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**Products of Polyaddition of 1,5-Pentanediol
Dithioglycolate with 2,4-Tolylene Diisocyanate
and with 4,4-Diphenylmethane Diisocyanate**

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Products of polyaddition of isocyanates with other components containing reactive atoms of hydrogen are of growing interest due to various possibilities of their application.

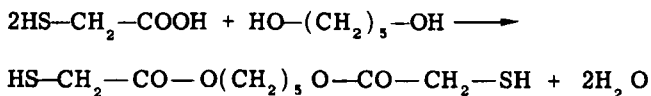
Polyurethanes and polyureas now being produced are appreciated by a great number of users. They are employed for the production of expanded plastics, film-forming plastics, flexible fibers, rubbers, glues, water emulsions, and other products [1-7]. The growing demand for polyurethane plastics also comes from the leather industry, where they are used for impregnating and improving leathers for manufacturing shoes.

The polarity of polyurethanes is due to their exceptionally high

resistance to the influence of water, atmospherical agents, oils, lubricants, organic solvents, and dilute solutions of acids and bases.

In our experiments polyurethanes were obtained from 1, 5-pentanediol dithioglycolate, synthesized in our laboratory, from 2, 4-tolylene diisocyanate and 4, 4-diphenylmethane diisocyanate.

The synthesis of 1, 5-pentanediol dithioglycolate was carried out by a standard method of esterification. *p*-Toluenesulfonic acid of (1, 3% by weight referred to the quantity of 1, 5-pentanediol) was used as a catalyst. The reaction was conducted for 2 hr until the theoretical amount of water was obtained in the azeotropic cap. The following percentage composition was determined in the ester obtained: C, 42.5%; H, 6.2%; and S, 25.1%. The reaction in which 1, 5-pentanediol dithioglycolate was obtained can be expressed by



The ester obtained constituted the component for the synthesis of polyurethanes with the diisocyanates enumerated above. The reaction in which polyurethanes were obtained, was conducted in the following manner: Into a three-necked flask provided with a mechanical stirrer and a reflux condenser, 0.1 mole (17.4 g) of 2, 4 tolylene diisocyanate, 150 cm³ of toluene, and 0.1 mole (25.2 g) of 1, 5-pentanediol dithioglycolate were introduced. The polyaddition reaction was carried out at the boiling point of the mixture. Continuous stirring was done for 4 hr until the polyaddition products were formed. The synthesis of 1, 5-pentanediol dithioglycolate with 4, 4'-diphenylmethane diisocyanate was carried out in an analogous manner.

The results of the elementary analysis given in Table 1 and the IF spectra curves (Figs. 1 and 2) confirm that the reaction in which

TABLE 1. Results of the Elementary Analysis of Resins

Resin	C (%)		H (%)		N (%)		S (%)	
	Calc	Found	Calc	Found	Calc	Found	Calc	Found
Resin 1	50.7	51.3	5.1	5.4	6.5	7.0	15.0	14.8
Resin 2	57.3	58.0	5.1	5.0	5.5	5.3	12.7	12.9

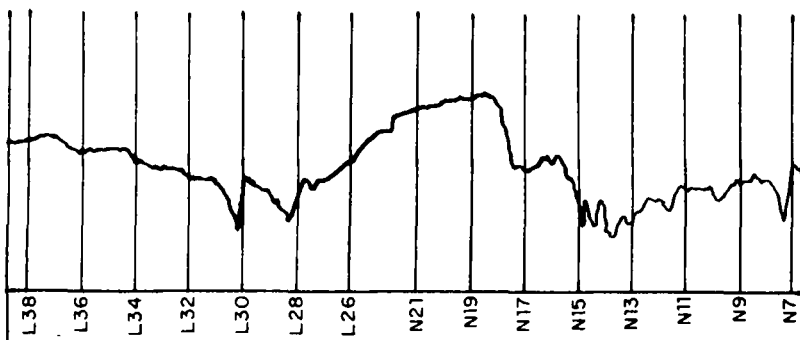


FIG. 1. Infrared spectrum of resin 1.

