Some Properties and Chemical Structure of Phenolic Resins and Their Derivatives

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Synopsis

Some physical and chemical properties of novolac and resole resins are described, IR spectra are given, and average structures of the examined resins are proposed. It was supposed that the gelation kinetics depend on the ratio of the reagents and on the structure of the resin.

INTRODUCTION

The methods of producing the reactive unmodified and modified o-novolac resins (ON) as well as some of their properties and applications have been described by Roczniak and Mastalerz.[1] Resin ON was used for preparation of orthoresole resin (ONR).[2]

On the basis of proton magnetic resonance (PMR) spectra, Woodbrey, Higginbottom, and Culbertson[3] identified structural fragments of the molecules of phenol–formaldehyde resin.

Siling and co-workers[4] studied the structure of phenol–formaldehyde resins using PMR spectrometry, infrared (IR) spectrophotometry, and paper chromatography. They attempted to establish a correlation between PMR data, concerning the position of methylene group relatively to hydroxyl group of phenol, and IR spectra, characterizing the type of aromatic substitution.

Dradi and co-workers[5] proposed a versatile method of synthesis of o,o-polyphenols with methylene bondings. The structure of ortho oligomers was examined using the NMR method.

Hetper and others[6] analyzed acetylated resole resins using PMR spectrometry, mass spectrometry, and gas chromatography. They identified 11 simple one-ring components constituting together over 20% of a resole resin. The authors proposed a method for calculating an average molecule of the components, comprising more than one aromatic ring.

In this paper some physical and chemical properties of novolac and resole resins are described. IR absorption spectra of the resins are given. The average structures of the resins are proposed.

The IR spectra give the information about the type of substitution of aromatic rings, the structure of methylene and oxymethylene bridges, and the presence of hydroxymethylene groups.[3,4,7–10] According to the correlations reported in the literature,[7,8,10,11] the deformation vibrations of C—H bonding in benzene rings substituted at the positions 1,2 and 1,2,3 (i.e., in the case of three or four adjacent unsubstituted C—H bondings) give the absorption bands in the 770–750 cm^{-1} range, while the rings substituted at the positions 1,4 and 1,2,4 (i.e., in the

systems with two adjacent unsubstituted C—H bondings) give their bands in the 830–790 cm^{-1}. The latter system[1,2,4] has an additional absorption band at approximately 900 cm^{-1}, corresponding to a single, isolated C—H bond. The bands characteristic for the oxydimethylene bridges appear at 1100 cm^{-1}, and those characteristic for the hydroxymethyl groups at 1250 and 1040 cm^{-1}.

The band pattern in the range 1500–1400 cm^{-1} can give information as to the nature of the substitution of methylene bridges.

EXPERIMENTAL

o-Resole resin ONR was prepared from o-novolac ON[1,2] and paraformaldehyde in ethyl alcohol solution in strongly alkaline medium. The mole ratio of phenol to formaldehyde was 1:1.05 (sample ONR-1) and 1:1.4 (sample ONR-2). The condensation was carried out at a temperature of 333 K for 3 h.[12]

The properties of resin ONR were compared with those of resole NR.[1] The content of dry substance in the examined resins was determined by the oven method[13]; the content of free phenol, iodometrically.[14] The average molecular weight ($\overline{M}_n$) was determined osmometrically in methanol vapor phase using a Packard (United States) osmometer. The gelation time was determined on a metal plate according to the Polish Standard.[15] The novolac resins were gelated with hexamethylenetetramine at a weight ratio 10:1.

