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Polyaddition Products of Desmodur L with Triethylene Glycol Glycolate, Thioglycolate, Lactate, and p-Hydroxybenzoate

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ABSTRACT

Investigations on the suitability of some hydroxyesters for the synthesis of new polyurethanes from Desmodur L were carried out. The products obtained were subjected to physicomechanical, thermal, dielectric, and analytical tests. IR, DTA, and TG analyses were also done.

The rapid development of polyurethanes is due chiefly to the large number of possibilities of shaping their internal structure. It is possible to synthesize thermoplastic polymers or duroplasts depending on reagents used. Foams, varnishes, rubbers, fibers, and glues [1] are among the most important polyurethane products, which in every one of the mentioned groups can be produced in forms widely varying in elasticity and flexibility, thermal and chemical resistance, and many strength and mechanical properties. Moreover, polyurethanes are widely used to produce stable water emulsions [2]

TABLE 1. Results of Elementary Analysis

Resin	C (%)		H (%)		N (%)		S (%)	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
Resin 1	54.6	53.9	5.1	5.0	7.9	8.2	—	—
Resin 2	52.2	53.0	5.3	5.5	7.6	7.2	8.7	8.1
Resin 3	55.8	55.1	5.9	5.6	7.6	7.0	—	—
Resin 4	60.9	62.1	5.2	5.3	6.7	6.2	—	—
Resin 5	57.2	56.1	6.0	5.9	9.5	8.9	—	—

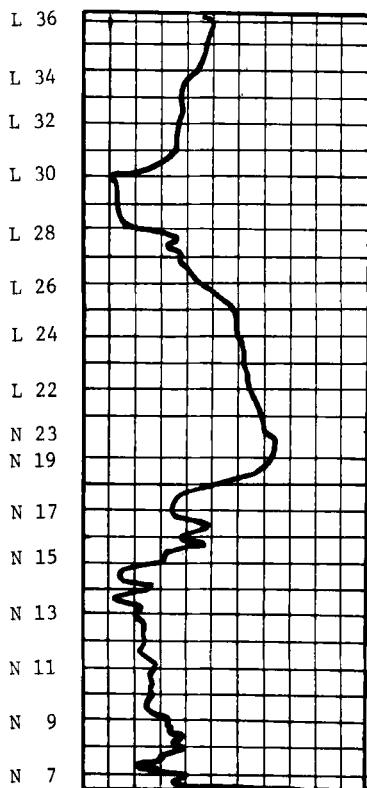


FIG. 1. Infrared spectrum of resin 1.

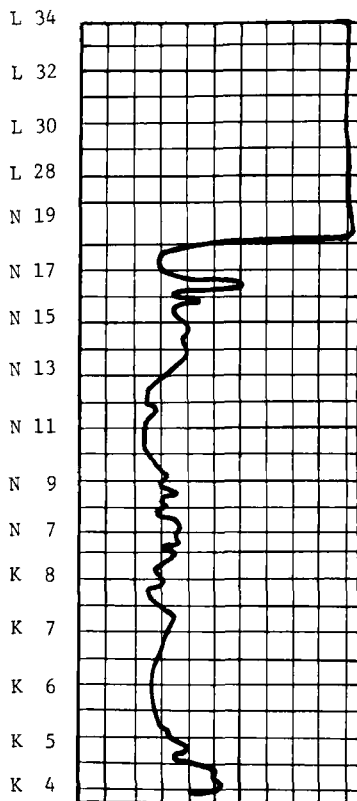


FIG. 2. Infrared spectrum of resin 2.

and surface-active compounds. Recently the use of polyurethanes synthesized from mono- and disaccharides as efficient antimetabolites has been investigated [3, 4].

Continuing studies on the synthesis of new polyurethanes [5, 6], we would like to present the results of investigations of polymers obtained from Desmodur L (a product of the reaction of 1 mole of trimethylpropane with 3 moles of tolylene diisocyanate) and triethylene glycol glycolate, thioglycolate, lactate, and *p*-hydroxybenzoate. All these esters were synthesized at our laboratory.

The polymerization of the esters with Desmodur L was carried out in a three-necked flask fitted with a reflux condenser and an electric stirrer with a ground joint seal.

