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ACCELERATING EFFECT OF 3-AMINOPROPYLOLIGOMERIC SILSESQUIOXANE ON FORMATION KINETICS OF THERMOSTABLE HYBRID NANOCOMPOSITES BASED ON POLYCYANURATE NETWORK.

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In this work, reactive 3-aminopropyloligomeric silsesquioxane (AP-OSS) was synthesized and studied, and the effect of AP-OSS depending on its content (0.1–1.0 wt.%) on the kinetics of polycyclotrimerization of dicyanate ester of bisphenol E (DCBE) was determined using the dynamic DSC method. AP-OSS was prepared in high yield by the hydrolysis and polycondensation of 3-aminopropyltrimethoxysilane in a mixture of acetonitrile and ethanol, with tetrabutylammonium hydroxide (But_4NOH) as a catalyst. The chemical structure of the synthesized AP-OSS was confirmed by the results of FTIR and ^1H NMR spectroscopies, as well as by MALDI-TOF method. The FTIR spectra showed broad and intensive stretching absorption bands centered at $\nu \approx 3431$ and $\nu \approx 3378$ cm^{-1} and bending absorption bands centered at $\delta \approx 1638$ and $\delta \approx 1599$ cm^{-1} of the N–H in NH_2 groups, as well as the absorption bands centered at $\nu \approx 1027$ and $\delta \approx 859$ cm^{-1}, attributed to the special characteristic vibrations of the silsesquioxane cage Si–O–Si. MALDI-TOF spectroscopy detected predominantly singly charged protonatedions, indicating that the degree of oligomerization in this silsesquioxane is between n = 3 and 10. It was found that AP-OSS accelerated the DCBE polycyclotrimerization allowing decreasing the final temperature and time of polycyanurate network (PCN) synthesis, the higher content of the AP-OSS the higher acceleration effect has been observed. It was supposed that during the in situ synthesis of the hybrid PCN/AP-OSS nanocomposites, the amino groups on a surface of AP-OSS nanoparticles chemically interact with –O–C≡N-groups of DCBE with formation of isourea fragments providing the covalent embedding of AP-OSS into the growing PCN matrix. Using DSC method, it was found that all synthesized hybrid PCN/AP-OSS nanocomposites possessed high glass transition temperatures ($T_g > 280^oC$) and can be classified as thermally stable polymer materials.

Keywords: cyanate ester resins, oligomeric silsesquioxane, polycyanurates, synthesis kinetics, accelerating effect.

INTRODUCTION. Modern technologies require multifunctional organo-inorganic polymeric nanocomposites for high-tech applications. Special interest is given to nanocomposites based on polymer matrices possessing high thermal, chemical, and moisture resistance. Among them polycyanurate networks (PCN) synthesized from cyanate ester resins have received much attention because of their unique combination of physical properties, including high glass transition temperatures (T_g ~ 210–400 °C), high thermal stability ($T_{d5\%}$ >340 °C), low dielectric constants (ε = 2.64–3.11) low toxicity and water absorption (< 3 wt.%), high adhesion to different substrates, etc.[1-6]. As a result, PCN are currently used as heat-, chemically- and radiation resistant matrices for carbon, glass and organic plastics in structural and functional materials applicable in microelectronics, aeronautics, space structures (composite strakes, fins, nose radar domes, heat shields, antennas), printed circuit boards, as well as adhesives [3, 7]. However, like for most thermosets, their main drawback is brittleness and long high temperature curing.To overcome this limitations, modification of PCN has been developed over the last decades, and it is still of great interest. PCN are modified by synthesis of nanocomposites of PCN with montmorillonite (MMT), carbon nanotubes, nanosilica, polyhedral oligomeric silsesquioxanes (POSS) and other nanofillers.

Nowadays, POSS attract much attention as one of the most important nanostructured materials owing to its excellent properties such as mechanical strength, thermal stability, and low dielectric constant[8].

