

## Phenol-Formaldehyde Type Polymers on the Basis of Bisphenols

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**ABSTRACT.** Methylol derivative on the basis of adamantane type bisphenols was obtained. Some kinetic regularities of reaction of interaction of polycyclic bisphenols and formaldehyde was studied. Bisphenol III is taken as an example. © 2009 Bull. Georg. Natl. Acad. Sci.

**Key words:** phenol, formaldehyde, adamantane, bisphenol, polycyclic polymer.

Heat-resistant and thermostable polymers, that are polymers possessing three-dimensional structure, especially those with rigid space lattice, have been widely used. Most significant representatives of polymers of this class are phenol-formaldehyde polymers [1-4].

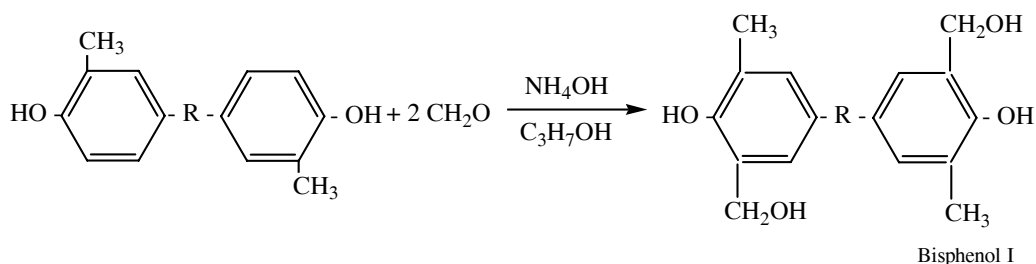
Recently, to increase some indices (heat- and thermal stability, strength at impact loads etc.) various bisphenols were used for the synthesis of phenol formaldehyde polymers. It enabled us to decrease cross-linking of macromolecules, which has a significant effect on physical-mechanical and other indices of polymers [5-7].

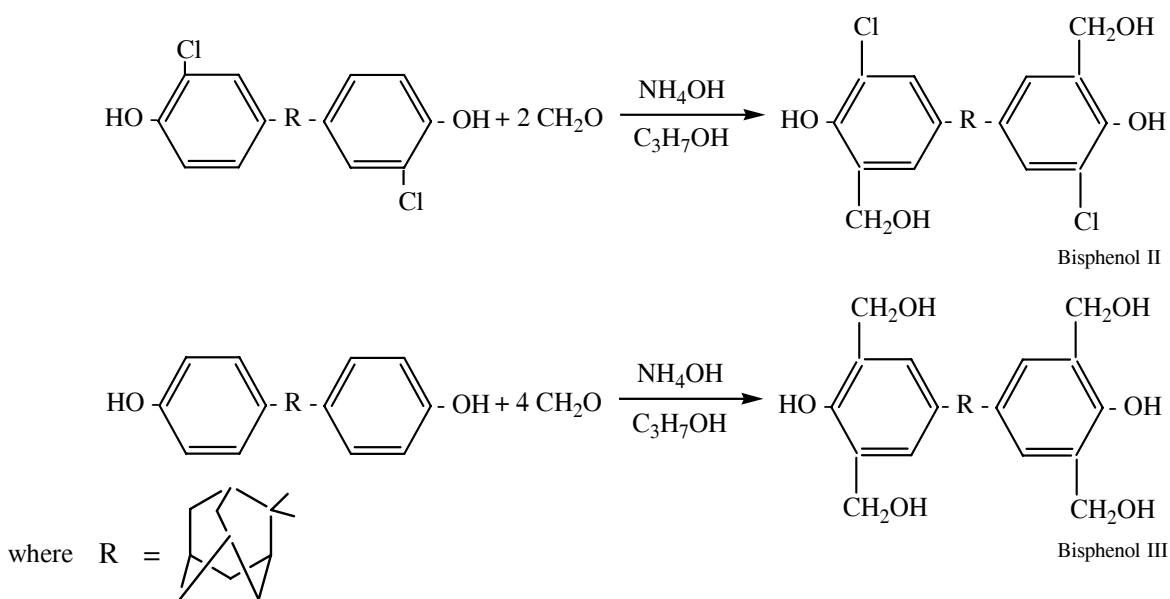
Thanks to the very interesting set of properties of other type polymers containing cycloparaffin card type

groupings [8-11], we considered it interesting and expedient to conduct investigations in the sphere of phenol formaldehyde polymers with adamantane type card groupings.