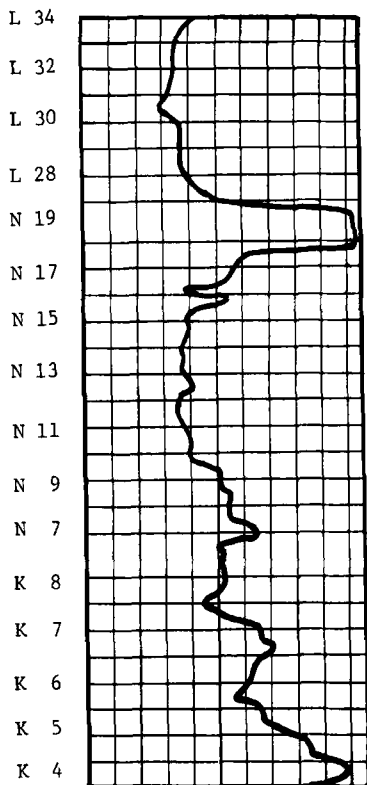


FIG. 3. Infrared spectrum of resin 3.

The reaction was carried out with and without anhydrous lead acetate as a catalyst in the following solvents: toluene, dioxane, and ethyl acetate. The reaction was continued until the polymer precipitated. The results of preliminary runs performed proved that the best products are obtained without the catalyst using toluene as the solvent. The presence of the catalyst causes almost immediate precipitation of the polymer at the boiling point of the system, which favors an increase in the degree of polydispersion of the polymer and results in a decrease in its strength.

The synthesis of Desmodur L with triethylene glycol alone was carried out in an analogous manner. This allowed us to compare

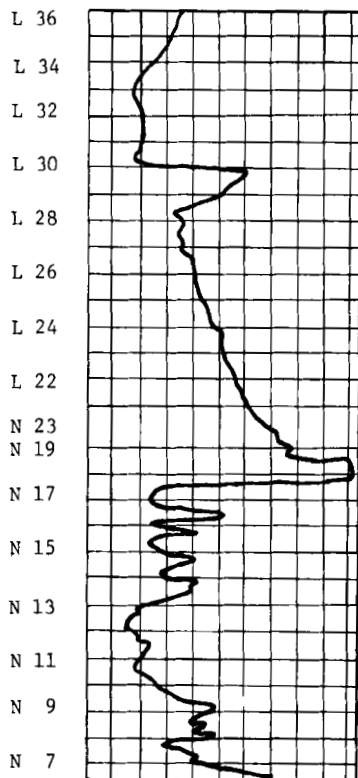
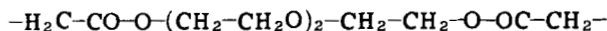


FIG. 4. Infrared spectrum of resin 4.

the properties of products obtained and to study the effect of ester groups incorporated into the polymers on the properties. Based on the results of the elementary analysis (Table 1) and the infrared spectra (Figs. 1-5) the course of the synthesis of the polymers may be assumed to be as shown in Eq. (1), where X is O or S.

When triethylene glycol glycolate (resin 1) or triethylene glycol thioglycolate (resin 2) is used, R is I,



I

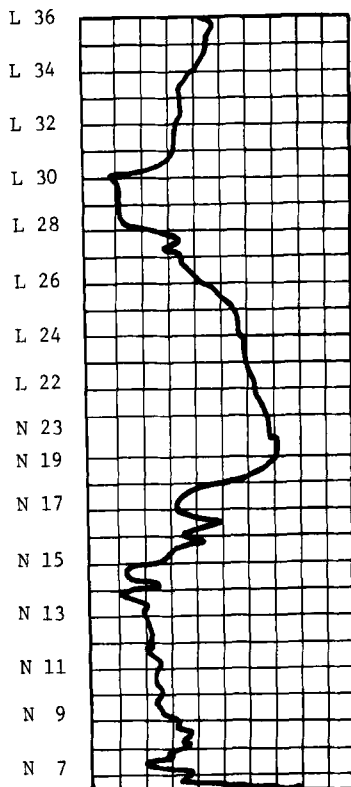
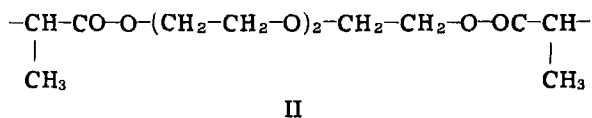
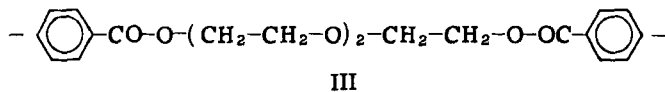


