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Polycondensation Products of Phloroglucine with Difunctional Aliphatic Amines

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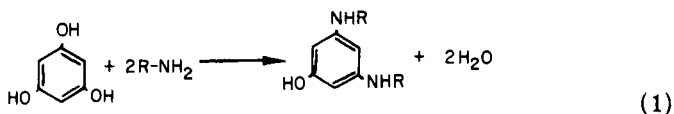
ABSTRACT

The known reaction of condensation of a strong amine with phloroglucine under quite mild conditions was the starting point for synthesis of a new series of macromolecular resins not previously described. Phloroglucine has been condensed with a series of nine aliphatic diamines in aqueous solution under atmospheric pressure. The resins obtained are dark powders, which can be molded under increased pressure in the temperature range of 175-310°C. The thermal, mechanical, chemical, and electrical properties of the new resins have been examined and their structure confirmed. Some properties of resins can be calculated by means of approximate mathematical formulas.

INTRODUCTION

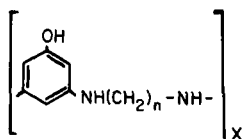
Phloroglucine is known to be very reactive due to its structure: a three-functional, symmetrical phenol existing in a tautomeric equilibrium with its ketonic form [1]. In addition to reactions typical of phenols, phloroglucine participates in some specific

reactions involving the exchange of two hydroxylic groups under the influence of strong amines, under very mild conditions [2] [Eq. (1)].



The above reactions were the starting point in the investigations on the possibility of their adaptation to the synthesis of macromolecular compounds, based on the new concept that the condensation of phloroglucine with difunctional amines must lead to resins belonging to the group of aliphatic-aromatic polyamines.

In the accessible literature we found no data on the possibility of preparing or the properties of such resins. In our earlier publication we described the condensation process and properties of products prepared from phloroglucine and hexamethyldiamine [3]. We examined the structure I of the resulting polycondensates.



I

In this paper the process of polycondensation of phloroglucine with a series of nine aliphatic diamines has been studied, including a complex investigation of the application properties of the resulting products.

EXPERIMENTAL

To prepare the macromolecular products, the previously described condensation process in organic solvent [3] was modified. The condensation was performed in aqueous solution at a 1:1 molar ratio of phloroglucine to diamines. Experiments showed that the yields of products in the aqueous phase were only slightly smaller than in organic solvents, but that the process used here was easier and simpler and the properties of products better. Therefore we continued to carry out the condensation in aqueous media but in the presence of 1% of a nonionic emulsifier. Stoichiometric amounts

of the above reagents were used at concentrations of reagents in the water solution of approximately 15%. After 10 hr of mixing at 20-25°C the mixture was heated to boiling under reflux for 2 hr.

The resulting dark sediments were filtered, rinsed with water, and dried.

The procedure and especially the time and temperature described and reaction medium permitted preparation of products with optimal physicomachanical properties.

Phloroglucine was reacted with the following amines: 1,2-ethanediamine, 1,3-propanediamine, 1,4-tetramethyldiamine (putrescine), 1,5-pentamethyldiamine (cadaverine), 1,6-hexamethyldiamine, 1,7-heptamethyldiamine, 1,8-octamethyldiamine, 1,10-decamethyldiamine, and 1,12-dodecamethyldiamine. The reagents were products of the following companies: POCh-Gliwice (Poland), Fluka (Switzerland), and Koch-Light (England).

Thus nine macromolecular compounds not previously described in the literature belonging to the poly(aliphatic-aromatic amines) were prepared. In order to simplify the nomenclature, we assigned to the new resins numbers corresponding to the number of methylenic groups in the diamine molecules used in the condensation with phloroglucine(Phl), i.e., Phl-1, Phl-2, etc.

The dark products were insoluble in organic solvent and partially soluble in aqueous NaOH solutions with partially gel formation. The yields of the individual resins were high, ranging from 91% for resin Phl-2 to 98% for resin Phl-12

The IR spectra of the resins were identical, and therefore a single IR spectrum typical of all the resins is shown in Fig. 1. The absorption band in the range of 3200-3400 cm^{-1} corresponded to the links in the resin chain between the phenolic OH group and the secondary NH group. Some frequencies in this range prove the existence of intra- and extramolecular hydrogen bonds. The bands in the ranges of 1500-1600, 1290-1310, 1140-1160, and 760-780 cm^{-1} correspond to bonds between the NH group and the aliphatic and aromatic radicals in the resin molecule. The existence of the 1,3,5-substituted benzene rings in the resin is proven by absorption bands occurring at 3100-3200, 1600-1700, 1020, 970-980, and 720 cm^{-1} [4].

