivity, 1/10; DTA sensitivity, 1/15; temperature range, 293–893°K. Weighed amounts of the resin samples were 358 mg (resin 1), 394 mg (resin 2), 294 mg (resin 3), 329 mg (resin 4), and 412 mg (resin 5). DTA, DTG, and TG curves are presented in Figures 6–10.

The polymers obtained are of a high chemical resistance. They do not dissolve in most organic solvents nor in concentrated solutions of mineral acids at room

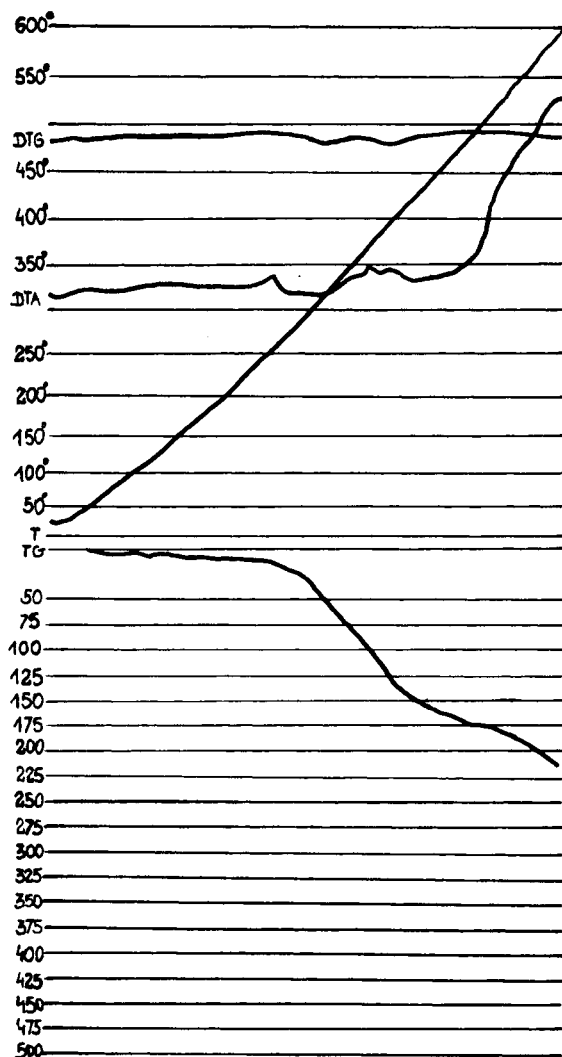


Fig. 8. DTA and TG curves for resin 3.

temperature. At higher temperatures, they dissolve in concentrated solutions of sulfuric and nitric acids. Water absorption of the synthesized polymers after 42 days is small, varying from 1.0% in the case of resin 3 to 7.8% in the case of resin 5. They have advantageous physicochemical and dielectric properties and high thermal resistance. The loss of mass at the test temperature range varied from 7.2% (resin 5, at 533°K) to 12.5% (resin 1, at 553°K).

The physicochemical properties of the polymers obtained from the synthesized hydroxy esters were more advantageous than the properties of the corresponding polyurethanes obtained from triethylene glycol alone (resin 3). This confirms their suitability for the synthesis of new polyurethanes. Especially noteworthy is the relatively high tensile strength and high impact strength of resin 3, a product of polyaddition of MDI with triethylene glycol lactate. The product having the highest hardness value was resin 2.