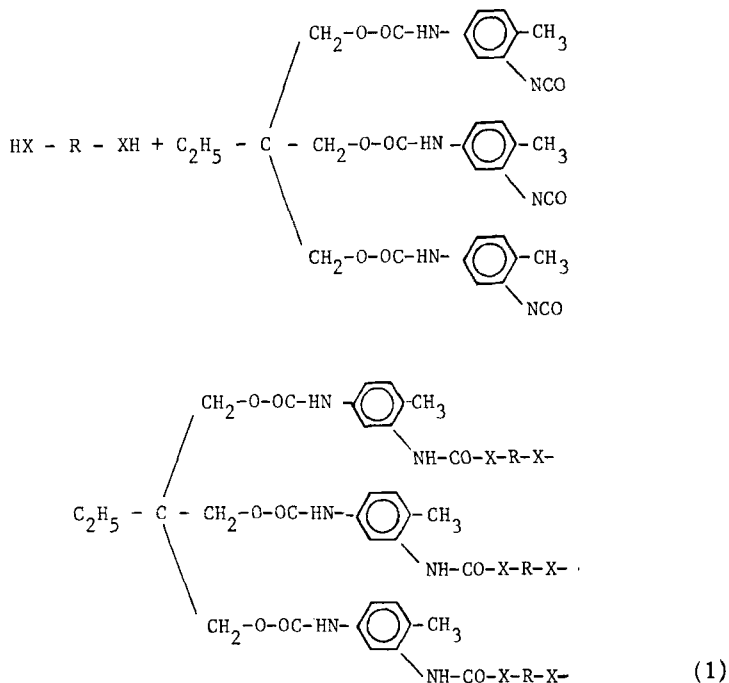
FIG. 5. Infrared spectrum of resin 5.

when triethylene glycol lactate (resin 3) is used, R is II,

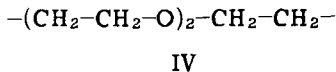


when triethylene glycol p-hydroxybenzoate (resin 4) is used, R has the structure III,





and when triethylene glycol (resin 5) is used, R is IV.



Duration of the process was 3-15 hr.

The absorption bands in the $1630-1720 \text{ cm}^{-1}$ range indicate the presence of CO groups; those in the $1450-1480 \text{ cm}^{-1}$ range indicate the presence of methylene ($-\text{CH}_2-$) groups, and those in at 1740 and $730-750 \text{ cm}^{-1}$ show the presence of urethane ($-\text{O}-\text{OC}-\text{HN}-$) groups and trisubstituted aromatic rings [7], respectively. The products precipitated, which were brown solids, were filtered off, ground, and dried. The yields of individual polymers varied from 82.1% (resin 5) to 99.3% (resin 1) of the theoretical yields. The small yield of resin 5 is due to the partial solubility of its oligomers in toluene. The polymers obtained were then subjected to certain analytical, physico-mechanical, thermal, and dielectrical tests. The results obtained are shown in Table 2.

TABLE 2. Results of 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)	2.73×10^7	0.21×10^7	0.91×10^7	1.98×10^7	1.43×10^7
2	Bending strength (N/m^2)	5.63×10^7	1.13×10^7	1.57×10^7	1.98×10^7	2.57×10^7
3	Impact strength (J/m^2)	4.61×10^3	0.71×10^3	2.52×10^3	1.41×10^3	1.76×10^3
4	Relative extension (%)	4	0.8	2	4	4
5	Hardness (N/m^2)	2.49×10^8	2.39×10^8	0.22×10^8	3.02×10^8	0.81×10^8
6	Thermal resistance (°K)	324	359	319	378	323
7	Melting point (°K)	483-514	493-538	513-543	483-543	523-543
8	Water absorption after 42 days (wt %)	11.8	2.6	20.8	1.4	15.5
9	Relative dielectric permeability	1.9	2.8	3.1	3.5	1.8
10	Dielectric loss coefficient	1.5×10^{-2}	1.5×10^{-2}	1.9×10^{-2}	1.8×10^{-2}	2.0×10^{-2}

