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Antoni Zochniak[a]; Stanislaw Gaika[a]
[a] Technical Department, University of Silesia, Sosnowiec, Poland

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# Products of Polyaddition of 1,1′-Isopropylidene-bis-(p-phenylene-oxy)-di-β-ethanol Thioglycolate with 4,4′-Diphenylmethane Diisocyanate and Desmodur L

ANTONI ZOCHNIAK and STANISLAW GAŁKA

Technical Department
University of Silesia
Sosnowiec, Poland



ABSTRACT

Esterification of dianol 22 by means of thioglycolic acid and some analytical tests of the product obtained were carried out. The synthesis of polyurethanes was then carried out using 4,4'-diphenylmethane diisocyanate and Desmodur L. The products of polyaddition were subject to some physicomechanical, thermal, and dielectric tests.

Pursuing the investigation [1-4] in search of new polymers and the raw materials for obtaining them, the reactions of polyaddition of 1,1'-isopropylidene-bis-(p-phenylene-oxy)-di-β-ethanol thioglycolate with 4,4'-diphenylmethane diisocyanate, commonly called MDI, and with Desmodur L were carried out.

1,1'-Isopropylidene-bis-(p-phenylene-oxy)-di-β-ethanol thioglycolate was synthesized in our laboratory using 1,1'-isopropylidene-bis-(p-phenylene-oxy)-di-β-ethanol (AKZO Chemie Nederland, Amsterdam) and thioglycolic acid (Polskie Odczynniki Chemiczne, Gliwice, Poland).

1'-Isopropylidene-bis-(p-phenylene-oxy)-di-β-ethanol, the commercial name of which is dianol 22, is a product of the reaction of polyaddition of 2 mol of ethylene oxide with 1 mol of 2,2'-di-(4-hydroxyphenylene)-propane.

The esterification of dianol 22 with thioglycolic acid was carried

TABLE 1. Test Results of Dianol 22 Thioglycolate

| No. | Test | Results | |
|---|---|---|---|
| | | Found | Calculated |
| 1 | Acid number, [mg KOH/g] | 63.6 | - |
| 2 | Saponification number, [mg KOH/g] | 283.2 | - |
| 3 | Mass density [$kg/m^3$] | $1.22 \times 10^3$ | - |
| 4 | Ester number [mg KOH/g] | 219.6 | 241.8 |
| 5 | Refraction of light coefficient | 1.5570 | - |
| 6 | Sulfur content, [%] | 12.90 | 13.85 |



out in the following way. Into a three-necked flask provided with an electric stirrer with a ground glass joint and with an azeotropic distillation head with the reflux condenser 0.5 mol (158.0 g) of dianol 22, 1 mol (92.0 g) of thioglycolic acid, 100 $cm^3$ of benzene, and 1 g of p-toluenesulfonic acid as a catalyst were introduced. The reaction was carried out for 7 h at the boiling point of the reaction mixture until the theoretical amount of water was distilled in the azeotropic head.

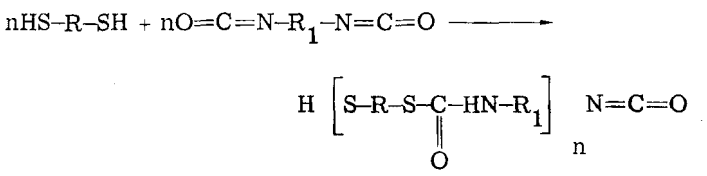
The product obtained was purified from benzene and p-toluenesulfonic acid by means of vacuum distillation. 227.5 g of dianaol 22 thioglycolate was obtained which was 98.0% of the theoretical yield. The ester was subjected to some analytical tests to assure the correct reaction run of polyaddition with MDI and with Desmodur L. Acid, saponification and ester numbers, mass density, refraction of light coefficient, and sulfur content were determined according to the requirements of the Polish Standard PN-68/C-89401.

The results are summarized in Table 1.

The product was then used in polyaddition reactions with MDI and Desmodur L for the synthesis of polyurethanes. The reactions were carried out in a three-necked flask with an electric stirrer, a ground glass joint and a reflux condenser.

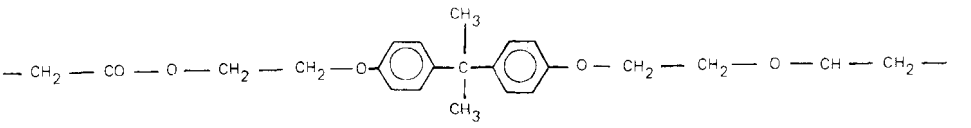
40.0 g of dianol 22 thioglycolate, 23.75 g of MDI solution with a 30.5% NCO group content, 200 $cm^3$ of benzene, and 1.5 g of lead stearate as catalyst were put into the flask. The process was conducted for 8 h until the polymer was precipitated from the solution. The product was filtered and dried. 63.0 g of polyurethane was obtained which was 98.8% of the theoretical yield.