POSS represent cage structures with the formula $(RSiO_{1.5})_n$ where n = 8, 10, 12 and R is hydrogen, reactive, or non-reactive organic groups. Each silicon atom is bonded to three oxygen atoms in a cage and to a single R substituent out of cage. These substituents improve compatibility of POSS molecules with polymers or monomers. In the case of reactive R, 3-D POSS molecules with diameters of 1–2 nm may graft chemically to polymer structures. New hybrid organic–inorganic PCN-based thermosets with hydroxy- [9–12], amino- [6, 13–15] or epoxy-functionalized [16–21] POSS units have thus been obtained with improved thermal and mechanical properties.

In the last decade, Zhang and co-authors [11] investigated the effect of amino-POSS with eight primary amino groups on the curing behavior of dicyanate ester of bisphenol A (DCBA) with PCN formation.They concluded that both temperature and POSS content influence on the curing reaction of DCBA. Authors noted that amino-POSS displayed the catalytic effect mainly at high temperature and the peculiarities were more complex at lower temperature. The incorporation of amino-POSS into PCN matrix led to the improvement in thermal stability and hot/wet resistance. Nanocomposite sample containing 1 wt.% of amino-POSS showed the best dielectric properties: the lowest dielectric constant and the lowest dielectric loss.

In previous work [6] we studied the effect of amino-POSS on structure-property relationships of thermostable hybrid cyanate ester resin based nanocomposites. We discovered that the addition of a small quantity (0.1 wt.%) of three different reactive amino-POSS chemically grafted to the PCN network led to increasing thermal stability of PCN matrix by 12–15 °C, depending on the type of amino-POSS. A significant increase of the glass transition temperature, T_g (DSC data), and the temperature

of α relaxation, T_α (DMTA data), by 45–55 °C of PCN matrix with loading of the nanofillers was evidenced. PCN/POSS films exhibited a higher storage modulus than that of neat PCN in the temperature range investigated. It was evidenced that PCN/aminopropylisobutyl (APIB)-POSS, PCN/*N*-phenylaminopropyl (*N*PAP)-POSS, and PCN/aminoethylaminopropylisobutyl (AEAPIB)-POSS nanocomposites demonstrated a more homogenous α relaxation phenomenon with higher T_α values and an enhanced elastic behavior. The value of storage modulus, E', at 25 °C increased from 2.72 GPa for pure PCN matrix to 2.99–3.24 GPa for the nanocomposites with amino-POSS nanoparticles.

Recently, some authors investigated[22] the kinetic regularities of forming thermostable polycyanurate networks (PCN) from dicyanate ester of bisphenol E (DCBE) with reactive APIB-POSS. They found that even 0.1 wt.% of APIB-POSS catalyzed high-temperature polycyclotrimerization of DCBE, enabling polymerization at lower temperatures and within a narrower time frame, resulting in a PCN/APIB-POSS nanocomposite with a higher T_g value. Notably, small amounts of APIB-POSS did not introduced effects into the PCN matrix. Additionally, the catalytic effect of *N*PAP-POSS, containing eight reactive secondary amino groups, was examined[23] in synthesizing hybrid nanocomposites based on PCN from DCBE. FTIR and DSC analyses revealed a reduced on set time for auto-acceleration, accelerated conversion of cyanate groups, increased maximum reaction rates, and decreased polycyclotrimerization duration. Dynamic DSC measurements confirmed *N*PAP-POSS's catalytic impact, showing significant changes in exothermic maximum temperature, increased reaction enthalpy, and non-monotonic variation in induction period and reaction rate based on nanofiller content.

Oligoaminopropylsilsesquioxanes (OSS) are very promising reactive compounds, which can be used as initial components for synthesis of different polymer materials, oligo- or polysiloxanes, as effective modifiers, or as hardeners for thermosetting resins, for preparing nanocomposites via reactive amino groups [24–26]. For the best of our knowledge, no papers were published on PCN/OSS synthesis and characterization.