The first stage of the study deals with the synthesis of methylol derivatives of adamantane-containing bisphenol. The initial components of the synthesis were 2,2-bis-(3-methyl-4-oxophenyl)adamantane, 2,2-bis-(3-chlor-4-oxophenyl)adamantane and 2,2-bis(4-oxophenyl)-adamantane (as phenol components) and alcoholic solution of formaldehyde.

Schematically the reaction can be presented as follows:





In order to realize successfully the reaction of synthesis, to determine the optimal terms of the reaction, we considered it proper to investigate some kinetic regularities of the process.

Interaction of 2,2-bis(4-oxophenyl)adamantane with formaldehyde was investigated in n-propyl alcohol, at 115-135°C temperature interval, in the presence of ammonia as the catalyst, at bisphenol to formaldehyde molar ratio 1:4.

Control over the reaction process was realized according to the quantity of the used formaldehyde [12].

Fig. 1 offers kinetic curves of condensation reaction of bisphenol with formaldehyde at various temperatures. It was found that at 115-135°C temperature range, up to the high rate of conversion, the rate constants preserved values unchanged during the reaction, and were calculated by the quadratic equation of Arrhenius.

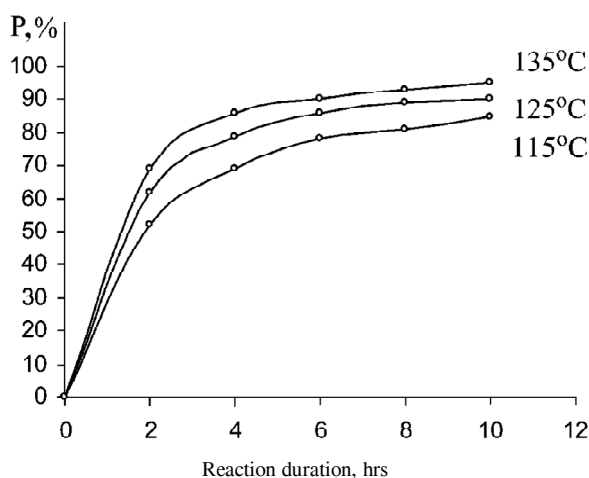


Fig. 1. Kinetic curves of interaction of formaldehyde and 2,2-bis(4-oxophenyl)-adamantane at 115-135°C. P - conversion rate.

Direct linear relation of the logarithm of the rate constant at inverse absolute temperature refers to the second order of the reaction. Activation energy of the given reaction, calculated from this relation (dependence) according to Arrhenius equation, equals  $69.6 \cdot 10^3$  J/mol.

The effect of various factors on the process of reaction, namely those of temperature and reaction length, quantity and nature of the catalyst, type of reaction medium, concentration and ratio of initial reagents were studied. As is seen from the kinetic curves (Fig. 1), by the increase of temperature, the rate and speed of conversion increase. The rate of conversion increases also at the increase of reaction duration. Reaction is mainly accomplished in 3 hours. 135°C is the limiting temperature value, over which conversion of methylol groups already takes place.

Kinetic curves of the reaction are significantly affected by the quantity and nature of the catalyst. At the increase of catalyst quantity (ammonia) from 1 to 2 mass %, with respect to bisphenol, the conversion rate at 135°C in 10 hours increases from 80 to 94%. Further increase of quantity of the catalyst does not affect the rate of conversion.

The reaction progress is also affected by the nature of the catalyst. By an increase of catalyst activity (pyridine, triethyl amine, ammonia) the conversion rate increases and in 10 hrs, amounts to 27.50; 83.10 and 86.25 %.

To determine the effect of the nature of the reaction medium, the reaction was carried out in various organic solvents: in n-paraffin, n-butanol, 1,2-ethyleneglycol, 1,4-butyleneglycol and glycerin. Experiments showed that for 5 hours of the reaction the conversion rate

equaled 88.00; 85.05; 93.00 and 95.50, respectively. The best results were obtained when the solvents glycerin and ethylene glycol were used.

But it is not expedient to carry out the process of reaction in these solvents, since separation of the reaction product is extremely complicated.