The x-ray spectra of the investigated resins contain no interferential lines, confirming their amorphous structure.

The elementary analysis data of the resins are shown in Table 1.

The IR spectra and the good agreement between elementary analysis data and the theoretical values prove the reaction path and the structure of the resins.

Samples of the resins were molded under a pressure of 200 kg/cm^2 ($1962 \times 10^4 \text{ N/m}^2$). The temperature of compression molding of the resin decreased with increasing length of the diamine chain used in the condensation with Phl. The dependence is shown in Table 2.

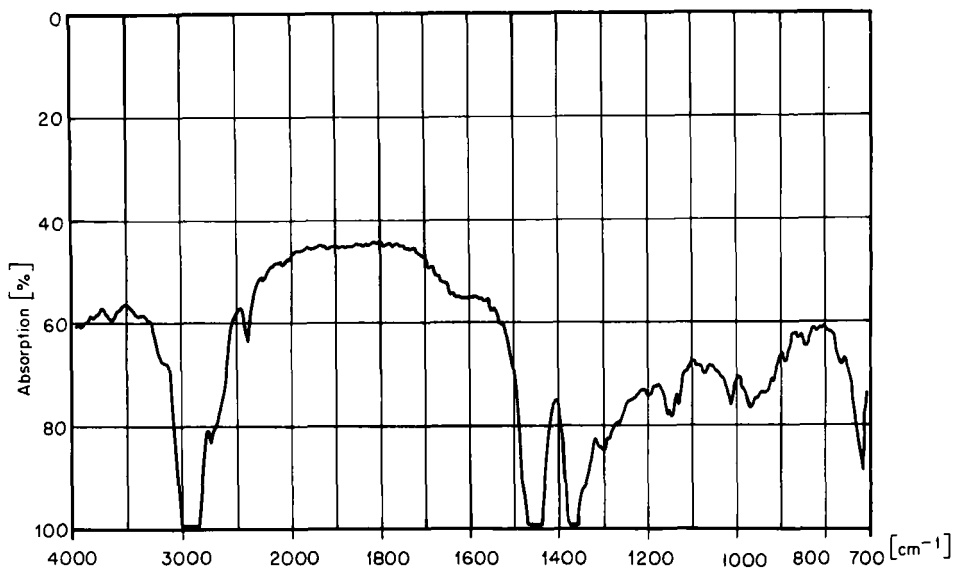


FIG. 1. IR spectrum of resins.

TABLE 1. Results of Elementary Analysis Resins

Resin	C (%)		H (%)		N (%)	
	Calcd	Found	Calcd	Found	Calcd	Found
2	64.0	63.5	6.6	6.8	18.6	18.2
3	65.8	65.7	7.3	7.5	17.0	16.9
4	67.4	67.1	7.8	7.8	15.7	15.6
5	68.7	68.8	8.3	8.0	14.6	14.2
6	69.9	69.0	8.7	8.9	13.6	13.2
7	70.9	70.1	9.1	9.1	12.7	12.5
8	71.8	71.0	9.4	10.0	11.9	11.4
10	73.3	73.1	9.9	9.6	10.7	10.5
12	74.5	74.0	10.3	10.4	9.6	9.6

TABLE 2. Compression Molding Temperature of Resins

Resin	Molding temperature ($^{\circ}\text{C}$)
2	310
3	325
4	300
5	275
6	240
7	220
8	205
10	190
12	175

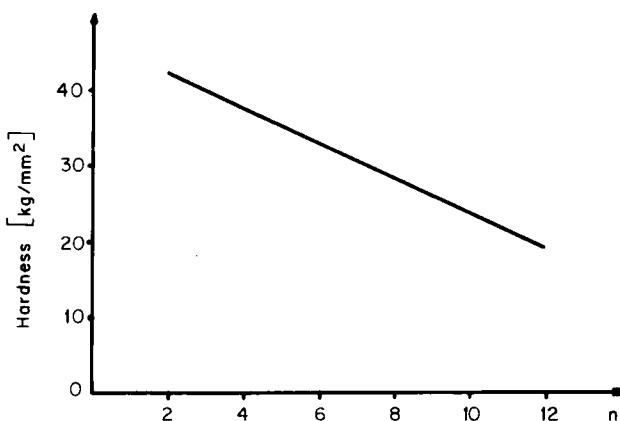


FIG. 2. Dependence of hardness of investigated resins on number of methylene groups in the amine moiety of the polymer chain.

