CHEMISTRY

SYNTHESIS OF THERMOREACTIVE OLIGOMERS ON THE BASIS OF POLYCYCLIC BISPHENOLS

Givi Papava, *professor, doctor*
Marina Gurgenishvili, *doctor*
Ia Chitrekashvili, *doctor*
Zurab Chubinishvili
Zurab Tabukashvili

Georgia , Tbilisi , Petre Melikishvili Institute of Physical and Organic Chemistry of Ivane Javakhishvili Tbilisi State University

DOI: https://doi.org/ 10.31435/rsglobal_ws/31102018/6178

ARTICLE INFO

Received: 15 August 2018
Accepted: 20 October 2018
Published: 31 October 2018

KEYWORDS

norbornane,
oligomer,
bisphenol,
formaldehyde,
hardening,
isothermal.

ABSTRACT

Novolac on the base of norbornane type bisphenol was obtained. Some cinetic regularities of reaction of interaction of norbornane type bisphenol and formaldehyde were studied. It was proved that the reaction proceeded according to the second order. IR-spectroscopy was used to study the process of thermal hardening of novolac at isothermal terms on the air.

Citation: Givi Papava, Marina Gurgenishvili, Ia Chitrekashvili, Zurab Chubinishvili, Zurab Tabukashvili. (2018) Synthesis Of Thermoreactive Oligomers On The Basis Of Polycyclic Bisphenols. *World Science.* 10(38), Vol.1. doi: 10.31435/rsglobal_ws/31102018/6178

Introduction. Most significant representatives of thermostable polymers are the phenol-formaldehyde tipe polymers [1-4].

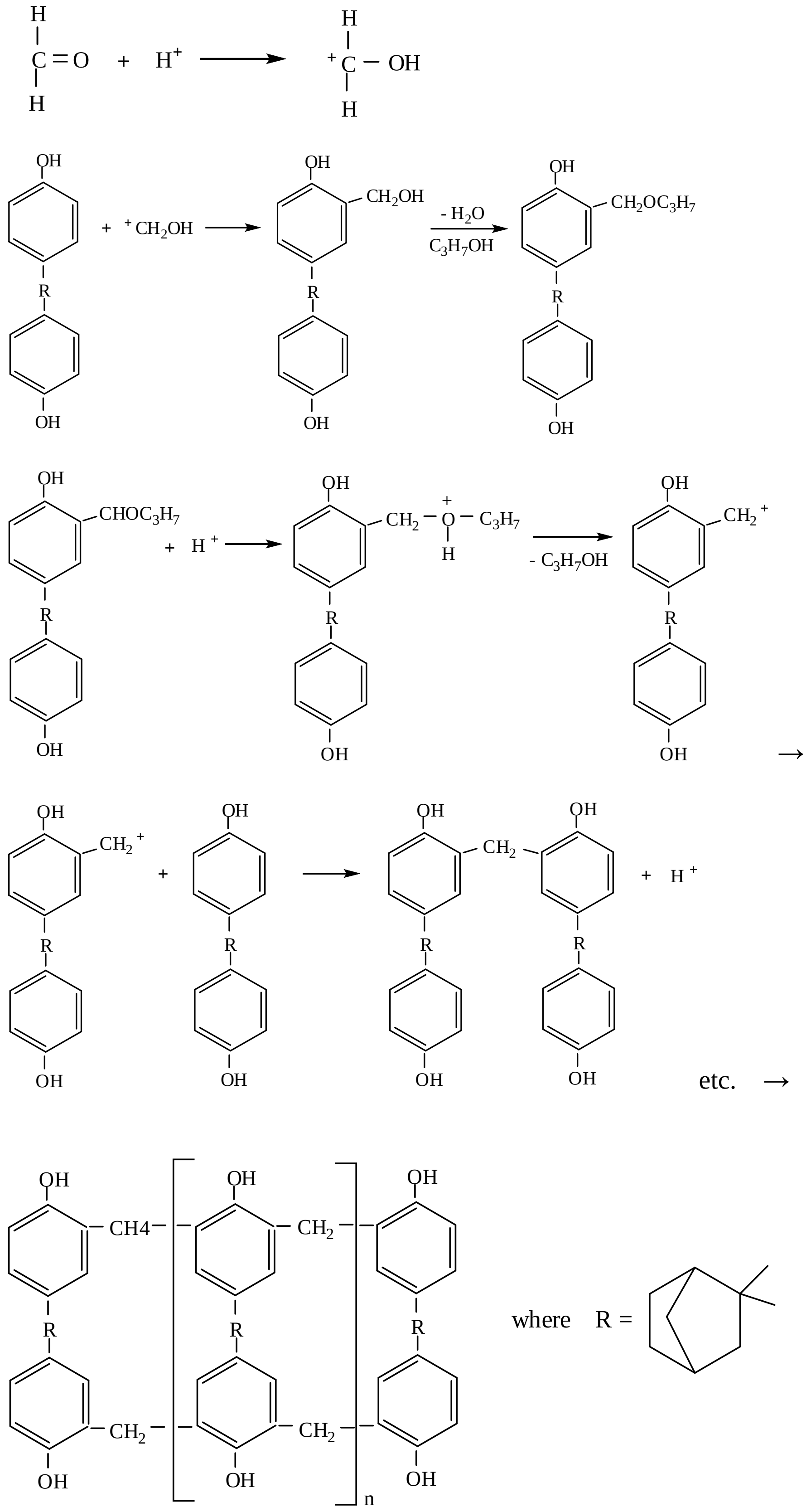
Recently, to increase some indices norbornane tipe bisphenols were used for the synthesis of phenol formaldehyde type polymers. It enabled us to decrease of cross-linking of macromolecules, which makes significant effect on physical-mechanical and other indices of polymers [3-5].