It was shown that at the increase of starting concentration of bisphenol from 0.1 to 0.6 mol./l in the reaction mixture, the maximum fractional conversion increases and by the end of 10 hrs it equals 70.50 and 94.50%, respectively.

At the interaction of formaldehyde and 2,2-bis-(4-oxyphenyl)adamantane the formaldehyde to bisphenol ratio 4:1 is optimal. All the above-referred regularities were studied at this ratio of starting components.

We have studied the effect of the amount of formaldehyde exceeding the equimolecular at the rate of formation of methyl derivative and fractional conversion bisphenol. Experiments were carried out by the use of various starting quantities of formaldehyde. Various molar ratios of bisphenol to formaldehyde, namely such as 1:4, 1:8 and 1:16 were tested, respectively. Experiments showed that by increasing the formaldehyde quantity over the equimolecular one, the rate and speed of bisphenol conversion markedly increased.

Studies to determine the effect of various factors on the rate of conversion, at the interaction of formaldehyde and 2,2-bis-(4-oxyphenyl)adamantane proved that the most optimal term for the process is carrying it out at 125°C in n-propyl alcohol, at molar ratio of starting components 1:8, in the presence of 2 mass % ammonia used as a catalyst (with respect to bisphenol), at the reaction duration 10 hrs and initial concentration of bisphenol – 0.6 mol./l.

Methyl derivative of 2,2-bis-(4-oxyphenyl)adamantane was separated from the reaction mixture by precipitation in water or by evaporation of the solvent under vacuum at 60°C temperature. The isolated product is solid powder, with yellowish hue, well soluble in acetone, alcohol, dioxane, dimethyl formamide, insoluble in aromatic hydrocarbons and water.

Roentgenostructural studies showed that, unlike 2,2-bis-(4-oxyphenyl)-adamantane, its methyl derivative is of amorphous structure.

According to the data of analysis, hydroxyl groups equal 6.08 %; molecular mass determined by ebullioscopy - 586; methylol group content - 25.56%. These data well conform to the calculated values of these indices for tetramethyl derivative of 2,2-bis-(4-oxyphenyl)adamantane, esterified by the use of propyl alcohol.

Formation of reaction products according to the above-referred scheme is confirmed by the data of IR spectroscopy. Spectra of methyl derivative show the absorption band in the zone of 1030 cm<sup>-1</sup>, which is characteristic of valence fluctuation of methylol groups. But the spectra give also an absorption band in the regions 1085 and 1110 cm<sup>-1</sup>, which is characteristic of simple ether bonds, referring to esterification of methyl groups by propyl alcohol. IR spectra of absorption show also the absorption bands in the regions 1380 and 3360 cm<sup>-1</sup>, characteristic of valence and deformation fluctuations of phenol hydroxyl hydrogen bonds of polymer.

Absorption bands in the regions of 2880 and 2970 cm<sup>-1</sup> are characteristic of valence fluctuations of methyl groups, while the band at 1600 cm<sup>-1</sup> corresponds to aromatic nuclei.

Irrespective of the fact that methylol groups in the process of formation of bisphenol methyl derivative suffer esterification, they affect significantly their reaction activity. They are thermo-reactive and suffer hardening at heating.

Fig. 2 presents a thermogravimetric curve of hardening of methyl derivative of 2,2-bis-(4-oxyphenyl)adamantane. Fig. 2 shows that bisphenol methyl derivative at heating up to 400°C in the air, the mass decreases by 32%. Decrease of the mass up to 400°C should be attributed mainly to the hardening process, which apparently proceeds up to 400-470°C. But, along with the hardening process, destruction processes start at the above-stated temperatures. At 560°C the whole polymer evaporates, without coke residue formation. The behavior of methylol derivative of adamantane-containing bisphenol should be attributed to polycyclic adamantane grouping.

Taking into consideration the results of thermogravimetric analysis we can state that in the temperature range 150-400°C the decrease of mass is mainly conditioned by polycondensation processes. Above this temperature, destruction processes prevail. Considering this fact, further thermal hardening was carried out using these data.