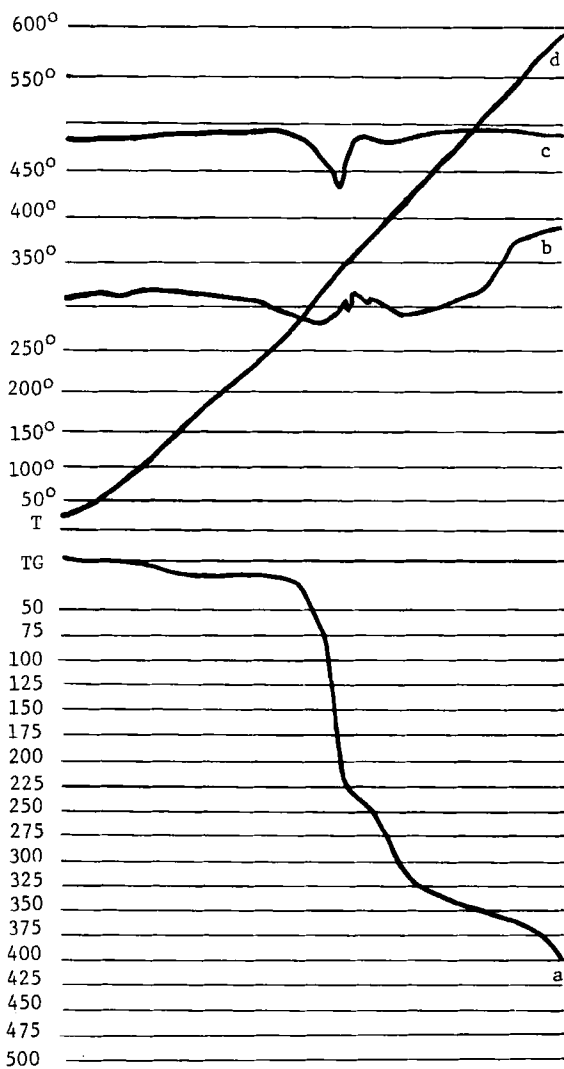


FIG. 6. Resin 1: (a) TG, (b) DTA, and (c) DTG with (d) T.