Therefore, the aim of the present work is to investigate the influence of reactive 3-aminopropyl oligomeric silsesquioxane (AP-OSS) on the kinetics of *in situ* synthesis of thermostable hybrid organic-inorganic nanocomposites based on PCN and thermophysical properties of the nanocomposites obtained depending on the content of the nanofiller used.

EXPERIMENT AND DISCUSSIONS OF THE RESULTS. The cyanate ester monomer used in this work was1,1-bis(4-cyanatophenyl) ethane (DCBE, Primaset LECy from Lonza, Switzerland). The nanosized reactive organically functionalized OSS, aminopropyl oligomeric silsesquioxane (AP-OSS) was synthesized by the hydrolysis and polycondensation of trifunctional monomer 3-aminopropyltrimethoxysilane (see below for thefurther details). 3-Aminopropyltrimethoxysilane (APTMS), ethanol, acetonitrile and tetrabutylammonium hydroxide were purchased from Sigma-Aldrich and used as received.

AP-OSS was prepared following the method described in the literature [24](with some modifications). 7 mL of distilled water, 4 mL

of anhydrous ethanol, 1 mL of acetonitrile, and 0,7 mL of tetrabutylammonium hydroxide (10% aqueous solution) were put into a three-neck flask equipped with a mechanical stirrer and a condenser, and mixed by stirring (1100 rpm). 3-aminopropyltrimethoxysilane (17.9 g) was added dropwise into the mixture for 10 min at vigorous stirring (800 rpm). The reaction was conducted at 50 °C for 24 h. A straw gelatinous product was yielded during the reaction. The product was washed with acetonitrile for three times, and finally, it was dried under reduced pressure at 70 °C for 24 h. A white crystalline product was obtained (the yield was 94%).

Different content of the nanofiller obtained, i.e. AP-OSS (0, 0.1, 0.5 and 1 wt %) was added to the liquid DCBE (~200 mg) and thoroughly grinded in an agate mortar for ~10 min at the ambient temperature until a transparent, i.e. homogenous, mixture was formed. Then the resulting mixture (~10 mg) was placed in a hermetic aluminium pan for dynamic curing during DSC measurements.

^{1}H-NMR spectra were performed using Varian VNMRS spectrometer (Agilent Inc., USA) at 400 MH zat temperature of about 20°C. The spectra were recorded in deuterated DMSO.

FTIR spectra were recorded using a Tensor 37 spectrometer (Bruker Daltonics Inc., Germany) at room temperature in the range of 4000–600 cm^{-1}. The sample was pressed into pellets with KBr.

Matrix-assisted UV-MALDI-TOF mass spectroscopy was performed using an Autoflex II (Bruker Daltonics Inc., Germany) equipped with a pulsed nitrogen laser (λ = 337 nm). The selected matrix was 2,5-dihydroxybenzoic acid. Sample was irradiated just above the threshold laser power to obtain molecular ions.

Differential scanning calorimetry (DSC) with Discovery DSC 25 Differential Scanning Calorimeter (TA Instruments, USA) was used to estimate the effect of the nanofiller on the kinetic characteristics of polycyclotrimerization of DCBE, *i.e.* the duration of induction period (τ_i) and total reaction time (τ_{tot}), the maximal rate of reaction (W_{max}), temperature of exothermic peaks ($T_{p(max)}$), total enthalpy of reaction (ΔH_{tot}), conversion of cyanate groups (α) *etc*. For nanocomposites synthesized the glass transition temperature, T_g, heat capacity jump, ΔC_p, and other thermophysical characteristics were found. The first and second scan with the heating rate of 5 and 20 °C/min, respectively, over the temperature range from 25 to 350 °C in nitrogen atmosphere were performed.