The process of thermal hardening of methylol derivative of 2,2-bis-(4-oxyphenyl)-adamantane was investigated in isomeric conditions, in the air, at temperatures 150, 200, 250, 300°C (Fig.2). At heating of methylol derivative of bisphenol of 2,2-bis-(4-oxyphenyl)adamantane for five hours the intensity of the absorption band in 1030 cm<sup>-1</sup>, characteristic of free non-esterified methylol group – weakens significantly. This is apparently connected with condensation of methylol groups and with the formation of ether bond -CH<sub>2</sub>-O-CH<sub>2</sub>-. The

intensity of the absorption band decreases significantly in the region of  $3360\text{ cm}^{-1}$  and the bands of absorption in  $3550\text{ cm}^{-1}$  characteristic of valence fluctuations of phenyl hydroxyl groups, participating in the formation of dimer hydrogen bonds increases.

Analogous changes were observed in deformation fluctuations of phenol hydroxyl in the regions  $1360$ ,  $1380\text{ cm}^{-1}$ .

Fig. 3 shows that by increasing the hardening temperature in isothermal conditions up to  $250^\circ\text{C}$ , at the starting section of the curves, the mass decrease rate is higher. At the increase of the length of heating, the intensity of decrease slows down for some time. Up to  $250^\circ\text{C}$  the decrease in mass is apparently conditioned by conversion of methylene ether groups, at a lesser degree, by conversion of methylol groups with the isolation of low molecular reaction products. The process of hardening apparently proceeds up to a deeper rate of completion, which can be explained by the formation of products with less rigid spatial, three-dimensional structure, owing to the large size of adamantane grouping.

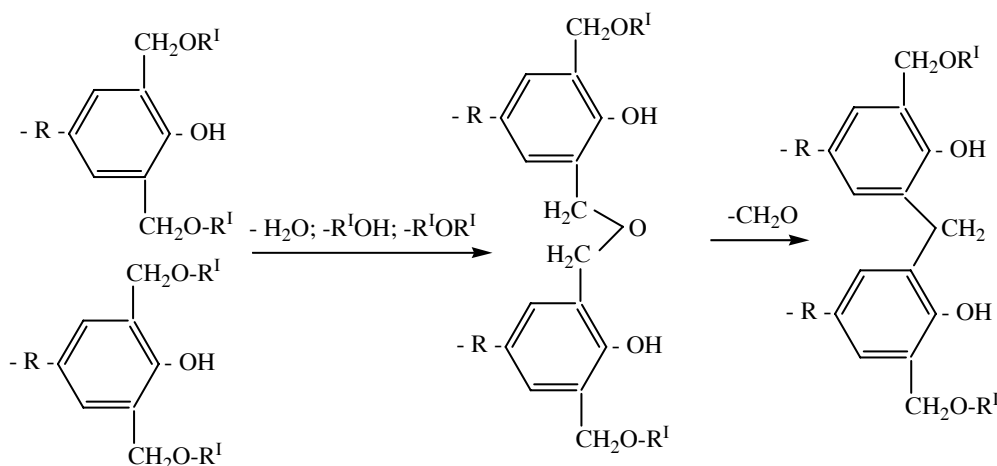
In IR spectra of the product of thermal treatment of methylol derivative of 2,2-bis-(4-oxy-phenyl)adamantane, carried out at  $200^\circ\text{C}$ , in isothermal conditions, the intensity of absorption bands at  $1085$  and  $1110\text{ cm}^{-1}$ , corresponding to simple ether bonds, greatly decreases. Destruction of these bonds takes place and infusible and insoluble product, resite is formed.

The intensity of the absorption band at  $825\text{ cm}^{-1}$  characteristic of extra-planar deformation fluctuations of two siding  $=\text{CH}$  groups of benzyl nucleus suffer significant decrease, which apparently refers to the formation of new bonds.

On the basis of the IR-spectral data the mechanism of the process of hardening of methylol derivative of bisphenol can be presented as follows: at the initial stages methylene ether bonds are formed. Then, at high temperatures, these bonds suffer destruction and an infusible and insoluble product is formed, which is confirmed by the decrease of the intensity of the absorption band in the region  $825\text{ cm}^{-1}$ .

