

Products of Polyaddition of Toluene 2,4-Dicarbonyl Chloride 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 toluene 2,4-dicarbonyl chloride were carried out. The products obtained were subjected to physicomechanical, thermal, dielectric, and analytical tests. IR, DTA, and TG analyses were also done.

Continuing our study^{1,2} on synthesis of new polyurethane structural materials, processes of polyaddition of toluene 2,4-dicarbonyl chloride (TDI) with triethylene glycol glycolate, thioglycolate, lactate, and *p*-hydroxybenzoate were carried out. The esters were synthesized by classical laboratory esterification methods.⁴ Elemental analyses of the esters obtained were carried out, and their saponification numbers, acid values, and hydroxyl group percentages were determined. The results obtained are compiled in Table I.

The esters obtained were used as starting materials for the synthesis of polyurethanes, which was carried on in a three-necked flask equipped with a reflux condenser and an electric stirrer with a ground joint seal. The reaction was performed using stoichiometric amounts of reactants in the presence as well as in the absence of a catalyst in the following solvents: toluene, dioxane, and ethyl acetate. Anhydrous lead acetate (about 2 wt % in relation to the TDI mass) was applied as a catalyst.

The process was continued until precipitation of the polymer was complete. Preliminary investigations have shown that optimal results can be attained by performing the process in toluene without a catalyst, which intensifies the reaction proceeding in this solvent so much that it terminates almost immediately at the boiling point of the system, giving products of worse mechanical properties. The reaction of polyaddition of TDI with triethylene glycol was performed under the same conditions in order to compare the properties of the products obtained with those of polyurethanes synthesized using triethylene glycol only, as well as to investigate the effect of ester groups upon these properties.

Based on the results of elemental analyses (Table II) and the IR spectra (Figs.

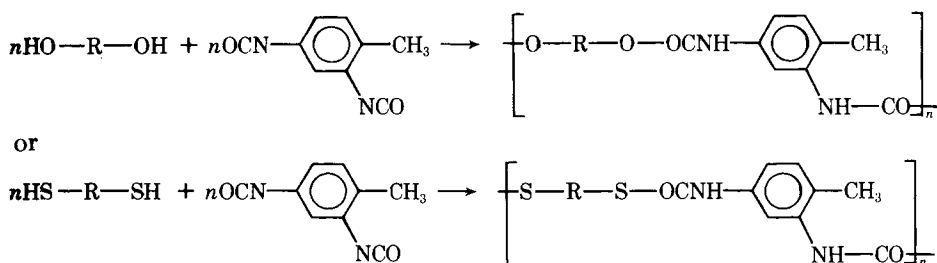
TABLE I
Results of Investigation of the Esters Obtained

No.	Ester	Analyses, %									
		C		H		S		Saponifi- cation no., mg KOH	Acid value, mg KOH	OH groups, %	
		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 <i>p</i> -hydroxybenzoate	60.5	60.1	5.6	5.6	—	—	580.3	295.0	8.1	

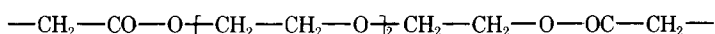
TABLE II
Results of Elemental Analysis of Polyurethanes

Resin no.	C, %		H, %		N, %		S, %	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
1	51.8	51.0	5.4	5.8	6.3	7.0	—	—
2	48.3	47.6	5.1	4.9	5.9	6.6	13.5	13.1
3	53.8	53.9	5.9	5.7	5.9	5.5	—	—
4	61.7	62.1	4.9	5.2	4.9	5.4	—	—
5	55.5	55.8	6.1	6.4	8.6	8.5	—	—

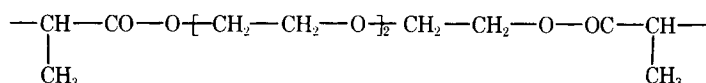
1-5), one can assume the following scheme of individual reactions for the polyurethanes obtained:



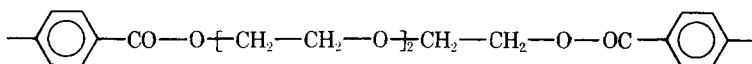
where R is
for glycolate (resin 1) and thioglycolate (resin 2):



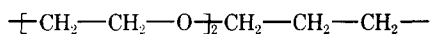
for lactate (resin 3):



for p-hydroxybenzoate (resin 4)



for triethylene glycol (resin 5)



Duration of the synthesis was 10-15 hr.