Fig.1 represents the FTIR spectrum of AP-OSS synthesized. The wide and intensive peaks at 3431 and 3378 $cm^{-1}$are attributed to the stretching vibrationand at 1638 and 1599 cm^{-1} to bending vibrationof N–H in NH_2 groups. There is also some weak shoulder at 3308 cm^{-1} that belongs to O–H stretching of the OH groups.The strong double peak at 2929 and 2866 cm^{-1} corresponds to the C–H stretching of the CH_2 groups in the aminopropyl fragment. The absorption band at 1122 cm^{-1} is the characteristic vibration of Si–O–Si bond. The absorption peaks at 1027 and 859 cm^{-1} are attributed to the special characteristic vibration of silsesquioxane cage Si–O–Si framework. The peak at 757 cm^{-1} relates to the bending vibration of Si–C bond in Si–CH_2. So, the FTIR spectrum of the product synthesized gives good assignment to the structure of AP-OSS [24].

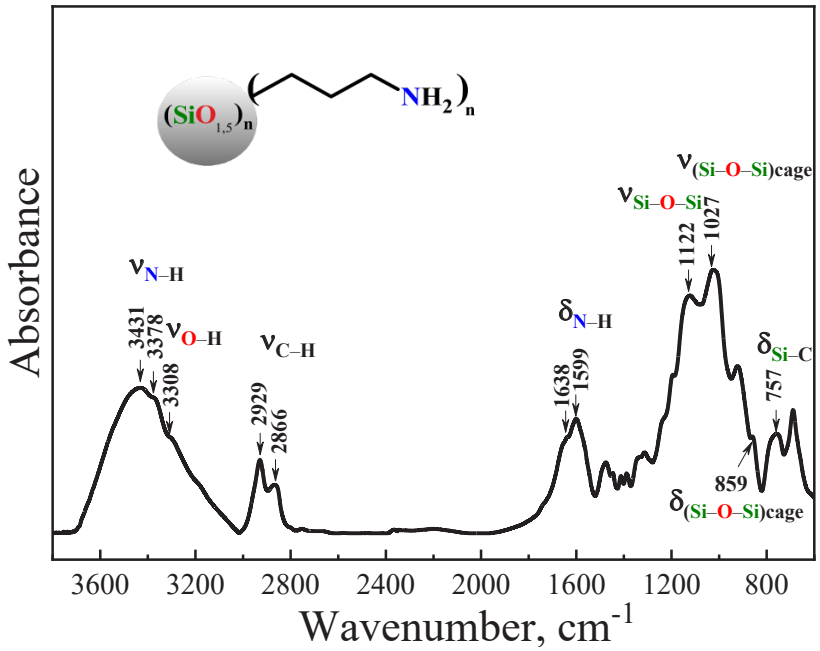

Fig.1. FTIR spectra of AP-OSS.

Fig.1 shows the ^{1}H NMR spectrum of AP-OSS in DMSO-d_6. Four peaks with chemical shifts of 0.56 ppm (CH_2 in the α position to the silicon atom *(a)*),1.43 ppm (CH_2 in the β position to the silicon atom (*b*), 2.67 ppm (CH_2 in the α position to the primary amino group *(c)*) and 3.26 ppm (OH-group *(d)*), appear in the spectrum [27]. Each of them is assigned to one type of the hydrogen atoms of the same chemical environment, further supporting the structure of AP-OSS prepared.

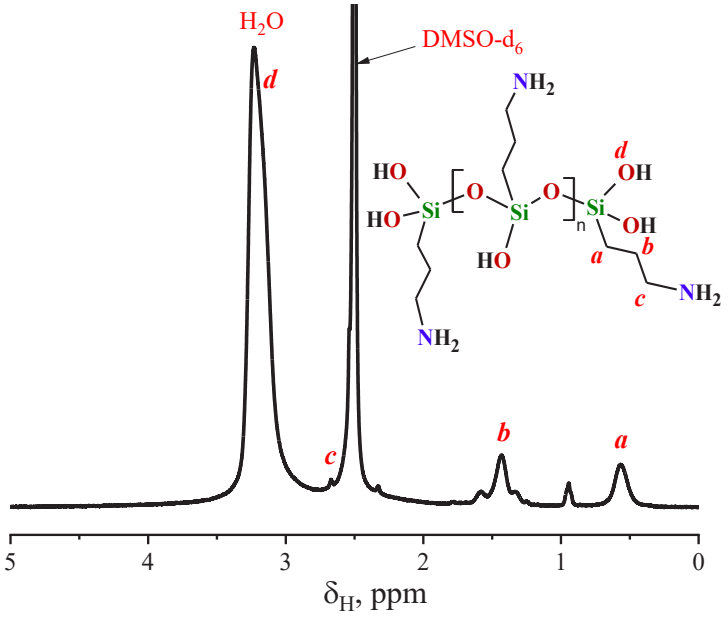

Fig. 2. ^{1}H NMR spectra of AP-OSS (DMSO-d_6).