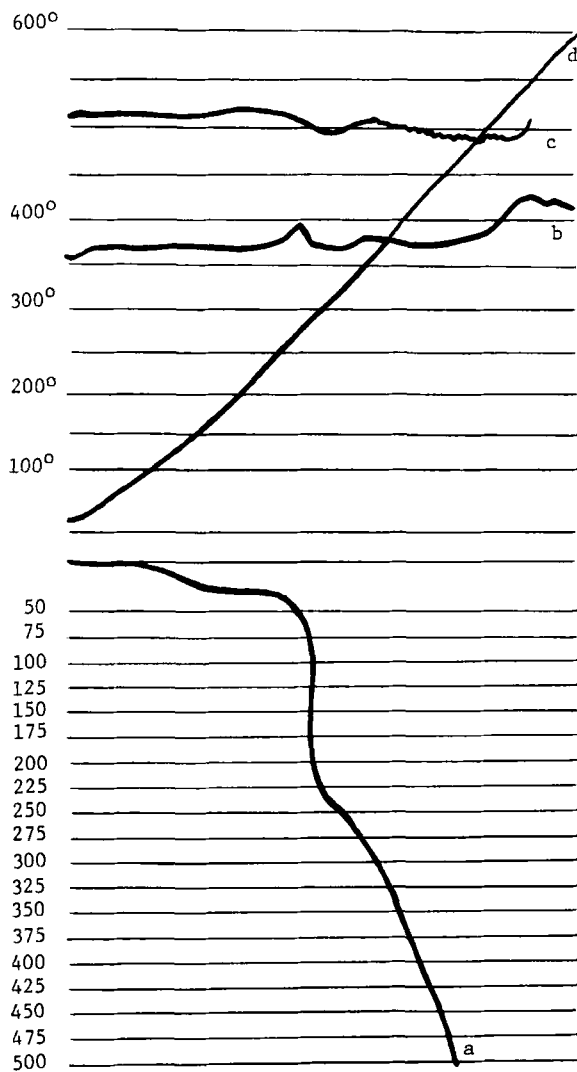


FIG. 7. Resin 2: (a) TG, (b) DTA, and (c) DTG with (d) T.

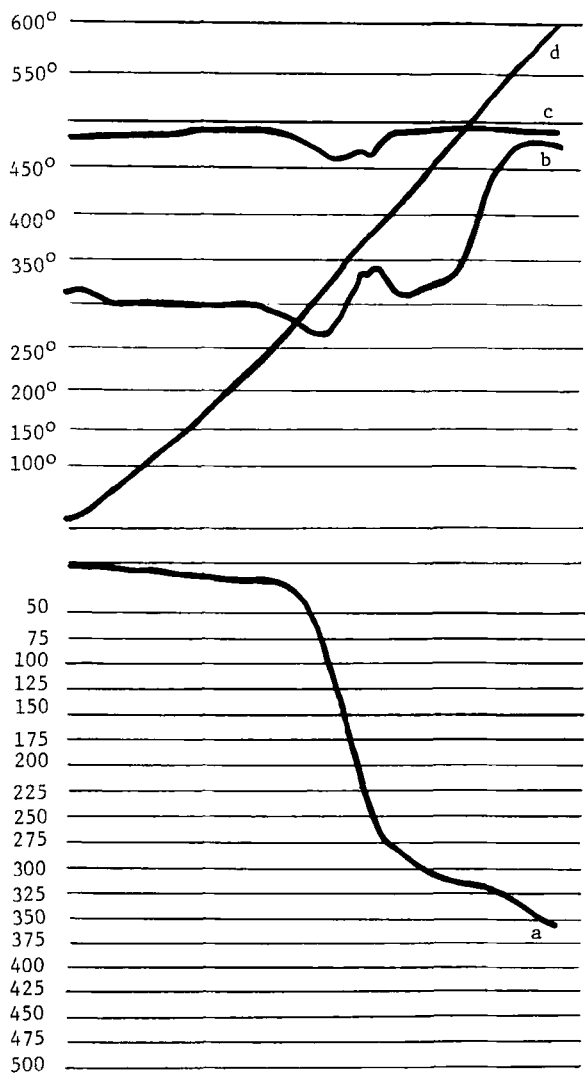


FIG. 8. Resin 3: (a) TG, (b) DTA, and (c) DTG with (d) T.