At thermal treatment of tetra-methylol derivative of 2,2-bis-(4-oxyphenyl)adamantane, at  $250^\circ\text{C}$ , in the air, at isomeric conditions the IR spectra show a band of adsorption corresponding to the aldehyde group, at  $1660\text{ cm}^{-1}$ , which is explained by partial oxidation of methylene group, and a band of absorption in the region of  $1680\text{ cm}^{-1}$ , which is characteristic of quinoid groups, and is accompanied by a decrease of absorption band intensity in  $2880$  and  $2970\text{ cm}^{-1}$ , corresponding to valence fluctuations of  $-\text{CH}_2-$  groups, which apparently is associated with the changes in adamantane structure.

According to the thermogravimetric curve (Fig. 2), at thermal hardening of methylol derivative of adamantane-containing bisphenol, mass decrease proceeds and increases up to  $400^\circ\text{C}$ . As it was stated above, mass decrease mainly takes place at the expense of the process of hardening. The presence of adamantane grouping contributes to the decrease of the effect of steric factors on the process of thermal hardening, as a result of which the degree of completeness shifts towards high values. In common phenol formaldehyde polymers, at the early stage of reaction the process of hardening stops due to rigidifying of the structure and formation of frequent cross-linking, which is a result of a decrease of the degree of completeness at a comparatively early stage.



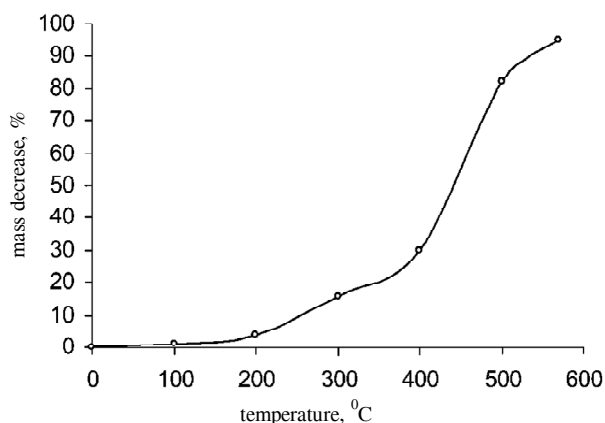


Fig. 2. Dynamic thermogravimetric curve of methylol derivative of 2,2-bis(4-oxyphenyl)adamantane (heating speed 5°C/min, in the air)

At thermal treatment of methylol derivative of 2,2-bis(4-oxy phenyl)adamantane, at 300°C, in isomeric conditions, in the air, IR spectra of the product of hardening show an absorption band in the region of 1600  $\text{cm}^{-1}$  (characteristic of the formed condensed aromatic hydrocarbons) and the increase of absorption band intensity in the region of 1720  $\text{cm}^{-1}$  (characteristic of carboxyl groups formed by oxidation of carbonyl groups).

The behavior of phenol hydroxyl groups at thermal treatment in the temperature range 250-300°C should be emphasized. Absorption bands at 3360 and 1389  $\text{cm}^{-1}$ , characteristic of valence and deformation fluctuations

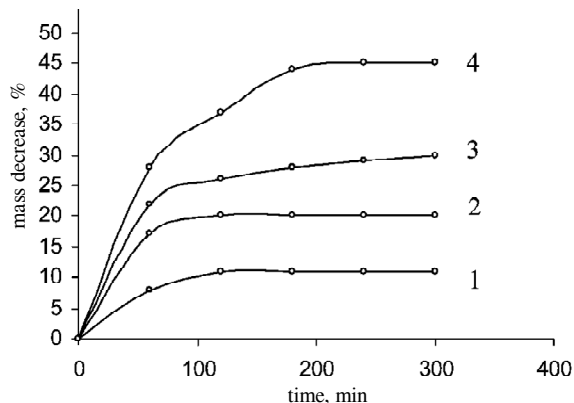


Fig. 3. Mass decrease at thermal hardening of methylol derivative of 2,2-bis(4-oxy phenyl)adamantane in the air, in isothermal conditions, at temperatures: 150 (1), 200 (2), 250 (3) and 300°C (4).

of phenol hydroxyls, linked by polymer hydrogen bonds, suffer great changes. Their intensity decreases, while the intensity of the bands at 3550 and 1360  $\text{cm}^{-1}$ , belonging respectively to valence and deformation fluctuations of phenol hydroxyl, participating in the formation of dimer hydrogen bonds - increases. This refers to regrouping of polymer hydrogen bonds towards those of dimers, characterized by high resistance.