The properties of the examined resins ON, ONR-1, ONR-2, and NR are pre-

TABLE I
Characteristics of Resins ON, N, ONR-1, ONR-2, NR[a]

Symbol	ON	N	ONR-1	ONR-2	NR
Molar ratio phenol/ CH$_2$O	1:0.76	1:0.76	1:1.05	1:1.4	1:1.05
Catalyst of polycondensation reaction	Zinc acetate	Hydro-chloric acid	Zinc acetate and —NaOH	Zinc acetate and NaOH	Hydrochloric acid and —NaOH
Resin properties: density at 293 K (g/cm^3)	—	—	1.0743	—	1.0541
Viscosity at 293 K (Pa·s)	—	—	2537	—	681.3
Content of dry substance (%)	100	100	72	—	72
Content of free phenol (%)	12.8	10.9	4.2	—	4.0
Melting point (K)	349	339	—	—	—
Number average molecular weight (M_n)	460 ± 46	455 ± 46	590 ± 86	—	600 ± 90
Gelation time (s) at					
373 K	1200	1200	153	—	142
403 K	134[b]	296[b]	137	—	133
423 K	56[b]	93[b]	135	110	126
443 K	33[b]	72[b]	116	—	117

[a] Sample designations: ON = orthonovolac resin; N = ortho-, paranovolac resin; ONR = ortho-resole resin; NR = ortho-, pararesole resin.
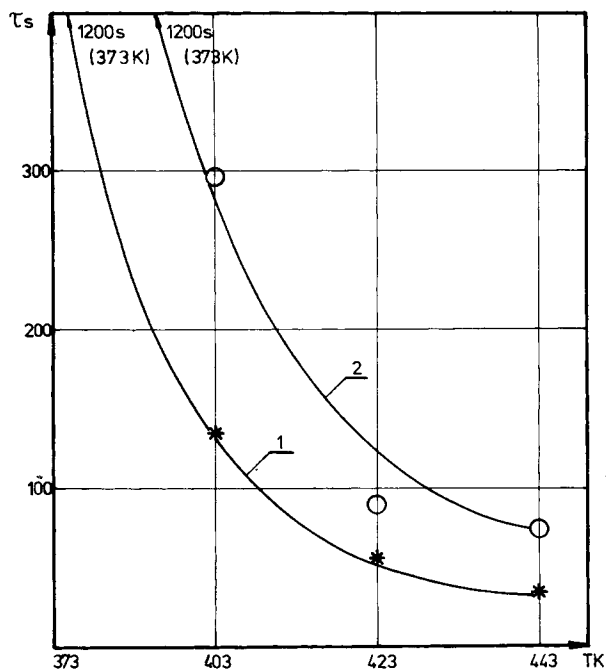
[b] Curing with hexamethylenetetramine.

Fig. 1. The effect of temperature of the gelation time of novolac resins: (1) o-novolac resin; (2) o,p-novolac resin.

sented in Table I. The effect of temperature on the gelation time is shown in Figures 1 and 2.

The IR spectra were taken using a UR-20 spectrophotometer (Carl Zeiss) in the 3800–700 cm^{-1} range. The samples of novolac resins were examined in the form of pellets with KBr (4 mg of resin were mixed with 800 mg of KBr and pelletized) while samples of resole resins were examined in the form of thin capillary films between KBr plates.

From the obtained IR spectra of the examined resins (Figs. 3 and 4) the absorbances of selected peaks were determined, while the background absorbance being eliminated as shown in the figures.

To diminish the errors caused by nonheterogeneous distribution of novolac resins in the KBr pellet and by unknown thicknesses of the films of the resole resins, the ratio of absorbance, measured at an analytical band to the absorbance measured at approximately 1,600 cm^{-1} (assigned to stretching vibrations of C=C bonding in benzene ring) was taken as a measure of the band intensity. It was assumed that possible changes in band intensities, connected with the stiffening of the molecule, were proportional to the intensities in all the bands of a given spectrum.

The PMR spectrum of resin ON was measured in deuterated acetone using spectrometer Jeol C-60 HL (60 MHz) at room temperature (Fig. 5).