Bands in the 1740 cm^{-1} range indicate the presence of urethane groups $-\text{O}-\text{OC}-\text{NH}-$,⁵ and those in the 1600 cm^{-1} range prove the presence of aliphatic groups. Absorption bands at 1370 cm^{-1} prove the presence of branched chains, whereas those in the $730-750\text{ cm}^{-1}$ range indicate the presence of trisubstituted aromatic rings.

The pale-yellow, orange, and brown products obtained during the synthesis were filtered off, ground, and dried. Their yields varied in the 92-97.5% range of theoretical yields.

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

No.	Test	Resin 1	Resin 2	Resin 3	Resin 4	Resin 5
1	Tensile strength, N/m ²	4.71 × 10 ⁷	2.65 × 10 ⁷	0.29 × 10 ⁷	0.12 × 10 ⁷	1.37 × 10 ⁷
2	Bending strength, N/m ²	8.02 × 10 ⁷	2.73 × 10 ⁷	crumbles	0.64 × 10 ⁷	3.85 × 10 ⁷
3	Impact strength, J/m ²	3.73 × 10 ³	4.68 × 10 ³	0.74 × 10 ³	0.32 × 10 ³	1.90 × 10 ³
4	Relative extension, %	6	4	crumbles	1.8	2
5	Hardness, N/m ²	1.97 × 10 ⁸	1.61 × 10 ⁸	crumbles	0.66 × 10 ⁸	0.56 × 10 ⁸
6	Thermal resistance, K°	320	321	318	314	308
7	Relative dielectric permeability	2.0	1.8	1.8	1.9	2.4
8	Dielectric loss coefficient	3.7 × 10 ⁻²	8.3 × 10 ⁻²	1.9 × 10 ⁻²	1.4 × 10 ⁻²	2.4 × 10 ⁻²
9	Molecular weight	9100	8600	4000	5600	4400

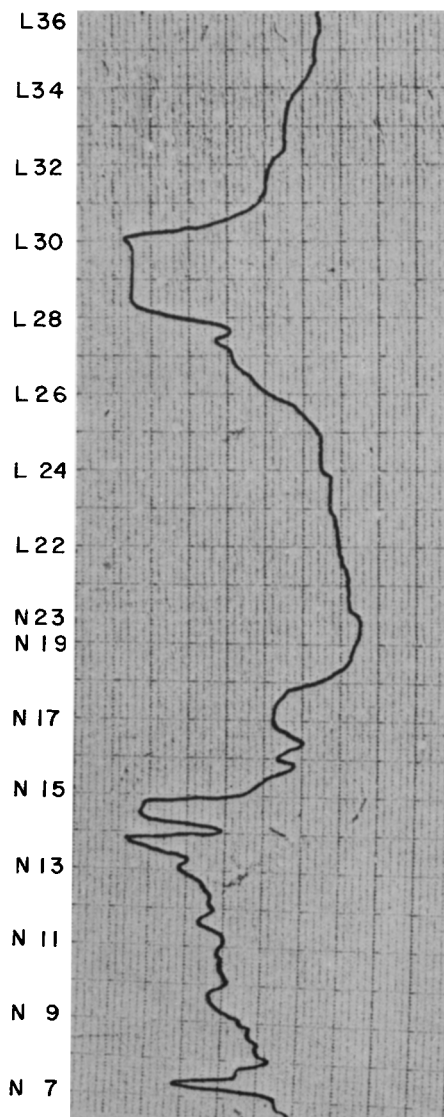


Fig. 1. Infrared spectrum of resin 1.

The polyurethanes obtained were then analyzed (Table II) and subjected to some mechanical tests and dielectric measurements (Table III). Differential thermal analysis (DTA) and thermal gravimetric analysis (TG) were also carried out (Figs. 6–10).

The derivatographic analysis was performed under the following conditions: initial tension, 50 V; heating rate, 3°C/min; sensitivity, TG—500, DTG— $\frac{1}{15}$, DTA— $\frac{1}{10}$; temperature range, 293–893°K. The TG analysis was performed for the following sample masses: resin 1, 363 mg; resin 2, 468 mg; resin 3, 442 mg; resin 4, 348 mg; resin 5, 405 mg.