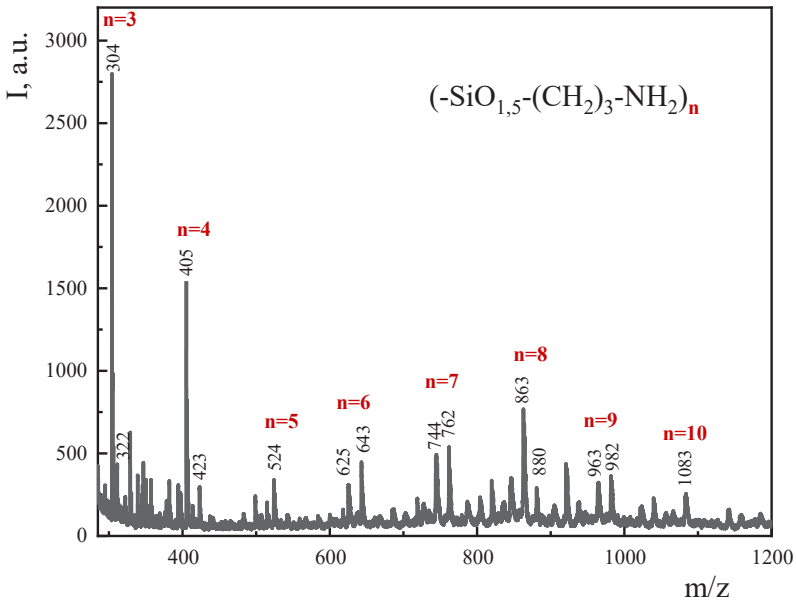

Fig. 3. Mass spectrum of the synthesized AP-OSS.

The analysis of the MALDI-TOF mass spectrum (Fig.3) of the synthesized AP-OSS shows the predominantly singly charged protonated ions, indicating that the degree of oligomerization within this silsesquioxane ranges from n = 3 to 10. It can be seen that the m/z signal peaks of AP-OSS are distributed between 300 and 1200, and the signal peaks with different m/z values correspond to AP-OSS with different numbers of Si atoms, means to the atomic fragments of the condensate $(SiO_{1.5}\text{-}(CH_2)_3\text{-}NH_2)_n$ with $m/z = (110\ D)_n$ at different values of the n index, as well as their products of altered composition due to incomplete synthesis reaction or destruction under the laser excitation. The spectrum shows the difference in the atomic composition of the synthesized fragments with even and odd n index. Thus, AP-OSS complexes with odd indices 7 and 9 include an atomic fragment with a lower oxygen content SiO – $((CH_2)_3\text{-}NH_2)$ with m/z 102 D. The presence of fragments with different oxygen content in the condensate structure leads to reduction in the atomic weight of the condensate and a shift of its mass line by m/z = 8 D.

Besides, there is AP-OSS structure with n = 9 and m/z 990 D, built only by complexes with m/z = 110 D, where the atomic group with m/z 27 D (NCH or CH_2CH) is absent. The complexes with even values of n = 6, 8 and 10 have the incomplete content due to vacancies of atomic groups with m/z = 17 (OH) and 26 D (NC or HCCH) in the AP-OSS space structures with n = 9 and m/z 990 D, built only by $(SiO_{1.5}\text{-}(CH_2)_3\text{-}NH_2)$ fragments.