The structure of resin ON was determined on the basis of the average molecular weight, PMR, and IR spectra. The structures of the other resins were determined on the basis of the average molecular weights, the contents of hydroxymethyl groups, and IR spectra. The structure of the resin ON was the basis for structural analysis of the other resins.
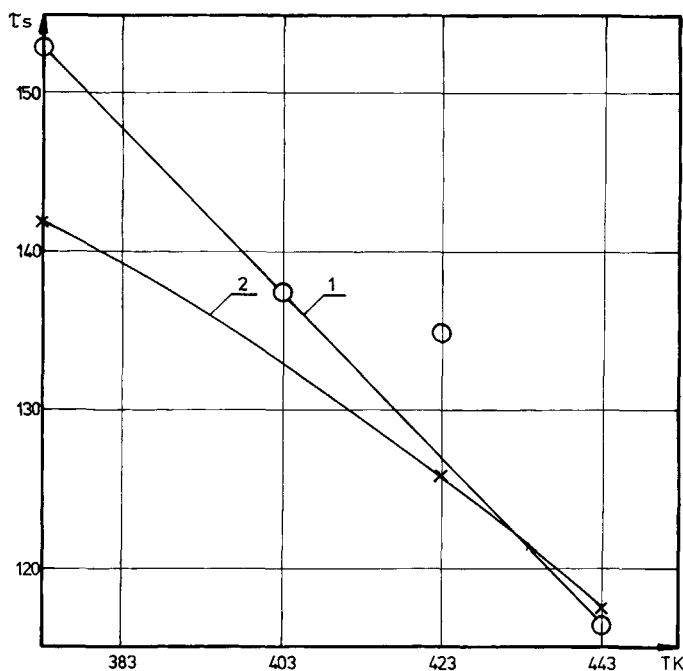
Fig. 2. The effect of temperature on the gelation time of resole resins: (1) ONR-1; (2) NR.

RESULTS AND DISCUSSION

General Characteristics of the Examined Resins

It has been found (Table I) that the resin ON contains the highest amount of free phenol and has a higher melting point than the resin N. Its gelation time with hexamethylenetetramine at a weight ratio of 10:1 is approximately twice shorter than that of the resin N (Fig. 1). This significantly shorter gelation time suggests high content of highly reactive unsubstituted para positions in aromatic phenolic rings. The gelation velocity of the resin ONR at temperature 373–425 K is slightly lower than that of resole resin NR (Fig. 2). At a temperature of 423 K the resin ONR-2, prepared at a mole ratio of phenol to CH_2O = 1:1.4 exhibits the shortest gelation time among the examined resole resins.

The values of the average molecular weights of novolac resins are smaller than those of resole resins, indicating that the average molecule of novolac contains four aromatic rings while that of resole contains five rings. In addition, resins ONR and NR contain small amounts of hydroxymethyl groups.