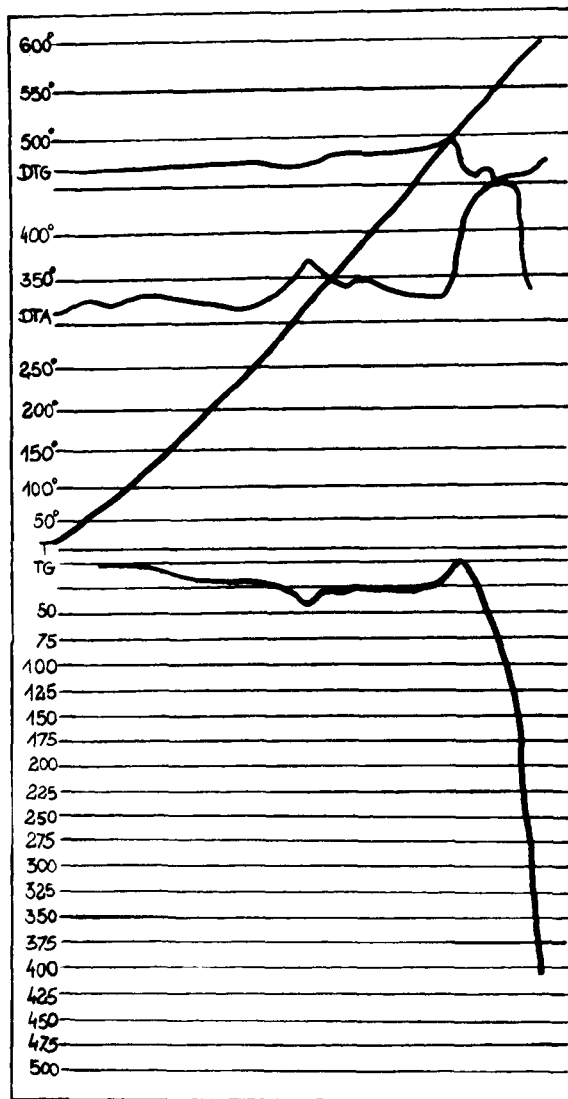


Fig. 9. DTA and TG curves for resin 4.

The polymers obtained, thanks to their high chemical and thermal resistances and good physicomechanical and dielectric properties, are likely to become products of interest for different branches of industry, the more so because of the possibility of changing their properties in the broad range.

Further investigations in this field will be aimed at improving the polymers by means of crosslinking and chain propagation.

Some properties—impact strength, tensile strength, and bending strength—of the products obtained are better than the corresponding properties of generally known and commercially available polyurethanes. They may find application in several fields of industry, especially as strengthening and filling materials in different types of constructions.

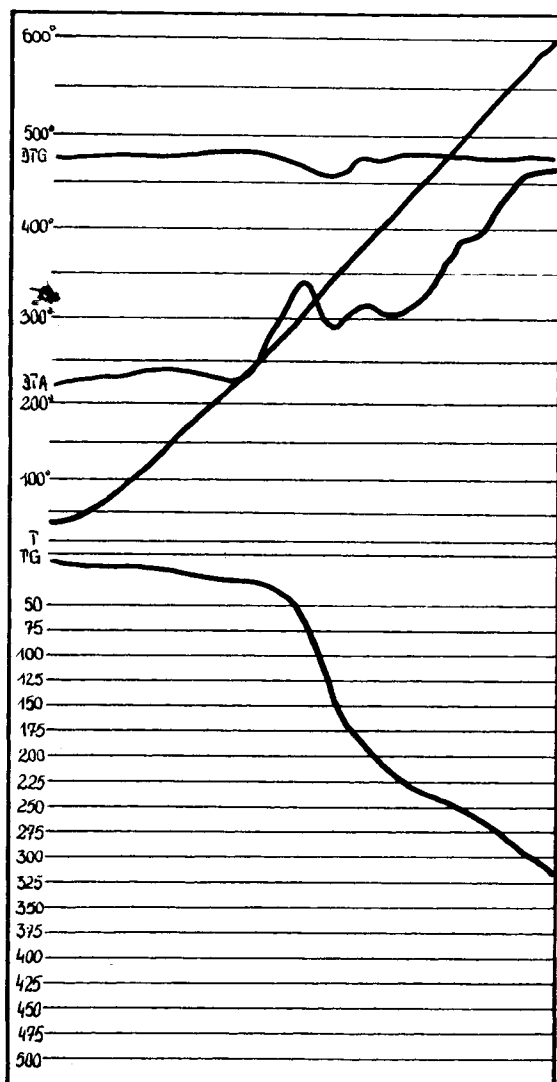


Fig. 10. DTA and TG curves for resin 5.

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