On the basis of the known mechanism [5, 6] of polymer formation, the following synthesis reaction may be assumed:

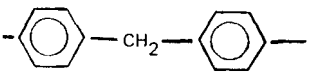


Resin 1

where R is



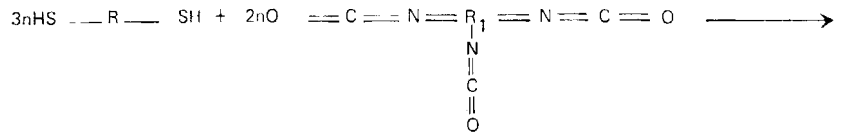
and $R_1$ is

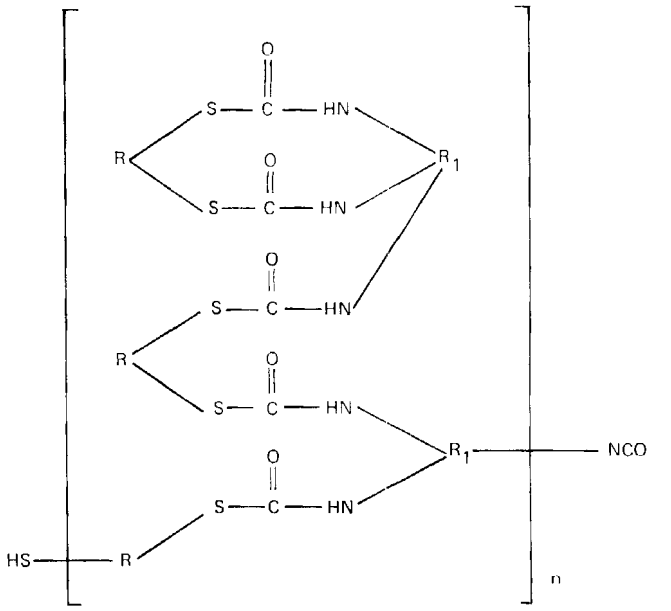


Dianol 22 thioglycolate with Desmodur L was synthesized in the same way.

From 0.1 mol (46.4 g) of dianol 22 thioglycolate and 129.2 g of the solution of Desmodur L with a 6.5% NCO group content, 76.0 g of the polymer was obtained which was 84.3% of the theoretical yield.

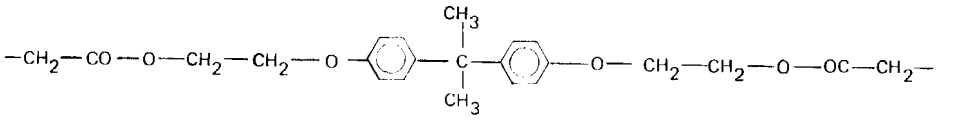
The synthesis may be expressed by





Resin 2

where **R** is



and $R_1$ is

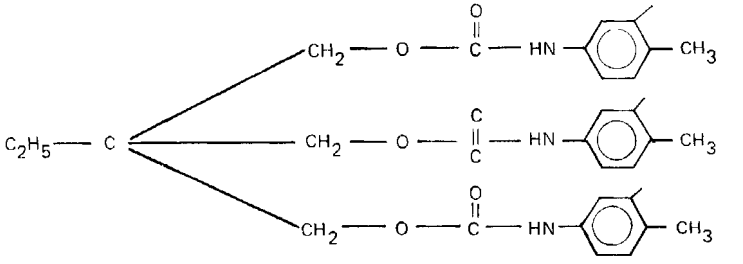


TABLE 2. Results of Physicomechanical, Thermal, and Dielectric Tests of the Products of Polyaddition

| No. | Test | Results | |
|---|---|---|---|
| | | Resin 1 | Resin 2 |
| 1 | Tensile strength, [$N/m^2$] | $8.01 \times 10^6$ | $6.57 \times 10^6$ |
| 2 | Unit elongation, [%] | 3.11 | 2.5 |
| 3 | Bending strength, [$N/m^2$] | $2.13 \times 10^4$ | $1.02 \times 10^4$ |
| 4 | Hardness, [HB] | 22.6 | 25.47 |
| 5 | Impact strength, [$J/m^2$] | $1.63 \times 10^3$ | $7.99 \times 10^2$ |
| 6 | Thermal resistance by Vicat, [K] | 432 | 371 |
| 7 | Breakdown temperature [K] | 513 | 510 |
| 8 | Molding temperature, [K] | 458 | 483 |
| 9 | Relative permittivity | 2.89 | 2.79 |
| 10 | Dielectric loss coefficient | $1.1 \times 10^{-2}$ | $7.2 \times 10^{-3}$ |
| 11 | Water absorption, [%]: | | |
| | After 24 h | 0.11 | 0.10 |
| | After 168 h | 0.42 | 0.54 |
| | After 672 h | 0.83 | 0.85 |



