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## NEW NETWORK POLYMERS BASED ON FURFURYLGLYCIDYL ETHER

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Received: December 26, 2007

**Abstract.** Among the activities done under the present work are the following: study of the kinetic regularities of the polymerization of new heterocyclic monomers and oligomers obtained from interaction between furfurylglycidyl ether and aliphatic monocarboxylic acids (saturated and unsaturated); determination of the polymerization mechanism in the absence of complex onium catalysts; determination of the structure and composition of monomeric and polymeric compounds by using chemical and physicochemical techniques and <sup>1</sup>H-NMR spectral analysis. The kinetic regularities for polymerization have been studied using differential scanning calorimetry (DSC); study of the thermal resistance and thermal stability employed the derivatography techniques (DTA and TGA).

**Keywords:** monomer, oligomer, network polymer, furfurylglycidyl ether, Diels-Alder adducts, complex onium catalysts.

### 1. Introduction

The furfural, furfuryl alcohol and other derivatives of furan are widely employed to obtain synthetic resins [1]; various furan compounds are used as solvents, plasticizers, pharmaceutical products, physiologically active substances, *etc.*

A wide base for pentosan-containing raw materials, which are essential for obtaining furfural and, consequently, other furan compounds, are determinative in obtaining synthetic polymer materials based on the furan derivatives, particularly, on furfurylglycidyl ether (FGE) [2].

Of special interest are the reactions forming network polymers based on the Diels-Alder adducts (DA), as in this case hyper-branched structures supported by the polyfunctionality of DA adducts are formed.

The oligomer DA adducts that include halogens (*e.g.* chlorine, bromine), form network polymers belonging to the self-extinguishing polymers group [3, 4].

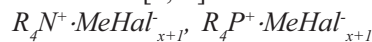
### 2. Experimental

FGE was synthesized according the procedure described in [5], and then vacuum-distilled. The refractive index is compliant with the published information (1.4810); the epoxide equivalent is 27.32 %; the main substance content (MSC) is 98 %. The acrylic acid (AA) was vacuum-frozen, the acidity index (AI) for the AA is 775.5 mg KOH/g. The MSC is 99.6 %. The linolenic acid (LA) was vacuum-dried, the iodine number (IN) is 272.4 mg, I<sub>2</sub>/100g, AI is 198.2 mg KOH/g. The MSC is 98 %.

The maleic anhydride was distilled prior to application, the AI is 1138.5 mg KOH/g, which is compliant with the MSC 99.5 %. Maleimide (Aldrich): melting point is 364–366 K, MSC is 99 %. 2,4,6-tribromoaniline (Aldrich): melting point is 393–395 K, the MSC is 98 %.

Producing 2,4,6-tribromophenylmaleimide, 0.1 mol of 2,4,6-tribromoaniline and 0.12 mol of maleic anhydride are suspended in a 70 g of polyphosphoric acid (content of P<sub>2</sub>O<sub>5</sub> is 72.5 mass %). The suspension is then mixed thoroughly and heated at 373 K until complete homogenization. After this step the reaction mass is kept at 383–393 K for 2 hours and then cooled and mixed with 30 ml of water. The sediment deposit is filtered out, washed and resolved in isoamyl alcohol; then activated charcoal is added, and the resulting substance is boiled "with backflow condenser" for one hour. After boiling, the product is cooled, filtered and re-deposited in water. The result is the product of the melting point of 415 K (more precisely, 415.5 K, according to published data).