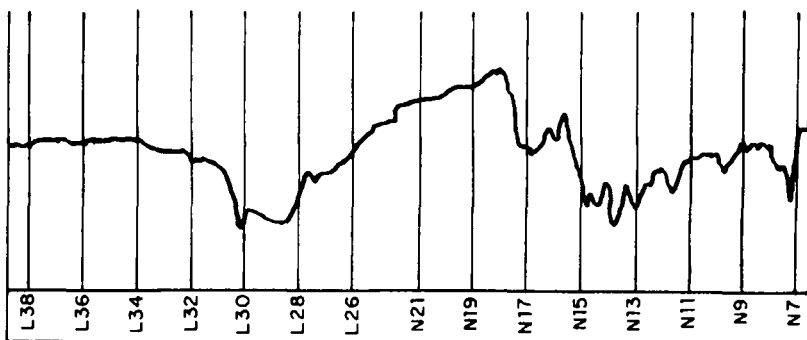
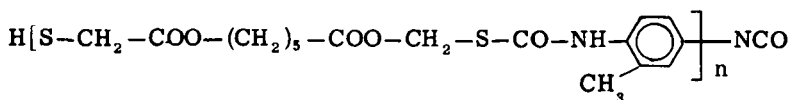
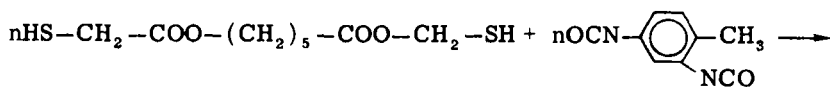


FIG. 2. Infrared spectrum of resin 2.

polyurethanes are obtained proceeded in a generally known way as expressed by

1. Reaction of 1, 5-pentadiole thioglycolate with TDI (resin 1):



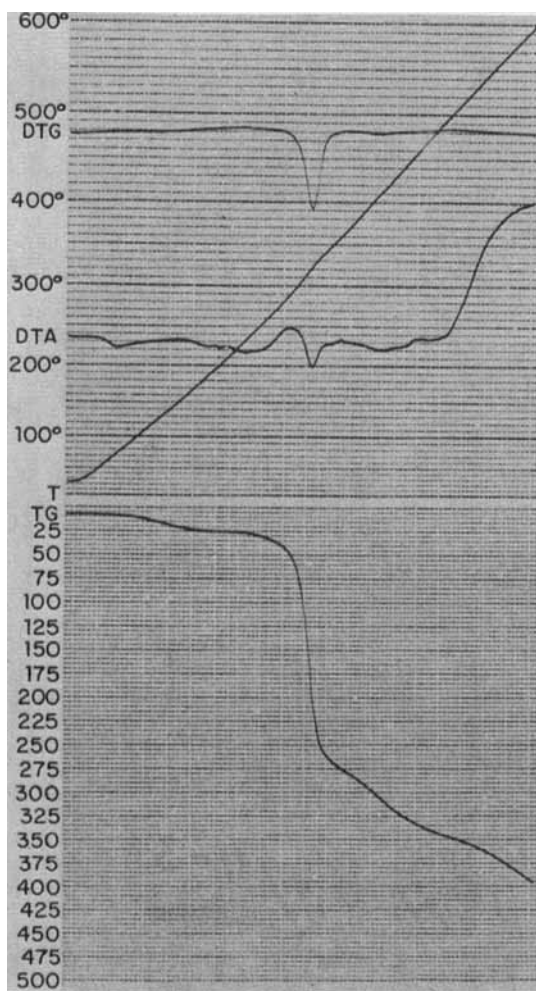


FIG. 3. DTA and TG curves for resin 1.

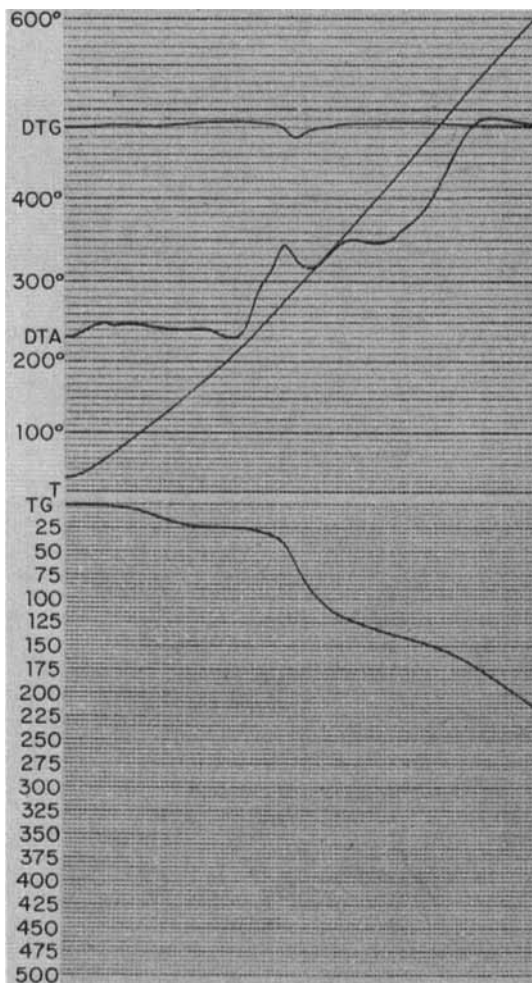
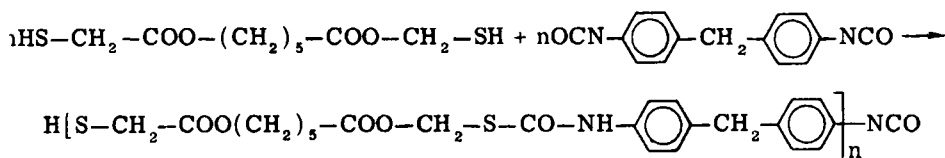