The resins were subject to physicomechanical, thermal, and dielectric tests. The following characteristics were determined according to Polish Standards (PN): tensile strength and unit elongation (PN-68/C-87034); bending strength (PN-72/C-04243); impact strength (PN-68/C-89029); hardness (PN-68/C-89030), thermal resistance by Vicat (PN-69/C-89024); breakdown temperature, molding temperature, and water absorption (PN-66/C-84032); relative permittivity (PN-61/E-04403); and dielectric loss coefficient.

TABLE 3. Tests of Solubility of the Products of Polyaddition[a]

| No. | Solvent | Resin 1 | | Resin 2 | |
|---|---|---|---|---|---|
| | | Room temperature | Solvent boiling point | Room temperature | Solvent boiling point |
| 1 | Acetic acid | - | - | - | - |
| 2 | Hydrochloric acid | - | - | - | - |
| 3 | Sulfuric acid | + | + | + | + |
| 4 | Nitric acid | + | + | + | + |
| 5 | NaOH 25% solution | - | - | - | - |
| 6 | Acetic anhydride | - | - | - | - |
| 7 | Pyridine | 0 | 0 | 0 | 0 |
| 8 | Benzene | - | - | - | - |
| 9 | Carbon tetrachloride | - | - | - | - |
| 10 | Toluene | - | - | - | - |
| 11 | Xylene | - | - | - | - |
| 12 | Dimethylsulfoxide | 0 | 0 | 0 | 0 |
| 13 | Dimethylformamide | 0 | + | 0 | 0 |
| 14 | Extraction naphtha | - | - | - | - |
| 15 | Nitrobenzene | - | 0 | - | 0 |

[a]Where - designates entire insolubility, + good solubility, and 0 weak solubility.

The solubilities of the synthesized polyurethanes in most typical organic solvents and in solutions of mineral acids and bases were also tested. The results are given in Tables 2 and 3.

DTA and TG analyses were done as well. Diagrams for Resins 1 and 2 are shown in Figs. 1 and 2, respectively.

For the measurements, 300 mg samples were taken. The heating rate was 20°/min. DTA sensitivity was 1/20, DTG sensitivity was 1/15, and TG sensitivity was 500.