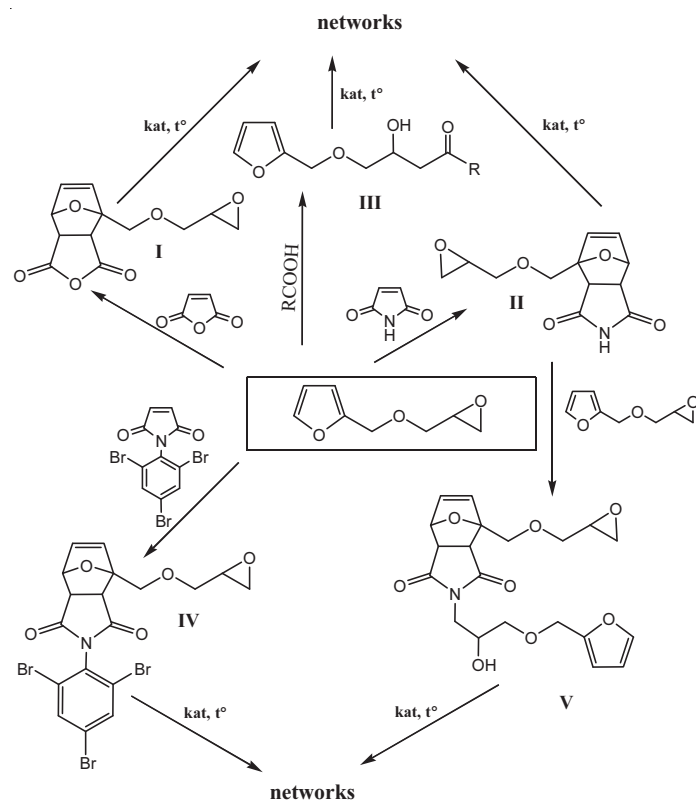
The catalysts – complex onium salts of the general formula given below, have been obtained according the procedure described in [6, 7].



where:  $R_4N^+$  and  $R_4P^+$  are the cations of the quaternary ammonium and phosphonium salts,  $R-ALk, Ar$ ;  $Me=Zn^{2+}, Fe^{3+}$

Furfuryl, hydroxypropylacrylat (FGPA) and furfuryl, hydroxypropyllinoleat (FGPL) have been synthesized using the above catalysts at  $T = 353$  K; the extent of reaction (96 %) was monitored as per the AI.

The Diels-Alder adducts have been synthesized at  $T = 313\text{--}333\text{ K}$ , with the molar ratio 1:1, in case of maleimide – 1:1 and 1:2; extent of reaction (90–95 %) was monitored as per the change of IN (Scheme 1).



**Scheme 1.** Heterocyclic polymers and oligomers based on furfurylglycidyl ether

The Differential Scanning Calorimetry (DSC) method was employed to determine the thermal effects and temperature limits for the course of reactions under analysis. The reactions were performed in vacuum-sealed ampoules, the shots weight ranged within 50–100 mg; heating rate is 2 K/min.

Thermogravimetric research of polymers was conducted using the “Paulik-Paulik-Erdei” derivatograph. A dry and solidified sample of polymer was analyzed in the dynamic mode; sample weight was 500 mg, heating rate – 5 K/min.

NMR spectra were recorded on a Varion Mercury VX-200 spectrometer in DMSO-D.

Content of the gel-fraction was defined through polymer extraction in the Soxhlet apparatus using toluene and propanone until their complete weight was reached.

The peroxide and iodine numbers were defined according to the procedure [8]. Application and testing of coatings was done in compliance with [8].

### 3. Results and Discussion

Previously, the authors have studied the kinetics of polymerization for unsaturated glycidyl ethers using glycidylmetacrylate, vinylglycidyl ether, and

furfurylglycidyl ether (FGE), as samples, in the presence of complex onium catalysts specified above. It was determined that a simultaneous polymerization of the double vinyl bonding and the oxirane ring occurred in the presence of the above catalysts.

Since the complex onium catalysts are related to the cation catalysts group, the polymerization of unsaturated glycidyl ethers occurs as a combined mechanism in the presence of the above catalysts, *i.e.* as a radical polymerization of the double bonding and cation polymerization of the oxirane ring.

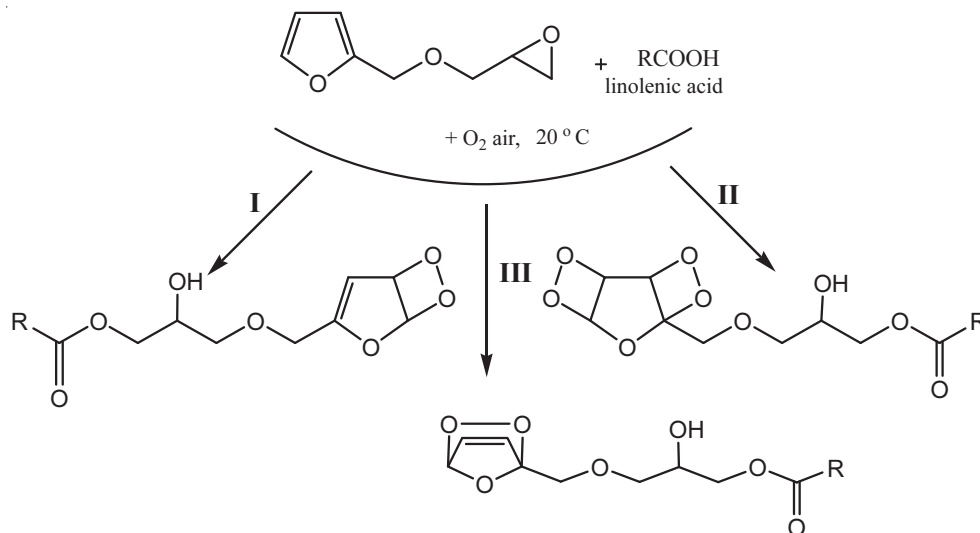
To verify the mentioned specific action of complex onium catalysts, we have polymerized the methylmetacrylate, which rejects polymerization as per the cation mechanism [9].