The properties of the investigated resins were examined, and results are presented in Table 3. The dependence of some mechanical properties of the resins on the kind of diamine used in the condensation with PhI are shown in Figs. 2-6 (where n = contents of CH_2 groups in the amine moiety of the polymer chain).

TABLE 3. Some Properties of Investigated Resins

Resin	Dielectric constant	Power factor $\tan \delta$ (120 kHz, 20°C)	Electric resistance (Ω -cm $\times 10^{12}$)	Specific gravity (g/cm^3)	Water absorption after 720 hr (%)	Vicat softening point (°C)	Brinell hardness (kg/mm^2)	Modulus of elasticity (kg/cm^2)	Tensile strength (kg/cm^2)	Elongation at break (%)	Flexural strength (kg/cm^2)	Charpy impact ($\text{kg}\cdot\text{cm}/\text{cm}^2$)
2	2.51	0.020	2.2	1.25	0.6	230	42.5	70938	197	6	184	4.9
3	2.50	0.020	2.1	1.24	0.6	225	40.1	50153	240	8	265	6.8
4	2.27	0.019	2.3	1.23	0.5	222	37.8	38990	342	8	305	7.6
5	2.25	0.019	2.6	1.23	0.5	190	35.7	31618	385	10	337	9.1
6	2.17	0.018	2.6	1.23	0.5	181	34.1	29523	420	11	388	10.0
7	2.15	0.018	3.0	1.21	0.4	168	30.6	27637	383	14	422	12.2
8	2.10	0.015	3.1	1.21	0.4	161	28.2	26034	349	14	490	13.2
10	2.10	0.015	3.3	1.21	0.4	155	25.7	24234	251	16	438	15.0
12	2.10	0.015	3.3	1.20	0.4	139	19.1	23134	210	16	408	16.1

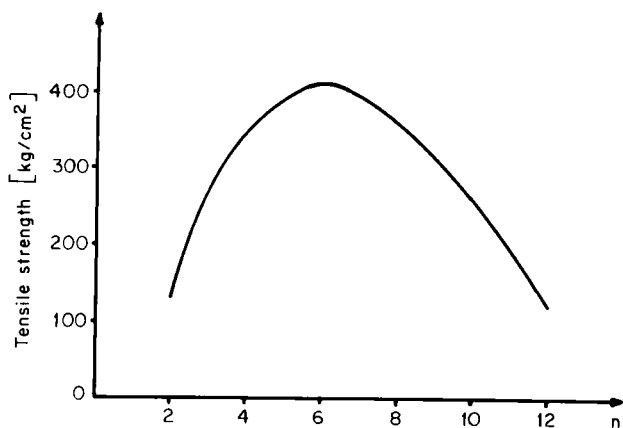


FIG. 3. Dependence of tensile strength of investigated resins on number of methylene groups in the amine moiety of the polymer chain.

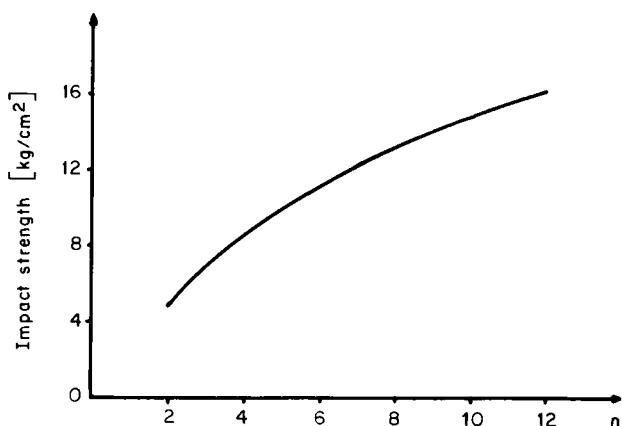


FIG. 4. Dependence of impact strength of investigated resins on number of methylene groups in the amine moiety of the polymer chain.