Note, that the condensate with n = 8 is completely formed by eight fragments of $(SiO_{1.5}\text{-}(CH_2)_3\text{-}NH_2)$ is detected. However, at lower index values, when n = 5, line m/z 524, the AP-OSS condensate is formed by five fragments with m/z 110 D without the NC or CHCH (m/z 26) atomic groups. The line with m/z 423 and n = 4 indicates the formation of an AP-OSS complex built by four fragments $(SiO_{1.5}\text{-}(CH_2)_3\text{-}NH_2)$ without one hydroxyl group.

Thus, as a result of the synthesis, an AP-OSS condensate was obtained, whose

the spatial structure is built by complexes ($SiO_{1.5}$-$(CH_2)_3$-NH_2), which include fragments of SiO - (($(CH_2)_3$-NH_2)) with a lower oxygen content and is characterized by the presence of vacancy clusters related with atomic groups OH, NC, CHCH, NCH, H_2CCH.

Tab. 1 gives the approximate structures of AP-OSS corresponding to different *m/z* calculated values. It can be seen that the *m/z* value of 880 represents the completely condensed cage T_8 structures; the *m/z* values of 763 and 863 represent the incompletely condensed polygonal cage T_7 and T_8 structures containing Si–OH.In the incomplete condensation structure, it is noted that the actual molecular mass of some structures is inconsistent with the *m/z* value. For example, in the T_9 structure, the calculated molecular weight is 999, but there is a signal peak with *m/z* value of 982 [28]. The difference between the *m/z* value of 982 and the calculated molecular weight of 999 is 17, which is exactly the mass number of 1 OH-group.Similarly, in the T_8 structure, the calculated molecular weight of the incomplete condensation structure with Si–OH is 898, and the actual *m/z* value is 863. The difference between the *m/z* value and the calculated molecular weight is 34, which is the mass number of 2 OH-groups.The reason for this phenomenon may be that a part of the incompletely condensed AP-OSS dropped OH-groups during the detection process [28].

Table 1.

Structures of AP-OSS.

m/z	Molecular structure	Molecular weight	Type
304	$Si_3O_3(C_3H_6NH_2)_3(OH)_3$ -3OH	357	T_3
322	$Si_3O_3(C_3H_6NH_2)_3(OH)_3$ -2OH	357	T_3
423	$Si_4O_5(C_3H_6NH_2)_4(OH)_2$-2OH	458	T_4
643	$Si_6O_7(C_3H_6NH_2)_6(OH)_4$ -3OH	697	T_6
744	$Si_7O_9(C_3H_6NH_2)_7(OH)_3$-3OH	797	T_7
762	$Si_7O_9(C_3H_6NH_2)_7(OH)_3$-2OH	797	T_7
863	$Si_8O_{10}(C_3H_6NH_2)_8(OH)_2$-2OH	898	T_8
880	$Si_8O_{12}(C_3H_6NH_2)_8$	880	T_8
982	$Si_9O_{13}(C_3H_6NH_2)_9(OH)_1$-1OH	999	T_9

Possible parallel and sequential chemical reactions, which can occur during the synthesis of AP-OSS are presented in Fig. 4. They include hydrolysis, alcohol condensation, water condensation of APTMS [24] followed by hydrolysis, polymerization, intramolecular condensation of the intermediate products obtained with formation of fully condensed POSS or silene structures (in the Fig. 5, as example, the structures with *n*=4 are shown). The formation of a fully condensed polyhedral silsesquioxane is favored in-solution as it is catalyzed by the acidic environment.On the other hand, the formation in solution of Si=C bonds in silenes is less possible [29].