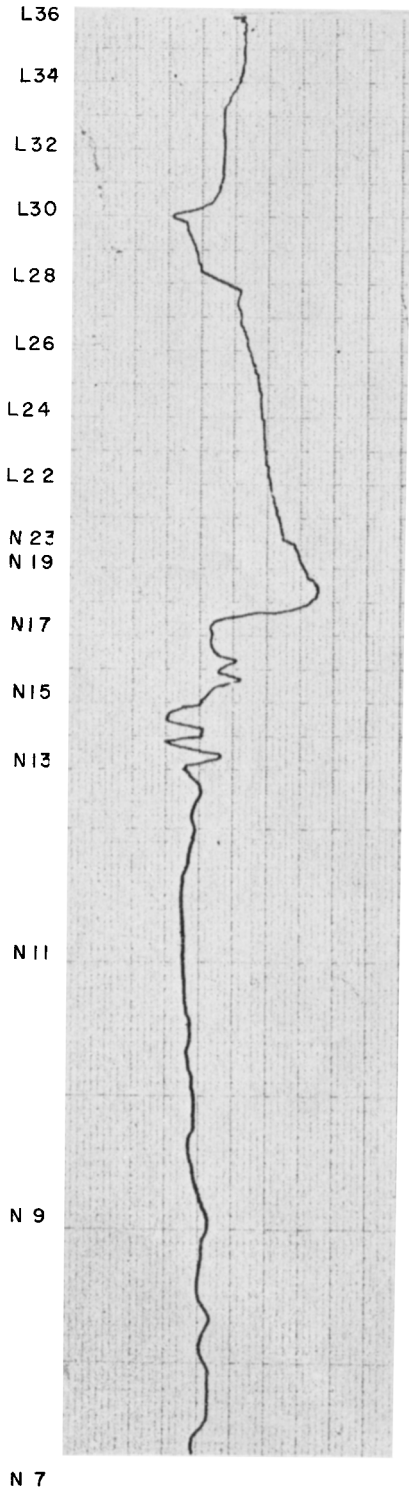


Fig. 2. Infrared spectrum of resin 2.

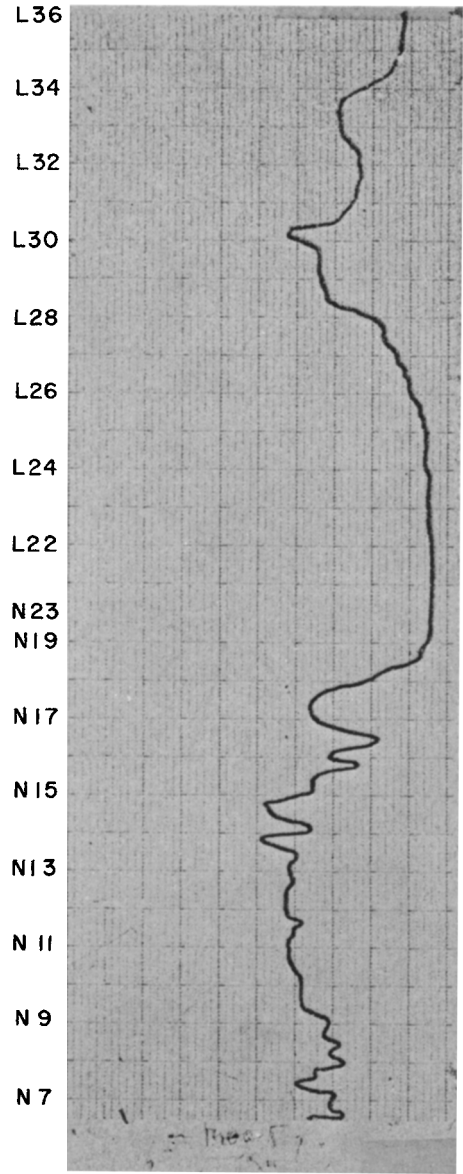


Fig. 3. Infrared spectrum of resin 3.