As was determined by using DSC technique FGE does not polymerize in the presence of complex onium catalysts of different composition and structure contained in vacuum in sealed ampoules or in a blanket of inert gas. This posed a question as to the mechanism of FGE polymerization in the presence of complex onium catalysts in the oxygen atmosphere, and the role played particularly by the oxygen.

The furan compounds – furfural, furfuryl alcohol, and others – are known to indicate a high chromophoric effect in the presence of atmospheric oxygen. Being totally

colorless after vacuum distillation, these compounds acquire a dark-brown tint when contacting with air, and a resinoid state when such contact is long-time, also under effect of the catalysts [10].

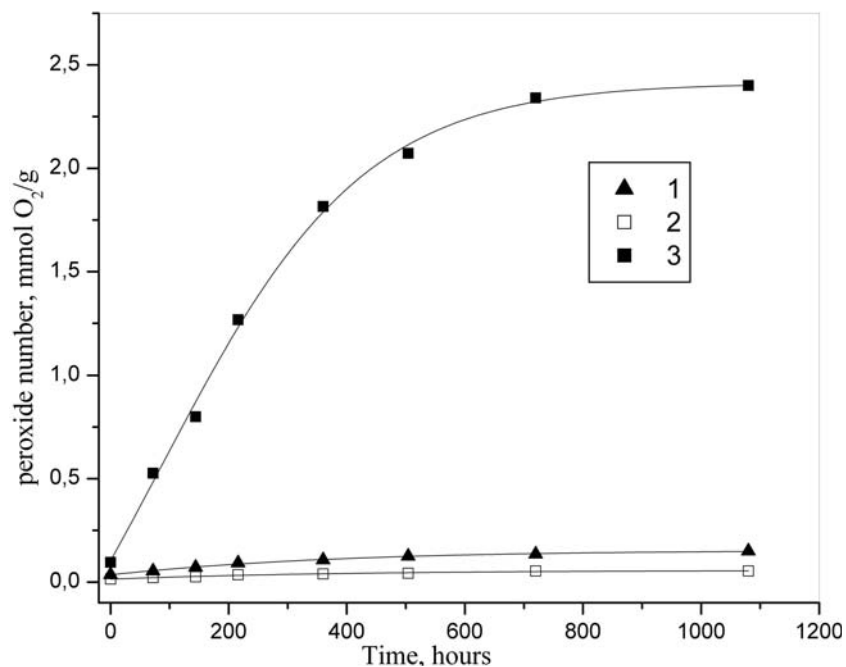
If we assume that the peroxide compounds occur in the double bondings of the furan ring, this would imply a scheme of possible routes for chemical reactions. The scheme is described below (Scheme 2):