Identification of the Structure of Resin ON

The analysis of PMR spectrum of resin ON according to literature data[3,4] shown the contents of o,o- and o,p-methylene bridges to be equal to 50% each. Then it was assumed that the content of all ortho substitutions in the average molecule of resin ON was 50 + 50/2 = 75%. The IR spectrum of resin ON, shown in Figure 3, and the calculated relative amount of ortho and para substitutions of phenol is in good agreement with Siling's data.
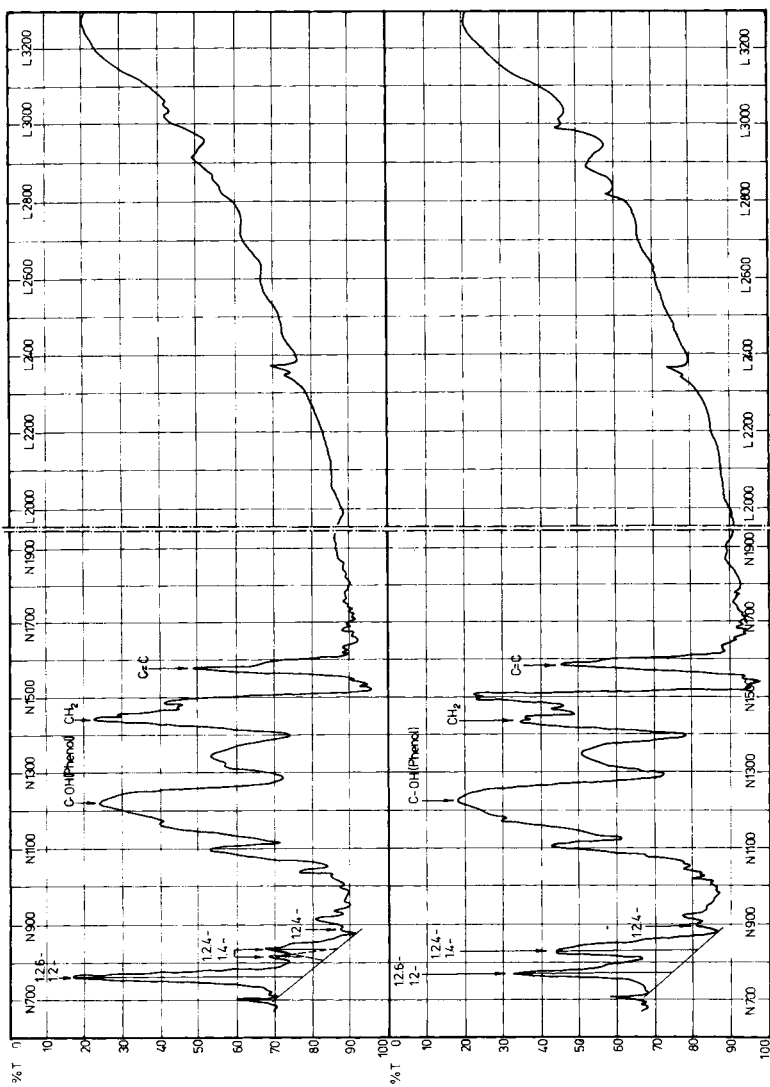
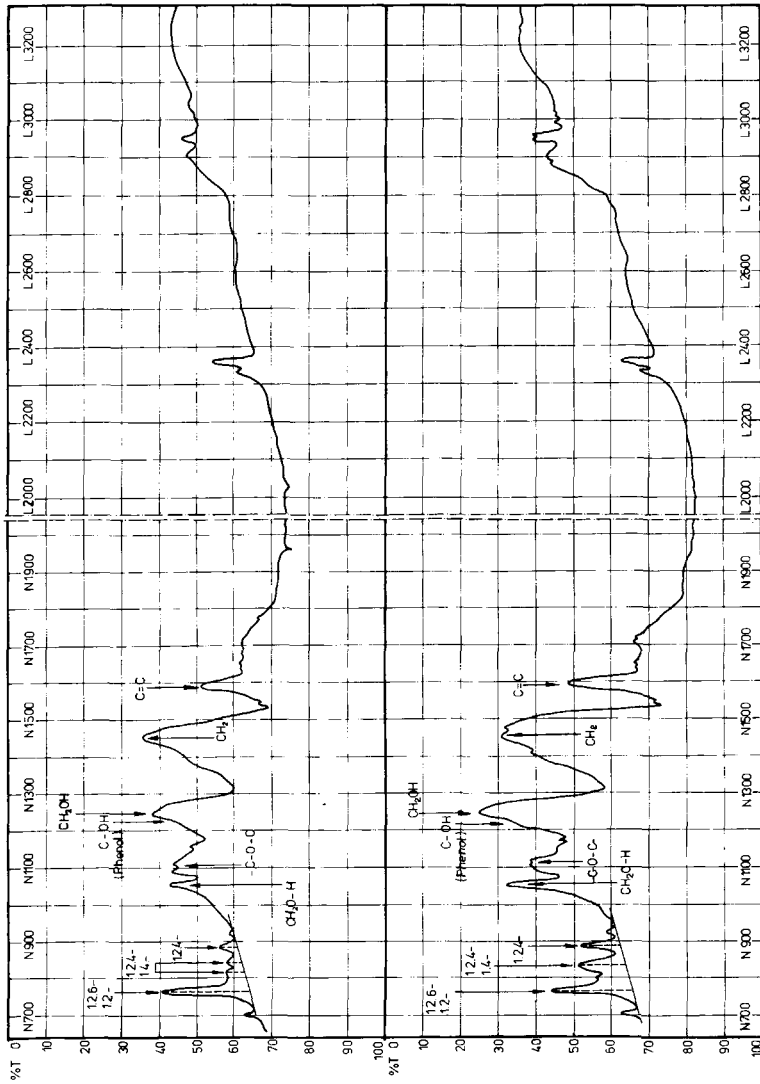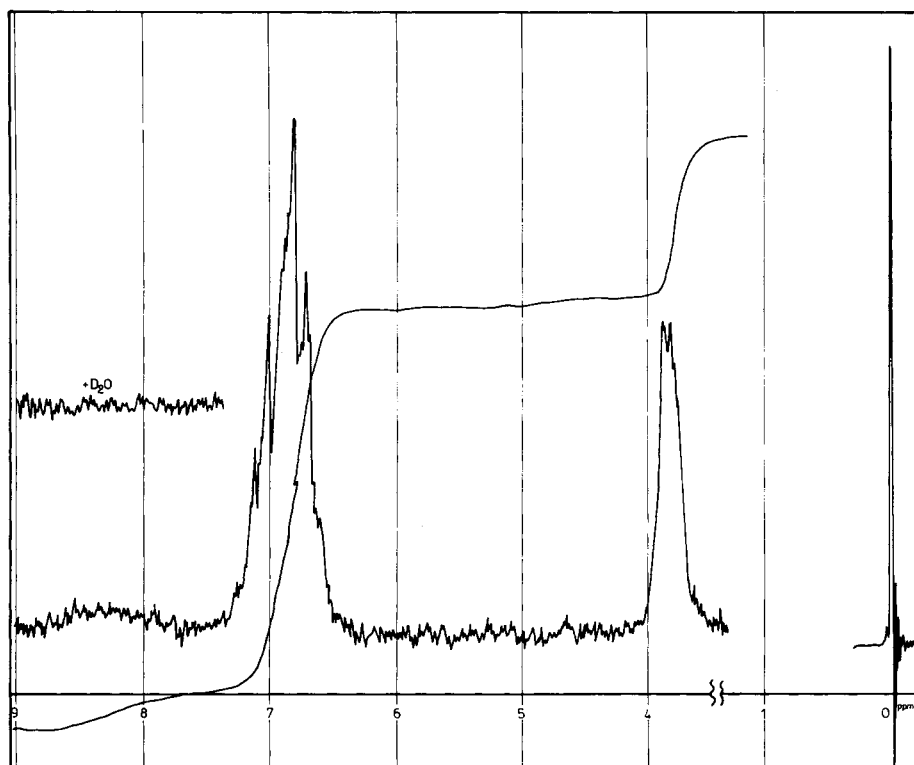Fig. 3. IR spectra of: (a) *o*-novolac resin; (b) *o,p*-novolac resin.