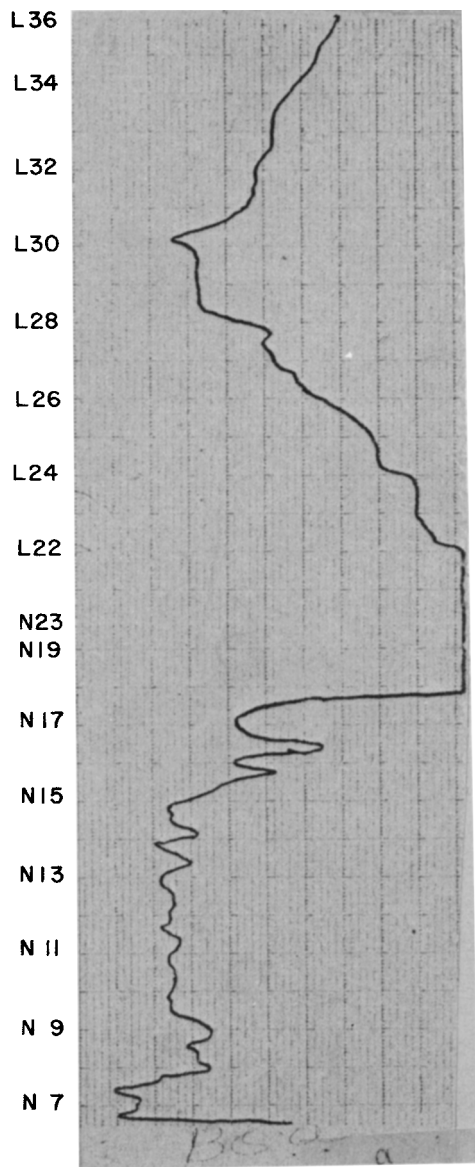


Fig. 4. Infrared spectrum of resin 4.

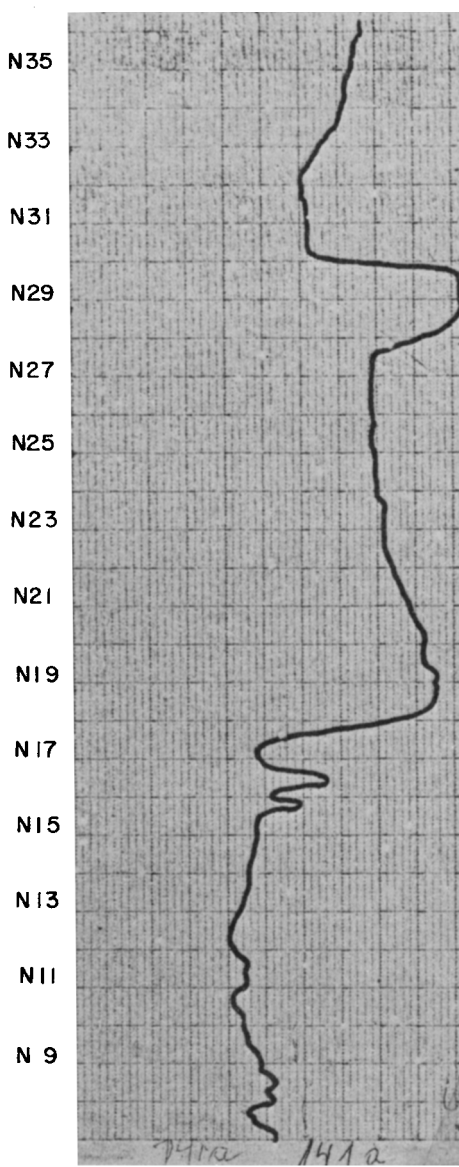


Fig. 5. Infrared spectrum of resin 5.