**Scheme 2.** Routes for chemical reactions in the polymerization mechanism

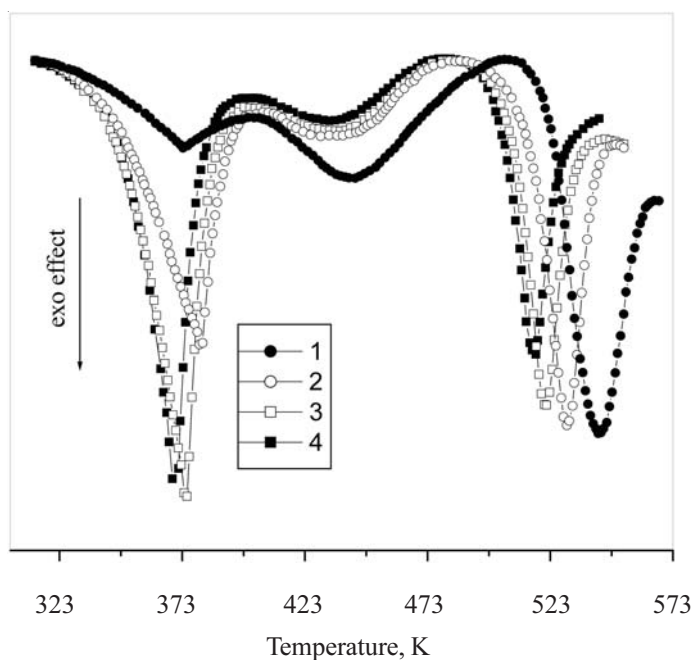
When studying the kinetics of accumulation of peroxide groups in the FGE, linolenic (unsaturated) acid and composition FGE+LA, it was determined that both the FGE, and the linolenic acid, form – to a slight extent – peroxide compounds, as shown in Fig. 1; the composition FGE+LA, upon a certain time period and at 293 K, reaches

the maximum value of peroxide number – 2.31 mmol O<sub>2</sub>/g, and is compliant with reactions 1 and 3 in the presented reaction route. From the viewpoint of thermodynamics, route 3 is preferred, since this route retains the most favorable distribution of electron density for the furan ring, similar to the formation of DA adducts.

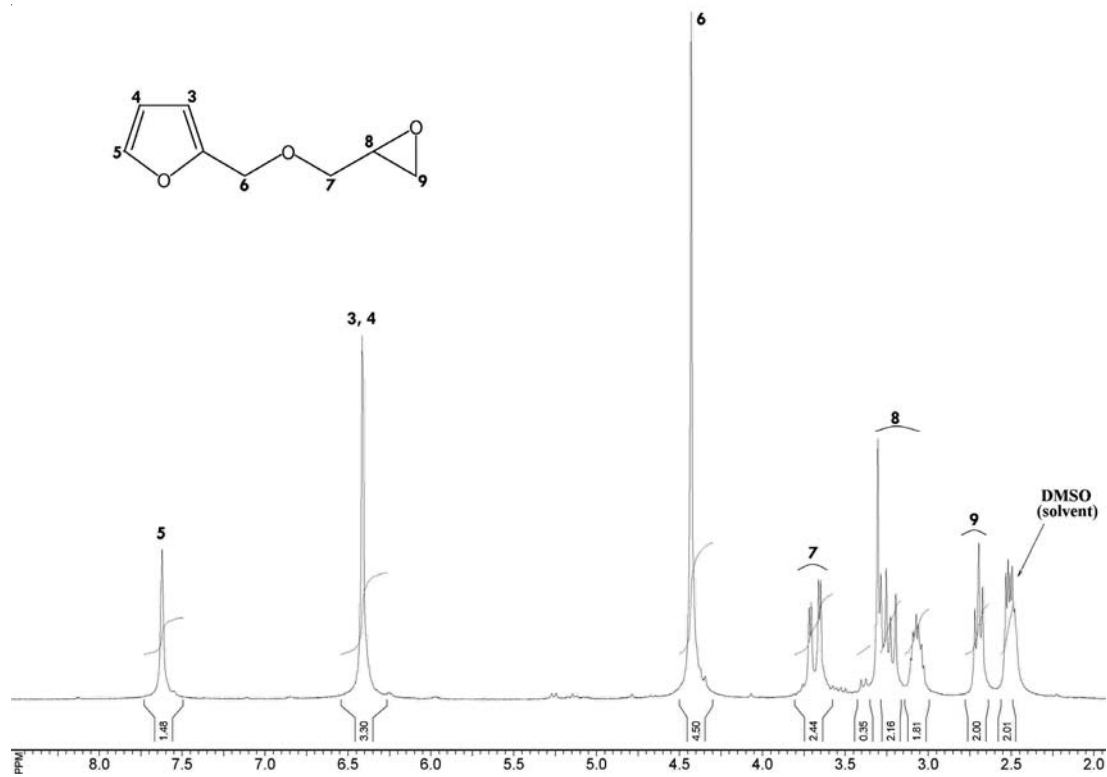


**Fig. 1.** Kinetics for accumulation of peroxide groups: FGE (1), LA (2), FGE + LA (1:1) (3)

The kinetic curves of DSC indicate the contribution of peroxide compounds at the FGE+LA polymerization. When the peroxide of furan ring is of maximum content (Fig. 2, curve 4), the activation energy decreases, and the polymerization temperature of double bondings of the furan ring is reduced by 40-50 K (Fig. 2, curves 1 and 4).