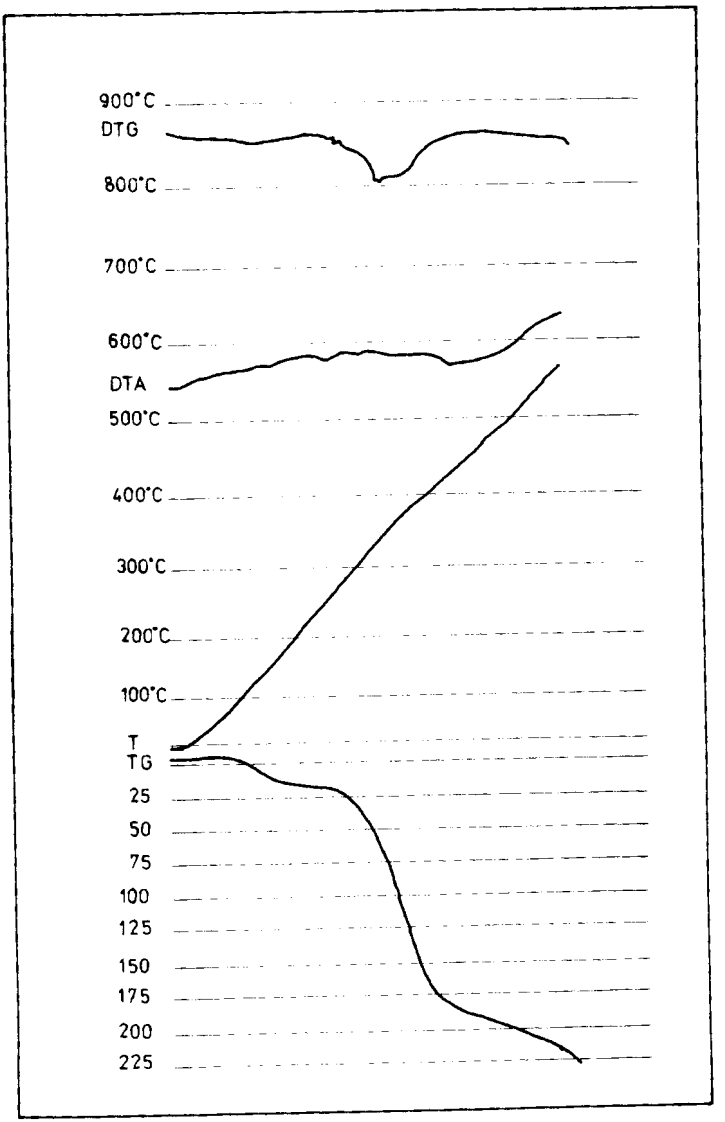



FIG. 1. DTA and TG curves for Resin 1.

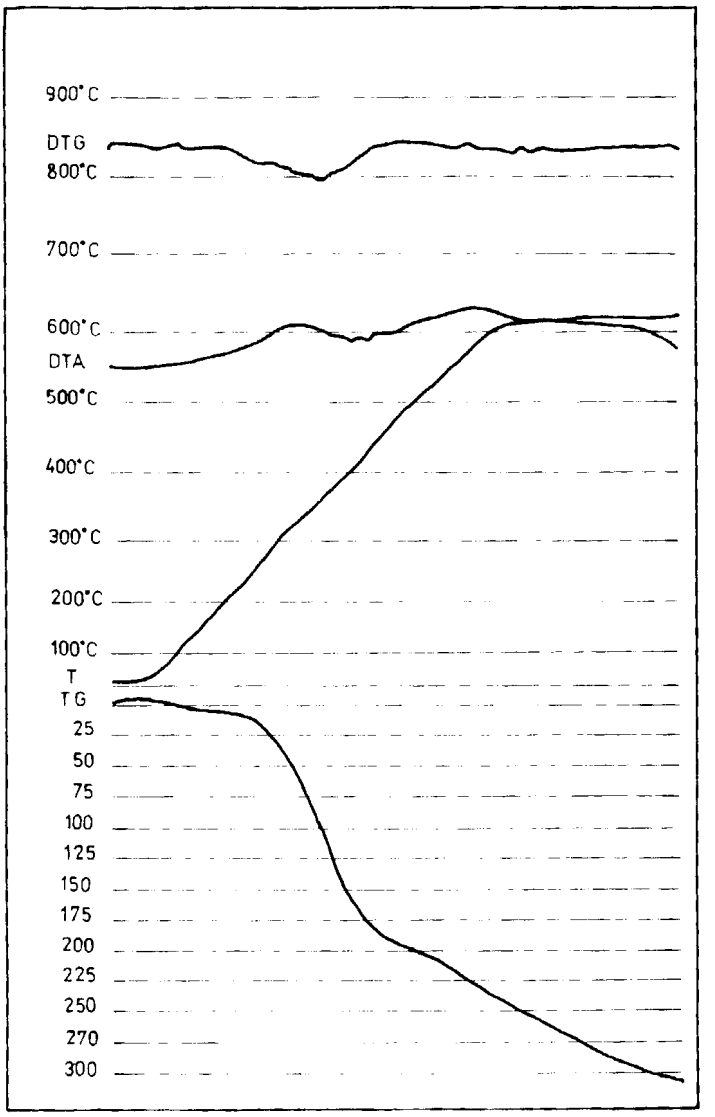



FIG. 2. DTA and TG curves for Resin 2.

It appears from the tests that the polymers obtained are of high thermal and chemical resistance (they are only subject to the action of concentrated solutions of sulfuric and nitric acids and strongly polar solvents). They have good physicomechanical characteristics, small water absorption, and excellent dielectric properties (Tables 2 and 3). Thanks to these advantageous characteristics, they may find various applications, particularly as structural materials.

## REFERENCES

[1] A. Zochniak, J. Appl. Polym. Sci., 22, 215-226 (1978).
[2] A. Zochniak, J. Macromol. Sci.-Chem., A11, 469-482 (1977).
[3] A. Zochniak, J. Appl. Polym. Sci., 21, 1869-1881 (1977).
[4] A. Zochniak, B. Kozbiał-Hołdyk, and J. Ossowski, J. Macromol. Sci.-Chem., A9, 1265-1271 (1975).
[5] W. Olczyk, Poliuretany, WNT, Warsaw, 1968.
[6] J. H. Saunders and K. C. Frisch, Polyurethanes: Chemistry and Technology, Wiley-Interscience, New York, 1963.

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