Fig. 4. IR spectra of: (a) o-resol resin ONR-1; (b) resol resin NR.

Fig. 5. PMR spectrum of *o*-novolac resin ON.

On the basis of these data as well as the average molecular weight, it has been established that the average structure of the resin ON is an equimolar mixture of the following compounds shown in structures I and II.

The molecule of type I contains two *o*,*o*′-methylene bridges and one *o*,*p*′ bridge. In the molecule of structure II this proportion is inversed. The mixture of compounds I and II at ratio 1:1 contains 50% of methylene bridges at *o*,*o*′ and 50% *o*,*p*′ positions. In the structure of the resin ON the relative content of the systems with three and four adjacent C—H bonds in the ring is approximately

TABLE II
Content of Substitutions 1,2-, 1,2,6-, 1,4-, and 1,2,4- (Systems with Free Adjacent Aromatic C—H Bonds) on Phenolic Rings of Novolac Resins Type ON and N and Resole Resins Type ONR and NR

Resin type	Absorbances			Relative content (%) of substitutions systems with free adjacent aromatic C—H bonds		
	760 cm^{-1}	815 cm^{-1} $\pm 840 \text{ cm}^{-1}$	890 cm^{-1}	Four and three	Two	Single
ON	2.2199	0.4211	0.0668	45	45	10
N	1.0000	0.6392	0.0806	20	68	12
ONR	1.0887	0.4000	0.2365	22	43	35
NR	0.7019	0.3693	0.3103	14	39	46
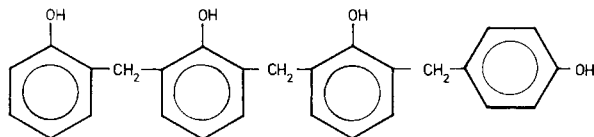
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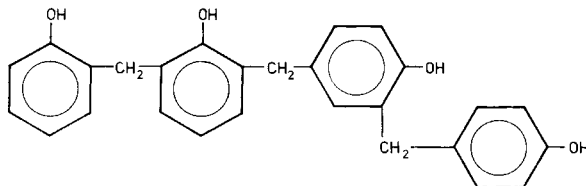
Formula II.

45%. The relative contents of the systems with two adjacent and single C—H bond are 45% and 10%, respectively (Table II).

In the IR spectrum of the resin ON (Fig. 3) the band at approximately 765 cm^{-1} was assigned to the substitution on the benzene ring at 1,2 and 1,2,6 positions. The bands at 815 and 840 cm^{-1} were assigned to the substitutions 1,4 and 1,2,4, and the weak band at 890 cm^{-1} to the substitution 1,2,4. The above-mentioned bands appear also in the resins N, ONR, and NR (Figs. 3 and 4); however, their intensities differ from those of the resin ON.

Taking the average structure of the resin ON as a reference, the respective absorptivities were calculated on the basis of the obtained absorbances at selected wave numbers (Table II). For C—H bondings in a substituted ring the following values were obtained: for 1,2- and 1,2,6-substituted positions, 0.0493 (band at 765 cm^{-1}); for 1,4- and 1,2,4-substituted positions, 0.0094 (band at 815 cm^{-1}); for 1,2,4-substituted positions, 0.0067 (band at 890 cm^{-1}). The values given refer to 1% relative content of the structural systems in question in resin ON. They made a basis for the determination of the relative contents of these systems in the resins N, ONR, and NR (Table III).

Identification of the Structure of Resin N, NR, and ONR

The spectrum of novolac N is shown in Figure 3. The spectra of resole resins NR and ONR are shown in Figure 4. The absorbances determined at selected analytical bands are given in Table II. These absorbances together with the data reported in Table I, and the determined absorptivities made a basis for assignment of average structures of the examined resins (Table III). In addition to the structures proposed, Table III contains the calculated relative amounts of

TABLE III

Unit Structures of Average Molecules of Examined Resins ON, N, ONR, and NR and Nature and Amounts of Substitutions on Phenolic Rings