**Fig. 2.** Thermal effects of interaction between FGE and LA, catalyst –  $\text{Et}_3\text{PhCH}_2\text{N}^+\text{ClFeCl}_4$  (1 mass %): in 7 days (1), in 14 days (2), in 30 days (3), in 45 days (4)



**Fig. 3.**  $^1\text{H-NMR}$  spectrum of freshly-distilled FGE

The analysis and interpretation of the  $^1\text{H-NMR}$  spectrums – FGE (freshly-distilled – Fig. 3), and FGE (kept in the air for two weeks – Fig. 4) also testify to the formation of peroxide group between the second and the

fifth carbons, since the initial singlet breakage forms of the fifth and the sixth carbons have changed into the triplet forms, and the protons of the third and the fourth carbons have transferred from the initial singlet form to the multiplet form.

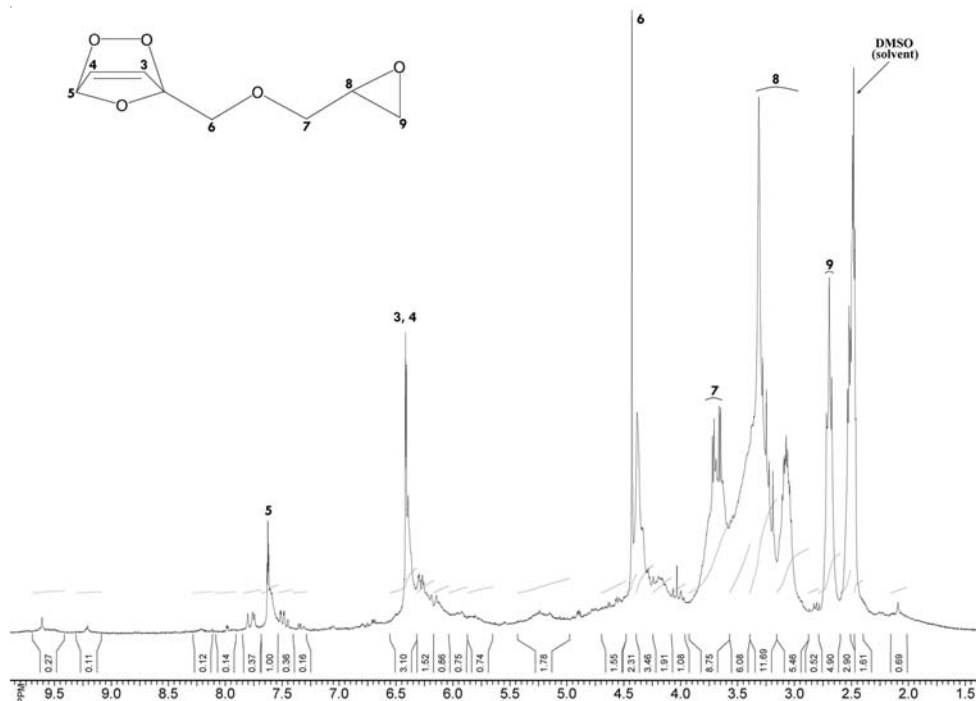


Fig. 4.  $^1\text{H-NMR}$  spectrum of FGE after keeping in the air for 2 weeks

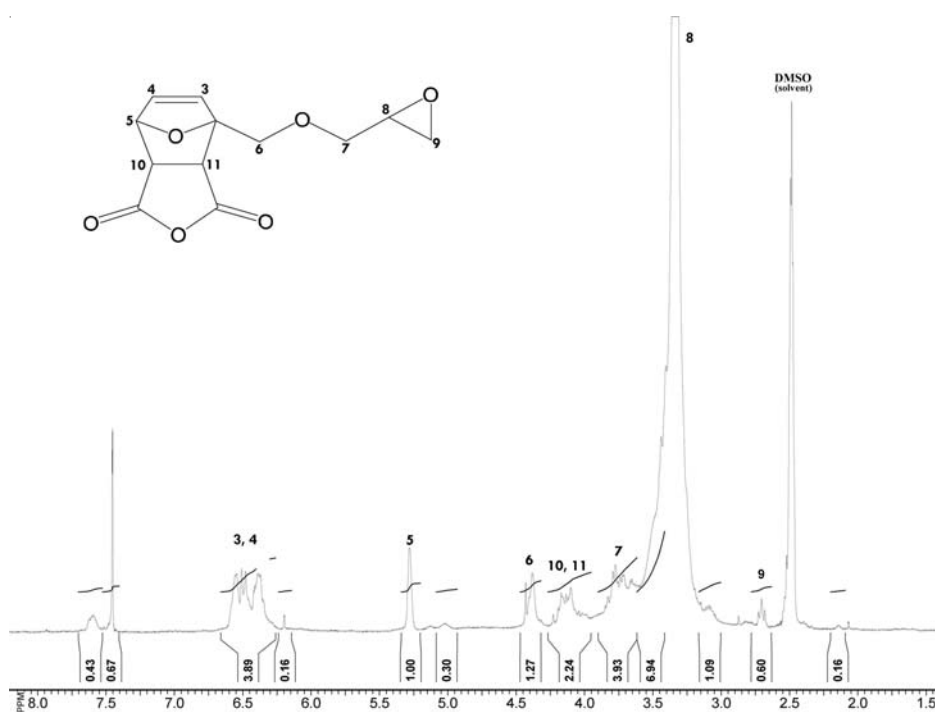
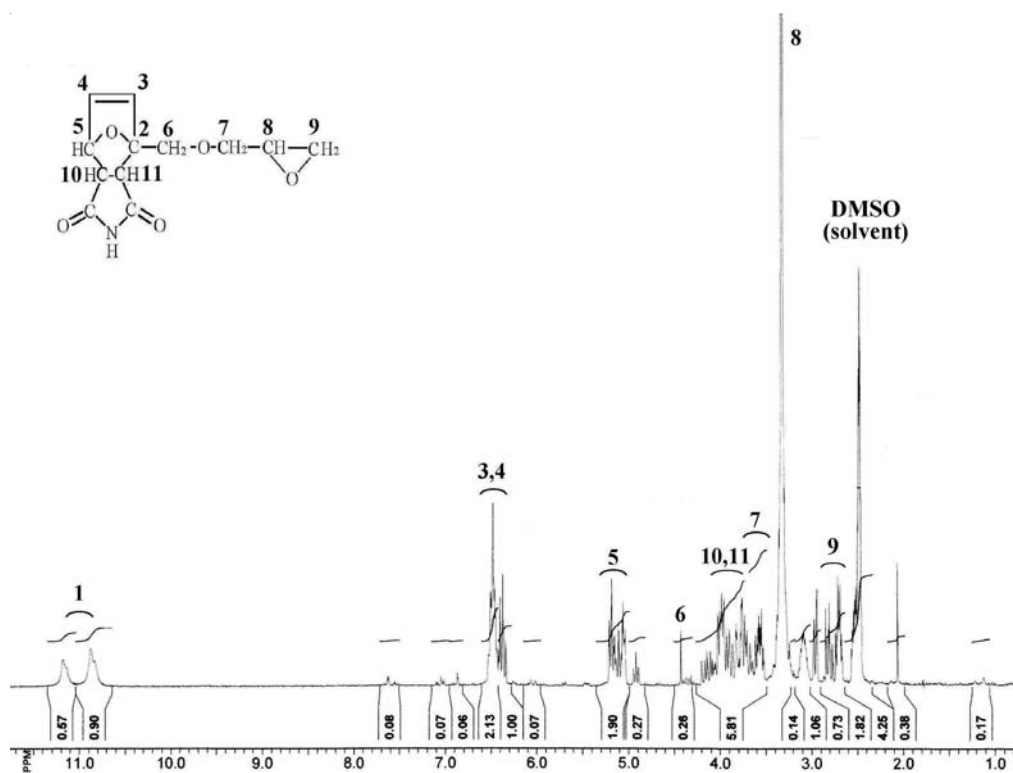
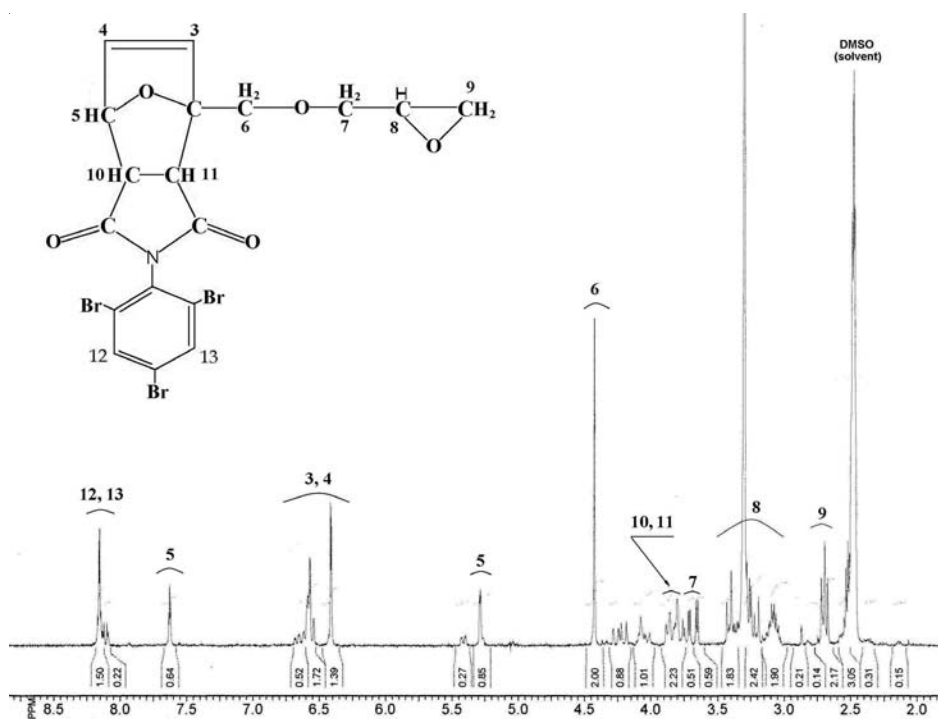
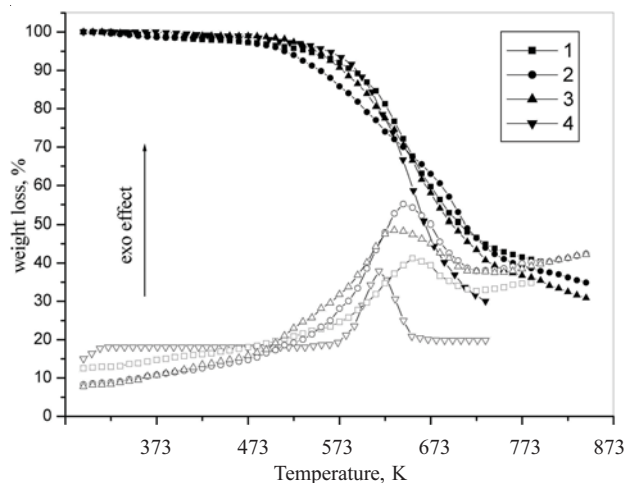