We have stated above that the presence of card groups increases the thermal indices of other class polymers. To evaluate the thermal stability of adamantane-containing bisphenol aldehyde polymer, we prepared resite of the corresponding polymer.

Table

Mechanical properties of some polymers and phenol formaldehyde type glass-reinforced plastics

| # | Sample type  | Relative impact strength, n, $\text{cm}^2/\text{cm}^2$ | Static bending MPa | Brinell hardness number MPa |
|---|--|--|--------------------|-----------------------------|
| 1 | Polymer on the basis of methylol derivative of bisphenol II  | 30   | 33                 | 330                         |
| 2 | Mixed polymer on the basis of methylol derivatives of bisphenols I and III (at bisphenol I to bisphenol III molar ratio 3:7)   | 35   | 37                 | 340                         |
| 3 | Mixed polymer on the basis of methylol derivatives of bisphenols II and III (at bisphenol II to bisphenol III molar ratio 3:7) | 38   | 40                 | 350                         |
| 4 | Phenol formaldehyde polymer  | 25   | 39                 | 343                         |
| 5 | Glass-reinforced plastic on the basis of methylol derivative of bisphenol III*   | 1600   | 216                | 412                         |
| 6 | Glass-reinforced plastic on the basis of methylol derivatives of bisphenols I and III  | 1700   | 230                | 420                         |
| 7 | Glass-reinforced plastic on the basis of methylol derivatives of bisphenols II and III   | 1900   | 250                | 440                         |
| 8 | Glass-reinforced plastic on the basis of phenol formaldehyde oligomer  | 170  | 63                 | -                           |
| 9 | Glass-reinforced plastic on the basis of phenolphthalein - formaldehyde oligomer   | 690  | 204                | -                           |

\* Relative elongation at rupture - 0.6%; tensile strength -  $441 \cdot 10^6$  Pa, resilience module  $216 \cdot 10^8$  Pa; tangency of angle of dielectric losses at  $10^3$  Hz - 0.016; dielectric transmissivity - 3.7-3.8

Resite was prepared as follows: weighted amount of a methylol derivative sample was heated to 180-200°C 10-15 min prior to its melting. When the melt started hardening, it was subjected to thermal treatment at 250°C for 1 hour. Preliminary experiments, by extraction of dispersed sample of resite from boiling acetone within 5 hours, showed that it didn't contain low molecular products and that thus the hardening process is practically brought to an end.

We carried out thermogravimetric and thermomechanical studies of resite. Structural changes taking place at thermal treatment were evaluated according to the data of IR-spectroscopy.

Resite, obtained by hardening of methylol derivative of 2,2-bis-(4-oxyphenyl)-adamantane, unlike common phenyl formaldehyde resites, as is shown by thermogravimetric studies, up to 300°C don't reveal mass decrease practically, while in case of common phenol formaldehyde resite, the mass decrease in this case equals 10%. Resite with adamantane grouping suffers intense decomposition in the temperature range 450-550°C, and

for common resite, this interval falls within 400-500°C.

Adamantane-containing resite suffers decomposition without formation of coke residue, which enables us to recommend it for making heat-eliminating covers.

Thermomechanical studies of adamantane-containing resite showed that the polymer revealed insignificant deformation (~ 2%) when it was treated up to the temperature of thermal decomposition. At the temperature about 500°C an increase of deformation is observed, which apparently is connected with resite destruction.

High thermal indices of a polymer on the basis of methylol derivative of 2,2-bis-(4-oxy phenyl)adamantane, enables us to use it as a binder for the creation of heat and thermally stable materials. Glass-reinforced plastic on the basis of methyl derivative of 2,2-bis-(4-oxyphenyl)adamantane, according to its dielectric and mechanical characteristics, significantly exceeds glass-reinforced plastic on the basis of common phenol formaldehyde oligomers, currently produced in industrial conditions (see Table).

*ორგანული ქიმია*

## ფენოლ-ფორმალდეჰიდური ტიპის პოლიმერები ბისფენოლების საფუძველზე

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ადამანტანის ტიპის კარდული ბისფენოლებისა და მათი ფენილწარმოებულების საფუძველზე სინთეზირებულია მეთილოლწარმოებულები. შესწავლილია ხსნარში ბისფენოლებისა და ფორმალდეჰიდის ურთიერთმოქმედების ზოგიერთი კინეტიკური კანონზომიერება.

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