Thanks to the very interesting set of properties of other type polymers containing cycloparaffin card type groupings [6,7] we considered interesting and expedient to lead investigations in the sphere of phenol formaldehyde polymers with other bisphenols.

Experimental part. Initial component of the synthesis was norbornane tipe bisphenol (as the phenol component) and alcoholic solution of formaldehyde.

Interaction of norbornane tipe bisphenol with formaldehyde was investigated in n- propyl alcohol, at 125-145°C temperature interval, in the presence of ammonia as the catalyst, at bisphenol to formaldehyde molar ratio 1:4.

Schematically the reaction can be presented as follows:



Control over the reaction process was realized according to the quantity of the used formaldehyde [7].

It was found that at 125-145°C temperature interval, up to the high rate of conversion, the rate constants preserved constant values during the reaction, and were calculated by the quadratic equation of Arrhenius.

Direct linear relation of 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 to $67{,}0 \bullet 10^3$ J/mol.

Effect of various factors on the process of reaction, and 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.

By the increase of temperature, the rate and speed of conversion are increased. Rate of conversion increases also at the increase of reaction duration. Kinetic curves of the reaction are significantly affected by the quantity of the catalyst to determine the effect of nature of the reaction medium, the reaction was carried out in various organic solvents: n-butanol, 1,2-ethyleneglycol, 1,4-butyleneglycol and glycerin. Experiments showed that for 5 hours of the reaction the conversion rate equaled to 90,00; 95.00; 95.00 and 98.10, correspondingly. The best results were obtained when the solvents glycerin was used.

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 is increased and by the end of 10 hrs it equals to 75 and 98,1%, correspondingly.

At the interaction of formaldehyde and bisphenol the formaldehyde to bisphenol ratio 4:1 is optimal.

The most optimal term for the process is its carrying out at 145^0C in n-propyl alcohol, at molar ratio of starting components 1:4, in the presence of 1 mass % HCI used as a catalyst, at the reaction duration 10 hrs and initial concentration of bisphenol – 0.6 mol./l.

Results and discussion. Formation of reaction products is confirmed by the data of IR spectroscopy. IR spectra of absorption show the absorption bands in the regions 1380 and 3360 cm^{-1}, characteristic to valence and deformation fluctuations of phenol hydroxyl hydrogen bonds of the polymer. Absorption bands in the regions of1600 cm^{-1} corresponds to aromatic nuclei. They are thermo-reactive and suffer hardening at heating.

Novolac at heating up to 400°C on the air, the mass is decreased by 40%. Decrease of the mass up to 400°C should be attributed mainly to the hardening process, which apparently proceeds up to 400-440°C.

Above this temperature, the destruction processes are prevailing. At 500°C the whole polymer is evaporated, without coke residue formation.