Fig. 5.  $^1\text{H-NMR}$  spectrum of monomer I (Scheme 1)

Fig. 6.  $^1\text{H-NMR}$  spectrum of monomer II (Scheme 1)Fig. 7.  $^1\text{H-NMR}$  spectrum of monomer IV (Scheme 1)

The furan [1] and furfuryl alcohol [11] are known to form the DA (Diels-Alder) [12, 13] adducts with the maleic anhydride and maleimide.

The paramagnetic spectrography approach for the  $^1\text{H-NMR}$  has helped determining the structure for the DA adducts formed: monomer I (Scheme 1, Fig. 5), monomer II (Scheme 1, Fig. 6).



**Fig. 8.** Dependence of the thermogravimetric analysis of network polymers: FGPA (1), FGPL (2), monomer II (3), monomer IV (4). Nontransparent signs are TGA curves, transparent signs are DTA curves

The area 5.15–5.5 ppm is related to the DA adduct; the singlet of protons of the third and the fourth carbons in the initial maleimide within 6.8 ppm of the DA adduct has split to the multiplet 6.3–6.6 ppm in Fig. 6. The Fig. 7 presents the spectrum of the  $^1\text{H-NMR}$  monomer IV (Scheme 1).

In the presence of the complex onium catalysts, all DA adducts form network polymers at the temperature of 433–453 K.