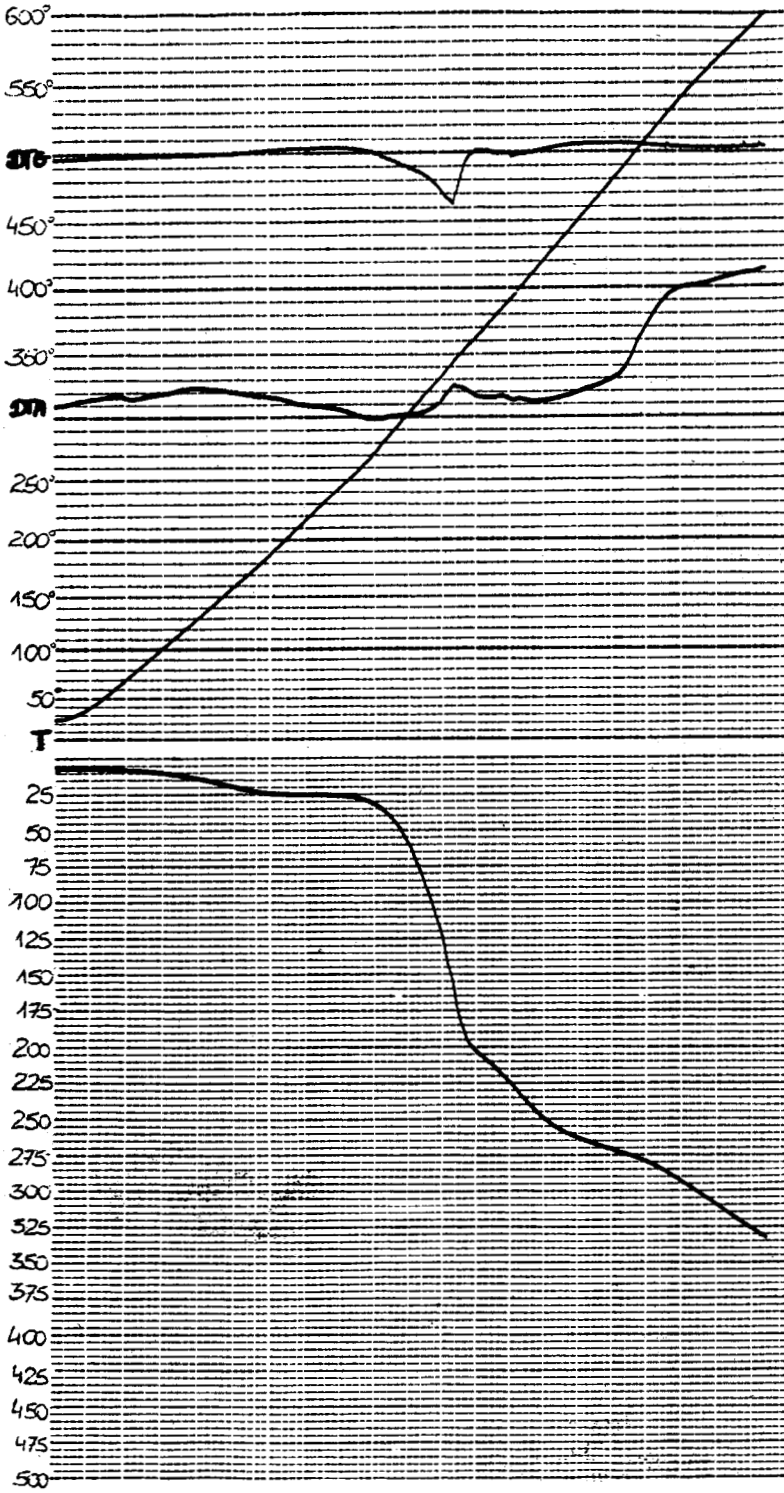


Fig. 6. DTA and TG curves for resin 1.