| Resin type	Unit structures of average molecules and their 1:1 mixtures	Relative content (%) of systems with free adjacent atom: C—H bonds			content (%) of —CH_2— bridges at positions			Relative content (%) of C—H groups of phenolic rings at positions		$\overline{M}_n$
		Four and three	Two	Single	o,o-	o,p-	p,p-	o-	p-	
ON	Structure I	60	40	—	75	25	—	50	50	418
	Structure II	33	50	17	25	75	—	67	33	418
	Equimolar mixture of I and II	46	45	9	50	50	—	59	41	418
N	Structure III	33	67	—	33	67	—	67	33	418
	Structure IV	14	57	29	33	33	33	83	17	418
	Equimolar mixture of III and IV	24	62	14	33	50	17	75	25	418
ONR	Structure V	43	29	29	75	25	—	50	50	586
	Structure VI	11	56	33	50	25	25	72	29	616
	Equimolar mixture of V and VI	27	43	31	63	25	13	61	39	601
NR	Structure VII	25	37	38	25	75	—	60	40	616
	Structure VIII	—	40	60	25	50	25	100	—	616
	Equimolar mixture of VII and VIII	13	39	49	25	63	13	80	20	616
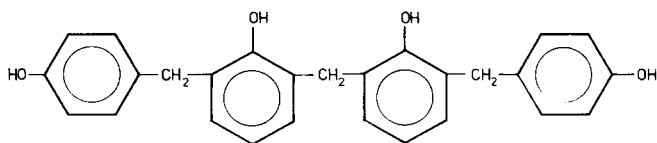
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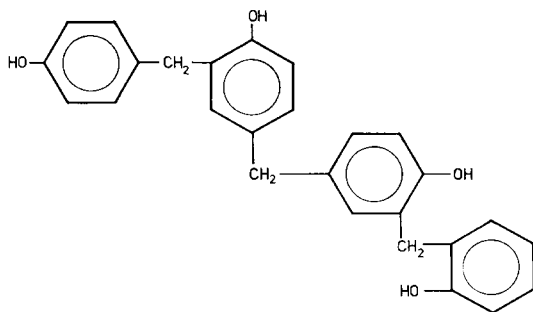
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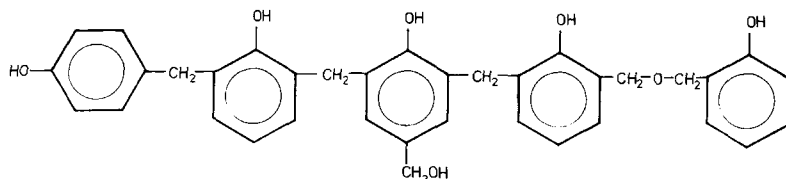
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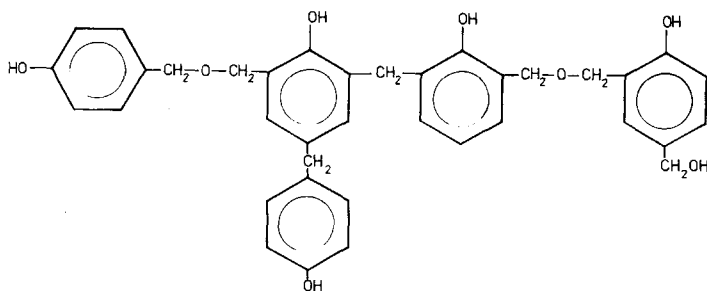
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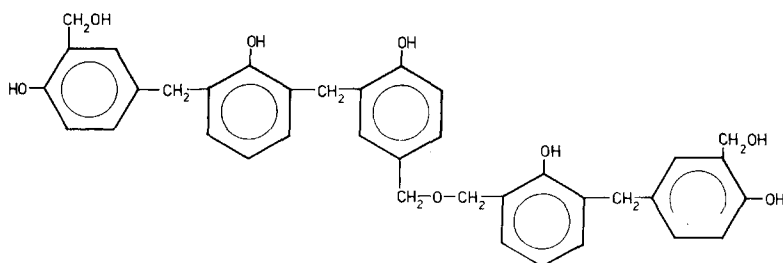
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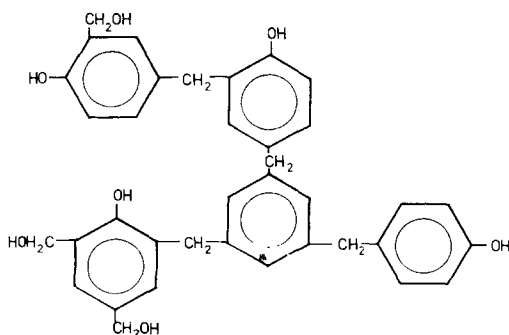
Formula VIII.

unsubstituted C—H bonds at ortho and para positions to hydroxyl group at aromatic rings. As can be seen, the resins ON and ONR have high contents of free *p* positions. The spectra of resole resins in contrast to those of novolacs, shows an additional absorption at approximately 1100 cm^{-1} due to the presence of

C—O—C bonds in oxydimethylene bridges. The band at approximately 1055 cm^{-1}, corresponding to C—OH bonding in hydroxymethyl group, is more clearly pronounced in the resin NR than in the resin ONR. This is in agreement with the data given in Tables I and III.