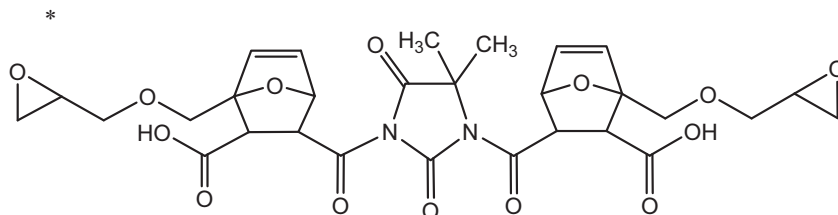
Derivatography was used to indicate the regions of thermal stability and thermal resistance for the network polymers. The loss of 5 % of the weight of a network polymer occurs at the temperature of 533 K; thermal decomposition is accompanied by the exothermic effect reaching its maximum at the temperature of 633 K. The information for DTA and TGA is presented in Fig. 8.

Since the resulting heterocyclic monomers and oligomers are easy-flowing or thick-flowing liquids, they are of considerable interest as chemically resistant protective coatings with high physico-mechanical indices as opposed to the known furan resins based on furfuryl alcohol polycondensation products [10, 14].

The properties of coatings based on heterocyclic monomers and oligomers are presented in Table.

#### Physico-mechanical properties of coatings

Monomers	Drying time until degree 3 is reached at 423 K, min	Hardness, conventional units	Impact, kg·s/cm	Flexural resilience, mm	Content of gel-fraction, %
Catalyst $\text{Et}_3\text{PhCH}_2\text{N}\cdot\text{FeCl}_4$ (1 % of weight)					
FGPA	20.0	0.72	45	1.0	97.5
FGPL	25.0	0.65	50	1.0	96.0
Catalyst $\text{Et}_3\text{PhCH}_2\text{N}\cdot\text{ZnCl}_3\cdot\text{H}_2\text{O}$ (1 % of weight)					
FGPA	20.0	0.68	50	1.0	96.0
FGPL	25.0	0.55	50	1.0	95.0
Catalyst $\text{Ph}_4\text{P}\cdot\text{FeBr}_3\text{Cl}$ (1 % of weight)					
FGPA	20.0	0.65	50	1.0	97.0
FGPL	30.0	0.59	50	1.0	95.0
Catalyst $\text{Et}_3\text{PhCH}_2\text{N}\cdot\text{FeCl}_4$ (1 % of weight)					
monomer II	45.0	0.55	30	5.0	95.0
DA adduct oligomer* 5, 5' - DMG+2MA+ 2FGE	20.0	0.70	–	–	99.0
monomer IV	3.0	0.70	5	25.0	96.0



MA - maleic anhydride; DMG - dimetilgidantoin



## 4. Conclusions

1. We have obtained new heterocyclic monomers and oligomers based on furfurylglycidyl ether, which provides for considerable increase of the initial range of substances to be used for paint and composition materials.

2. Under the conditions of polymerizing with the complex onium catalysts, we have synthesized new network thermally resistant polymers, which can be used as chemically resistant protective coatings. New network polymers feature enhanced physico-mechanical properties as opposed to the traditional alkyd plastics.

3. We have studied the kinetics and presented the polymerization mechanism of FGE derivatives.

4. Using the physico-chemical methods and the methods of <sup>1</sup>H-NMR spectrography we have determined the scope and structure of monomers and oligomers.

5. New monomers and oligomers are ecologically safe, since no organic solvents are involved when using them as coatings.

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### НОВІ СІТЧАСТІ ПОЛІМЕРИ НА ОСНОВІ ФУРФУРИЛГЛІЦИДНОГО ЕТЕРУ

**Анотація.** Вивчено кінетичні закономірності полімеризації нових гетероциклічних мономерів і олігомерів, отриманих взаємодією фурфурілгліцидного етеру з аліфатичними монокарбонowymi кислотами (насиченими і ненасиченими). Встановлено механізм полімеризації у присутності комплексних онієвих каталізаторів. Будова і склад мономерно-олігомерних сполук встановлені хімічними і фізико-хімічними методами та <sup>1</sup>H-ПМР-спектроскопією. Кінетичні закономірності полімеризації вивчені з використанням диференційної скануючої калориметрії (DSC), термостійкість і термостабільність – методами дериватографії (DTA, TGA).

**Ключові слова:** мономер, олігомер, сітчасті полімери, фурфурілгліцидний етер, адукт Дільса-Альдера, комплексні онієві каталізатори.