FIG. 4. DTA and TG curves for resin 2.

TABLE 2. Results of Certain Physicomechanical, Thermal, and Dielectric Tests for Resins 1 and 2

No.	Test	Resin 1	Resin 2
1	Hardness (N/m ²)	1.87 × 10 ⁸	2.02 × 10 ⁸
2	Tensile strength (N/m ²)	8.34 × 10 ⁶	46.7 × 10 ⁵
3	Impact strength (J/m ²)	0.59 × 10 ²	0.89 × 10 ²
4	Relative extension (%)	2	8
5	Molecular weight	8200	-
6	Thermal resistance (°K)	328	361
7	Water absorption after 7 days (wt%)	0.55	24.6
8	Relative dielectric permeability	2.4	3.2
9	Dielectric loss coefficient	0.032	0.015

2. Reaction of 1, 5-pentadiole thioglycolate with MDI (resin 2):



Bands in the 1450 cm⁻¹ zones confirm the presence of methylene groups (CH₂) [8]. Bands in the 1150 cm⁻¹ zones indicate the presence of an ester group (O-CO) [8]. Medium bands in the 1470 to 1500 cm⁻¹ zones confirm the presence of a NH-CO group [8].

The polymers obtained after filtration, drying, and breaking up are light yellow solids (when TDI is used) and dark brown solids (when MDI is used). Their characteristic feature is a high chemical resistance. At room temperature their properties do not change when subjected to the influence of concentrated solutions of sulfuric, nitric, and hydrochloric acids. They dissolve in concentrated solutions of sulfuric and nitric acids when heated. They do not dissolve in typical organic solvents. Resin 1 changes its properties at higher temperature only under the influence of solvents of high polarity such as nitrobenzene, dimethylformamide, aniline, and phenol.

The differential thermal analysis (DTA) and thermogravimetric (TG) analysis were also made. DTA and TG curves for resin 1 are shown in Fig. 3, and those for resin 2 in Fig. 4. Analysis was carried out in the following conditions: heating rate, 3°/min; DTA sensitivity, 1/5; TG sensitivity, 500; DTG sensitivity, 1/15; weighted amount of resin 1, 0.473 g; and weighed amount of resin 2, 0.288 g.

From the form of DTA curve (Fig. 3) it appears that there were no changes in resin 1 when it was heated up to 533°K. The loss of mass of resin 1 up to 533°K, 6.3%, is insignificant.

The form of the DTA curve (Fig. 4) indicates that resin 2 is stable up to 483°K. The loss of mass at this temperature is 8.6%.

The polyaddition products were also subjected to some thermal and electrical resistance tests. The results are shown in Table 2.

From the data in Table 2, it appears that resin 2 has better resistance properties and higher thermal resistance compared to resin 1. The synthesized resins are of high chemical and thermal resistance, and have advantageous dielectric properties.

REFERENCES

- [1] J. H. Saunders and K. C. Frisch, Polyurethanes. Chemistry and Technology, Wiley-Interscience, New York, 1963.
- [2] U.S. Patent 3,379,687 (1968).
- [3] P. W. Ryan, J. Elastoplast., 3, 57 (1971).
- [4] E. Windemuth, Kunststoffe, 57(5), 337 (1967).
- [5] Z. Wirpsza, Polimery, 18(6), 274 (1973).
- [6] P. Penczek, Ibid., 18(6), 277 (1973).
- [7] T. Lesiak, and J. Iwazkiewicz-Nowak, Chemik, 6, 220 (1972).
- [8] I. R. Dyer, Spektroskopia absorpcyjna w chemii organicznej, PWN, Warsaw, 1967.

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