In the region 1500–1400 cm^{-1} characteristic for the deformation vibrations of C—H bonds in groups —CH$_2$—,[15] some differences can be noticed. These differences can yield information as to the structure of methylene bridges.

When comparing the proposed structures (Table III) with the spectra shown in Figures 3 and 4, the following correlations could be observed:

—CH$_2$— position p,p'	band at approximately	1450 cm^{-1}
o,o'		1460 cm^{-1}
o,p'		1480 cm^{-1}

Methylene groups in oxydimethylene bridges and in hydroxymethyl groups show an absorption at approximately 1410 cm^{-1}.

CONCLUSIONS

1. The studies permited to determine the chemical structure of average molecules of some phenolic resins.

2. The obtained IR and PMR spectra confirmed Siling's data[4] on the structure of o-novolac resin. This structure was used as reference in the further studies.

3. The significantly higher reactivity of the o-novolac resin ON as compared to the novolac resin N is due to a relatively high content of unsubstituted p positions on phenolic rings. Owing to its high reactivity, the resin ON can be used as a quickly gelating moulding binder.

4. The resole ONR contains more free para positions on phenolic rings than resole resin NR. However, the reactivities of both the resins are similar. On this basis it is supposed that the gelation kinetics depends, in addition to unsubstituted p position, on such factors as a mole ratio of reagents, the presence of oxydimethylene bridges, and active hydroxymethyl groups. The IR spectra suggest higher content of OH groups in the resin NR than in the resin ONR.

5. The obtained IR spectra show also some differences in the bands pattern in the region 1500–1100 cm^{-1} characteristic for the deformation vibrations of C—H bonds in methylene and oxymethylene bridge systems and hydroxymethylene groups. The characterization of methylene bridges until now has been carried out solely on the basis of PMR spectra.

References

1. K. Roczniak and B. Mastalerz, *Polimery*, **26**(3), 106 (1981).
2. K. Roczniak and L. Popek, Polish Patent No. 215 082 (1982).
3. J. P. Woodbrey, H. P. Higginbottom, and H. M. Culbertson, *J. Polym. Sci.*, A3, 1079 (1965).
4. M. I. Siling, O. S. Matyukhina, O. A. Mochalova, V. P. Pshenitsyna, and I. Y. Slonim, *Vysokomol. Soyedin.*, A11, 1943 (1969).
5. E. Dradi, C. Casiraghi, G. Sartori, and C. Casnati, *Macromolecules*, **11**, 1295 (1978).
6. J. Hetper, I. Hetper, E. Pisarzewska, and H. Gryta, *Polimery*, **24**, 307 (1979).
7. *Analiza Polimerów Syntetycznych*, S. Pietras, Ed., WNT, Warsaw, 1971, p. 206.
8. D. O. Hummel and F. Scholl, *Atlas der Kunststoff-Anylyse*, Carl Hauser Verlag, Munich, 1968, Vol. II, p. 322.

9. H. A. Szymanski and A. Bluemle, *J. Polym. Sci.*, **15,** 63 (1955).

10. *Poradnik Fizykochemiczny*, WNT, Warsaw, 1974, part E, p. 180.

11. G. M. Kline, *Analiticeskaja Chimija Polimerov*, Moscow, 1962, Vol. II.

12. L. Popek, MSc. Thesis No. 1357, Institute of Plastics and Leather, Swiętokrzyska Technical University, Radom, 1978.

13. Polish Standard BN-75/6311-05.

14. Polish Standard PN-75/0-89044.

15. Polish Standard BN-75/6311-17.

16. S. Holly and P. Sohar, *Absorption Spectra in the Infrared Region*, Akademiai Kiado, Budapest, 1975, p. 51.