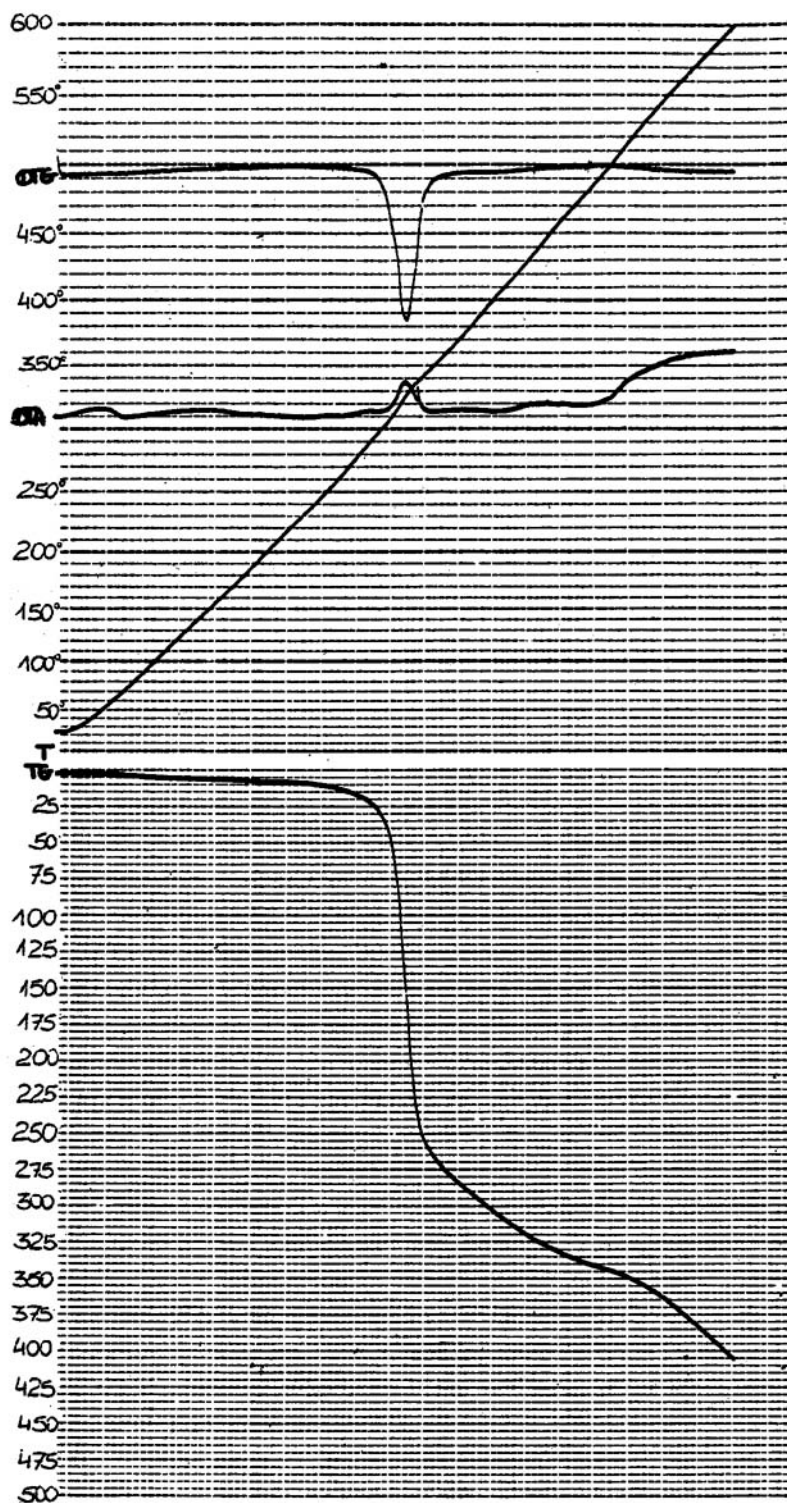


Fig. 7. DTA and TG curves for resin 2.