In IR spectra of the product of thermal treatment of novolac of bisphenol, carried out at 200°C, in isothermal conditions, the intensity of absorption bands at 1085 and 1110 cm^{-1}, corresponding to simple ether bonds, greatly decreases. Destruction of these bonds takes place and infusible and insoluble product, resite is formed

On the base of the IR-spectral data the mechanism of the process of hardening of novolac of bisphenol can be presented as follows: at the initial stages, at high temperatures the infusible and insoluble product is formed, which is confirmed by the decrease of intensity of absorption band in the region 825 cm^{-1}.

At thermal treatment at 250°C, the IR spectra show a band of adsorption corresponding to the aldehyde group, at 1660 cm^{-1}, which is explained by partial oxidation of methylene group, and a band of absorption in the region of 1680 cm^{-1}, which is characteristic to quinoid groups,

At thermal treatment of novolac olygomer of bisphenol, at 300°C, IR spectra of the product of hardening show absorption band in the region of 1600 cm^{-1} and the increase of absorption band intensity in the region of 1720 cm^{-1}. Behavior of phenol hydroxyl groups at thermal treatment in the temperature interval 250-300°C should be emphasized. Absorption bands at 3360 and 1389 cm^{-1}, characteristic for valence and deformation fluctuations of phenol hydroxyls, linked by polymer hydrogen bonds, suffer great changes. Their intensity is decreased, while the intensity of the bands at 3550 and 1360 cm^{-1}, belonging correspondingly to valence and deformation fluctuations of phenol hydroxyl, participating in the formation of dimer hydrogen bonds - increase. This refers to regrouping of polymer hydrogen bonds towards those of dimers, characterized by high resistance.

To evaluate thermal stability of norbornane-containing bisphenol aldehyde polymer, we prepared resite of the corresponding polymer.

Resite was prepared as follows: weighted amount of a novolac olygomer sample was heated to 180-200°C 10-15 min prior their melting. When the melt started hardening, it was subjected to thermal treatment at 250°C within 1 hour. We carried out thermomechanical studies of resite.

Resit, obtained by hardening of novolac olygomer of 2,2-bis-(4-oxyphenyl)norbornane, in distinct from common phenyl formaldehyde resites, up to 300°C don't reveal mass decrease practically, while in case of common phenol formaldehyde resite, the mass decrease in this case equaks to 10%. Resite with norbornane grouping suffer intense decomposition in temperature interval 450-480°C.

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

Thermomechanical studies of norbornane-containing resite showed that the polymer revealed insignificant deformation when it was treated up to the temperature of thermal decomposition.

High thermal indices of a polymer on the base of novolac olygomer of 2,2-bis-(4-oxy-phenyl)norbornane, enables us to use it as the binder for the creation of heat and thermally stable materials. Glass-reinforced plastic on the base of novolac olygomer of 2,2-bis-(4-oxy-phenyl)norbornane, according to its dielectric and mechanical characteristics significantly exceeds glass reinforced plastics on the base of common phenol formaldehyde oligomers, (see Table).

Table 1. Mechanical properties of some polymers and phenol formaldehyde type glas-reinforced plastics

#	Sample type	Relative impact strength, n, cm/cm^2	Static bending MPa	Brinnel hardness number MPa
1	Polymer on the base of novolac olygomer of 2,2-bis (4-oxyphenyl)-norbornane	30	35	280
2	Phenol formaldehyde polymer	25	39	343
3	Glass-reinforced plastic on the base of novolac olygomer of 2,2-bis (4-oxy phenyl)-norbornane [*]	1100	200	320
4	Glass-reinforced plastic on the base of phenol formaldehyde oligomer	170	63	-
5	Glass-reinforced plastic on the base of phenolphthalein – formaldehyde oligomer	690	204	-

[*] Relative alongation at rupture - 1.4%; tensile strength - 300.10^{6}Pa, resilience module 194.10^{8}Pa; tangency of angle of dielectric losses at 10^3 Hz – 0,020; dielectric transmissivity - 3,4 –3,7.

Conclusions.

Novolac olygomer on the base of norbornane type bisphenol was obtained. Some cinetic regularities of reaction of interaction of norbornane type bisphenol and formaldehyde were studied. It was proved that the reaction proceeded according to the second order. Resite with norbornane grouping suffer intense decomposition in temperature interval 450-480^{o}C**.** Norbornane-containing resite suffers decomposition without formation of coke residue, which enables us to recommend it for making heat-eliminating covers. High thermal indices of a polymer on the base of novolac olygomer of 2,2-bis-(4-oxy phenyl)norbornane enables us to use it as the binder for the creation of heat and thermally stable materials.

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