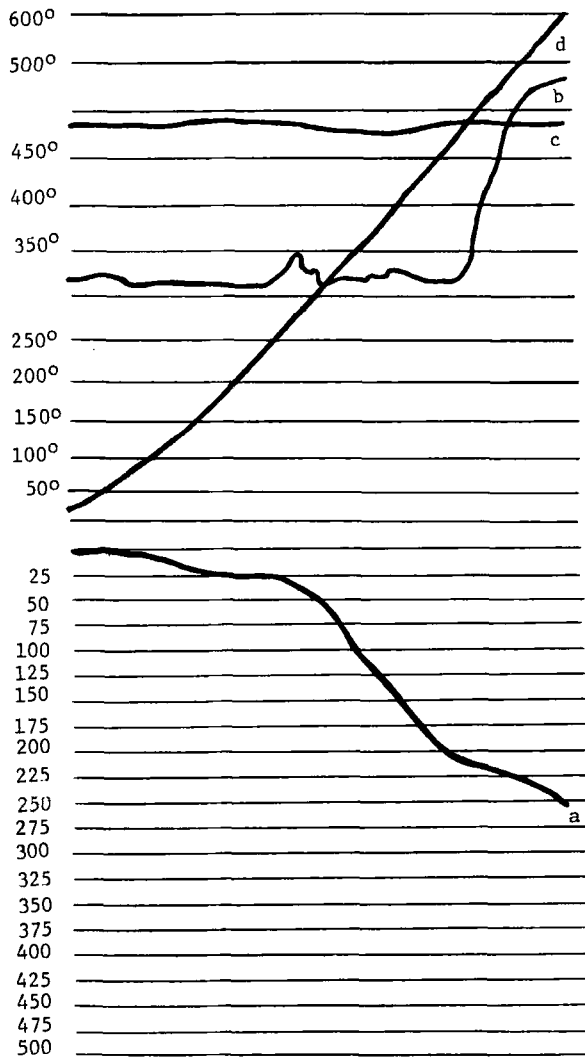


FIG. 9. Resin 4: (a) TG, (b) DTA, and (c) DTG with (d) T.

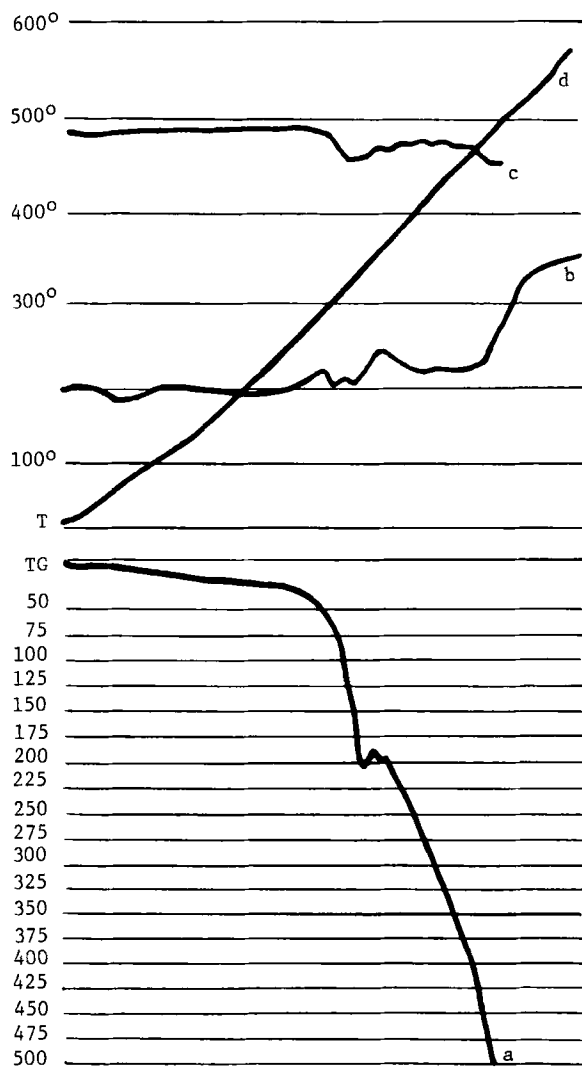


Fig. 10. Resin 5: (a) TG, (b) DTA, and (c) DTG with (d) T.

The resins were also characterized by DTA and TG methods. The analyses were conducted under the following conditions: initial voltage 50 V, heating rate 3° C/min, sensitivity for DTG, 1/15; for TG, 500; for DTA, 1/10; temperature range 293-893° K. The sample sizes were: for resin 1, 448 mg; for resin 2, 469 mg; for resin 3, 375 mg; for resin 4, 285 mg; for resin 5, 323 mg.

The DTA and TG curves are shown in Figs. 6-10. The temperature at which a distinct fall of the curves begins and the weight loss at temperature are: resin 1, 553° K, 5.5%; resin 2, 533° K, 9.5%; resin 3, 543° K, 6.6%; resin 4, 533° K, 10.5%; resin 5, 493° K, 7.7%.

The polymers obtained have adequate chemical resistance. They do not dissolve in most organic solvents, but do dissolve in strongly polar solvents, such as dimethylformamide or phenol. At room temperature the polymers are resistant to concentrated mineral acid solutions, but at elevated temperatures dissolve in concentrated sulfuric and nitric acids. Because the polymers have good dielectric properties and strength and high chemical and thermal resistivity and are amenable to further modification of their properties, they can find a variety of uses.

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