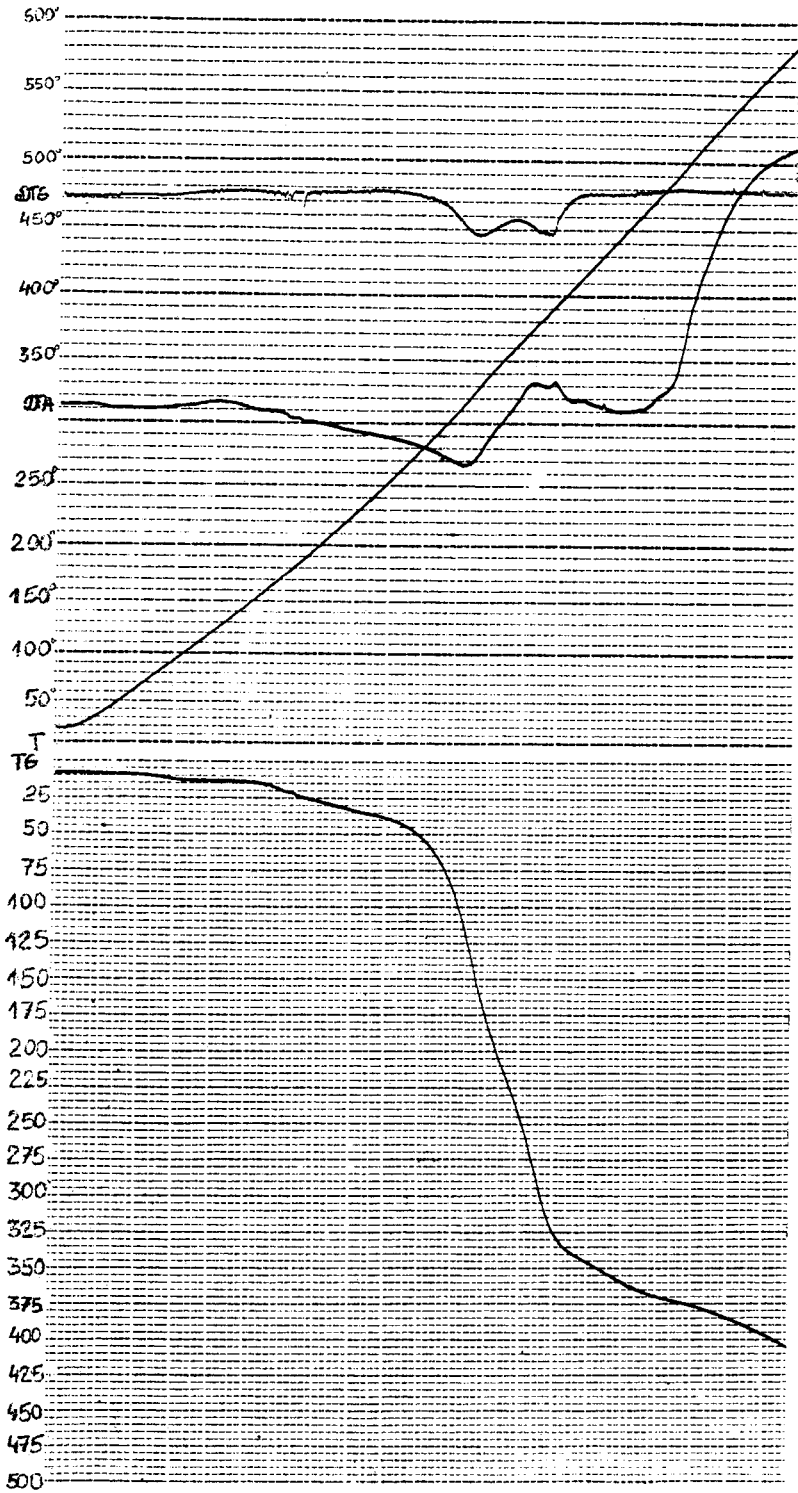


Fig. 8. DTA and TG curves for resin 3.

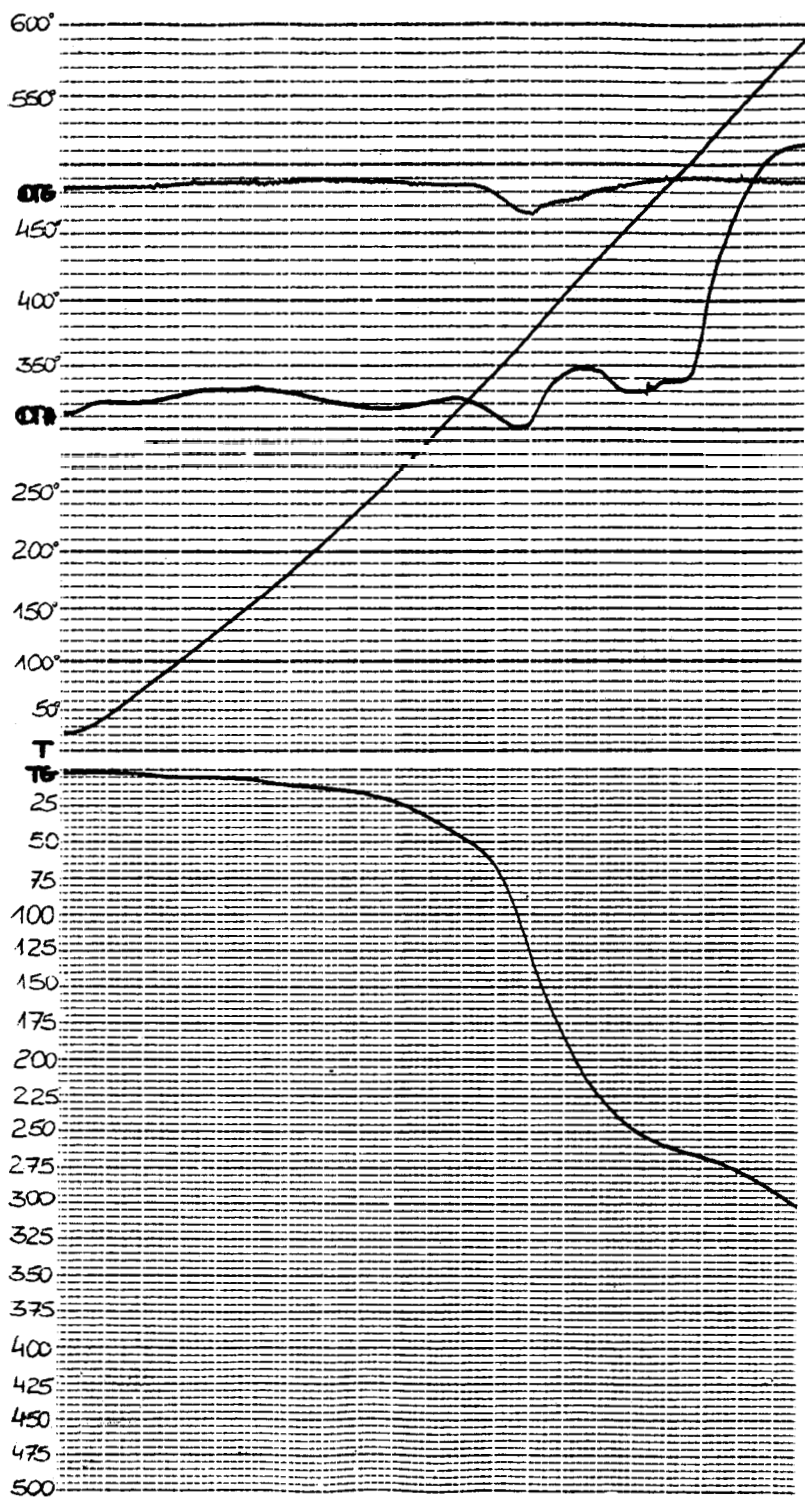


Fig. 9. DTA and TG curves for resin 4.