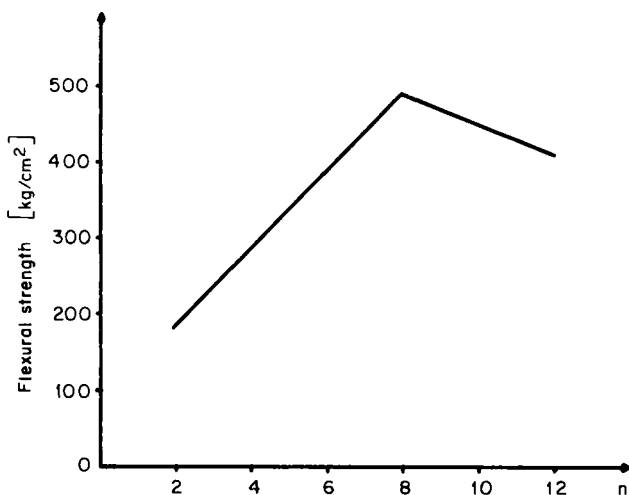


FIG. 5. Dependence of flexural strength of investigated resins on number of methylene groups in the amine moiety of the polymer chain.

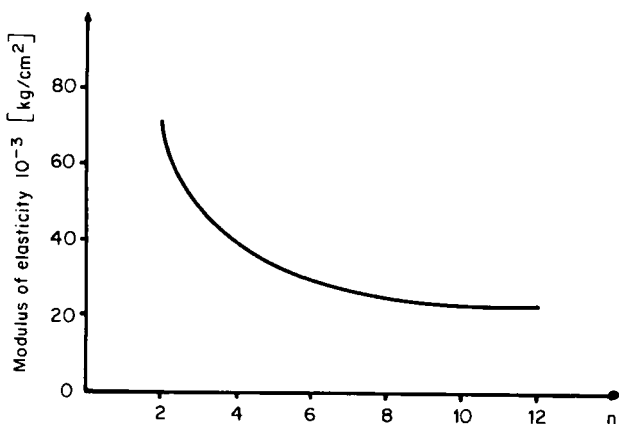


FIG. 6. Dependence of modulus of elasticity of investigated resins on number of methylene groups in the amine moiety of the polymer chain.

Some of the graphically stated dependences are described also by means of the following empirical mathematical formulas:

$$\text{Hardness of resins (kg/mm}^2\text{)} = -2.34n + 47.2$$

$$\text{Modulus of elasticity (kg/cm}^2\text{)} = (n^2 + 138)/n$$

$$\text{Tensile strength (kg/cm}^2\text{)} = n^3 - 32n^2 + 276n - 310$$

$$\text{Charpy impact strength (kg-cm/cm}^2\text{)} = 1/4n + 12 \log n$$

The studied resins are resistant to weak acids (3% CH_3COOH), bases (10% NH_4OH), and salts. In solutions of strong acids or bases, swelling and decomposition of the resins proceeds.

Thermographic and thermogravimetric measurements on the resins prove their high thermal resistance. Their thermal decomposition starts at approximately 360°C (633°K), and therefore they may be classified as thermoresistant resins.

DISCUSSION AND CONCLUSIONS

The previously published procedure for preparation of the resins in organic solvent, for example of Phl-6 [3], has substantially less potential for application than the method of condensation of Phl with diamines in the water phase presented here. Due to the insolubility of the resins, their molecular weights cannot be evaluated, but their good mechanical properties and resistance to chemical factors indicate that their molecular weights must be rather high.

Due to the broad interval between the temperatures of formation and decomposition of the resins no problems arise during their processing.

The dependence of the mechanical properties of the resins on the aliphatic chain length between the two aromatic rings in the polymer molecule was different for different properties. The hardness of resins decreased linearly from resin 2 to 12, but the best tensile strength was found for resin 6. The highest flexural strength we have established for resin 8 and the best impact resistance for resin 12, reaching a value of 16.1 kg-cm/cm^2 , which is a rather satisfactory one.

The investigated resins have distinctly better properties than

other polyamines, but their physicomachanical resistance is poorer than of many commercial resins. In some respects they are superior to some standard commercial resins, like polystyrene.

The polymers described constitute a new group of macromolecular, thermoreactive compounds. At the processing temperature, which is above the temperature of the reactivity of the third phenolic group of phloroglucine with secondary amines [5, 6], crosslinking of the resin proceeds. The resins also have good electric properties. All the above properties show that the resins show good potential for use and further investigation may be successful.

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