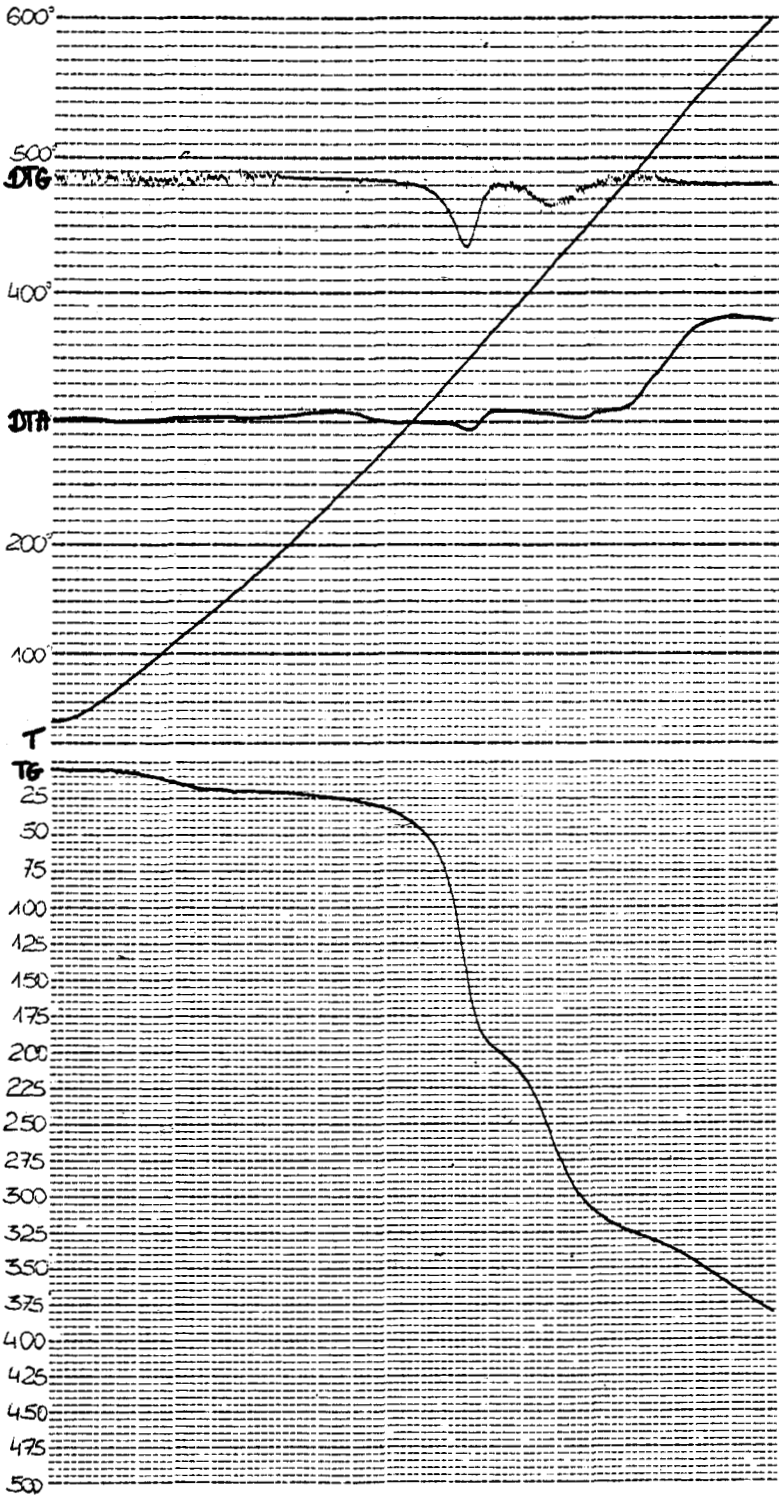


Fig. 10. DTA and TG curves for resin 5.

The results of investigations have shown that resin 1 synthesized from triethyl glycol glycolate possesses the best utilitarian properties. Its mass losses at 423°K amount to 6.5%. The polyurethanes obtained are characterized by great chemical resistance and are resistant to most organic solvents. They dissolve only in strongly polar solvents such as nitrobenzene, aniline, and phenol. At room temperature, they resist also concentrated sulfuric, hydrochloric, and nitric acids. Their good dielectric properties are also worthy of notice.

References

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