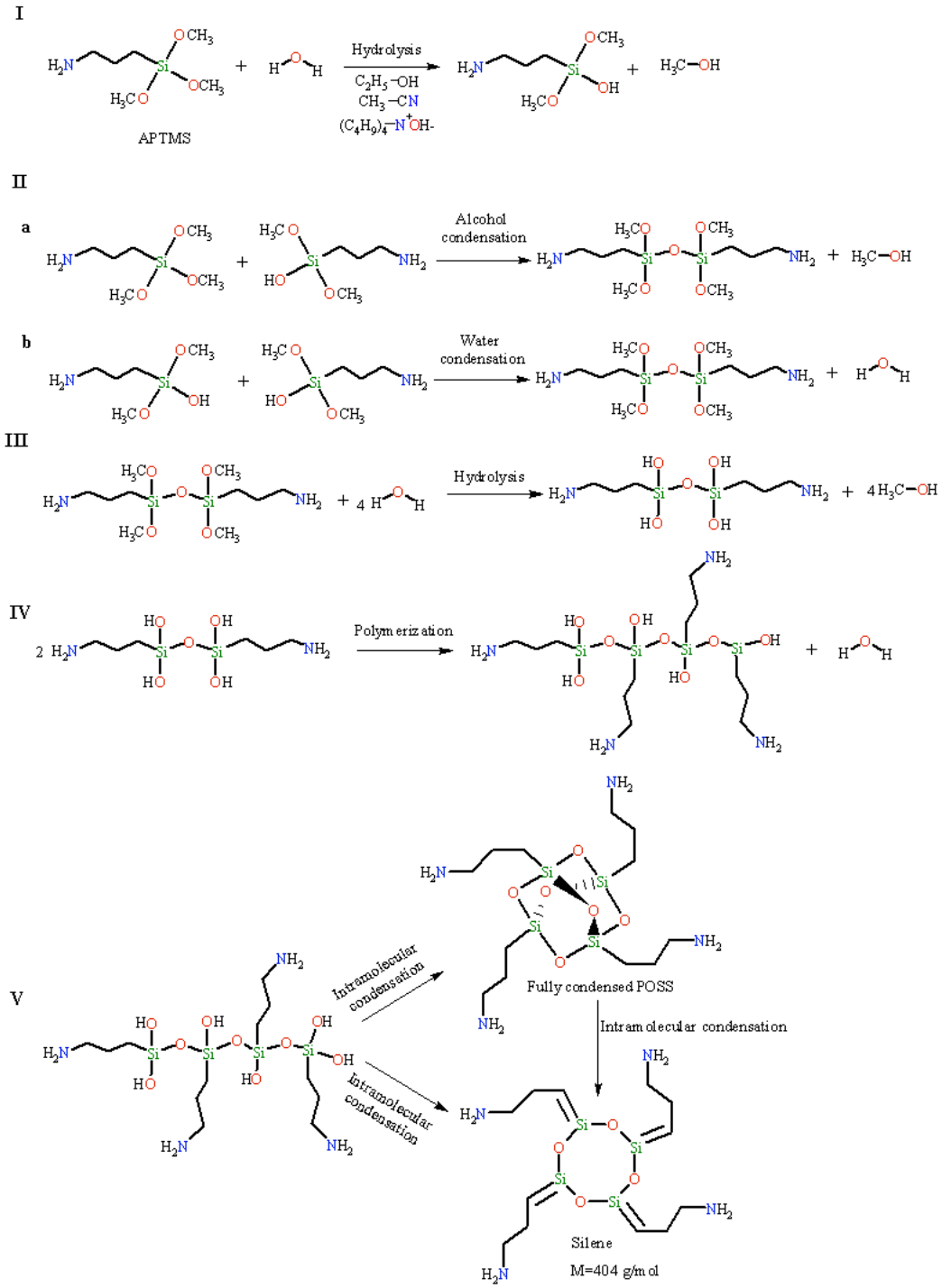

Fig. 4. Possible reactions, which occur during synthesis of AP-OSS (n=4) from APTMS with formation of a fully condensed POSS or silene by intramolecular condensation [24, 29].

The acceleration effect of the AP-OSS on polycyclotrimerization of DCBE[1, 2] was observed at DSC investigation. Fig. 5 shows the DSC thermograms of polycyclotrimerization and the time dependence of the conversion of cyanate groups for the individual DCBE and DCBE/AP-OSS compositions with different AP-OSS content. The main kinetic characteristics are provided in Tab. 2.

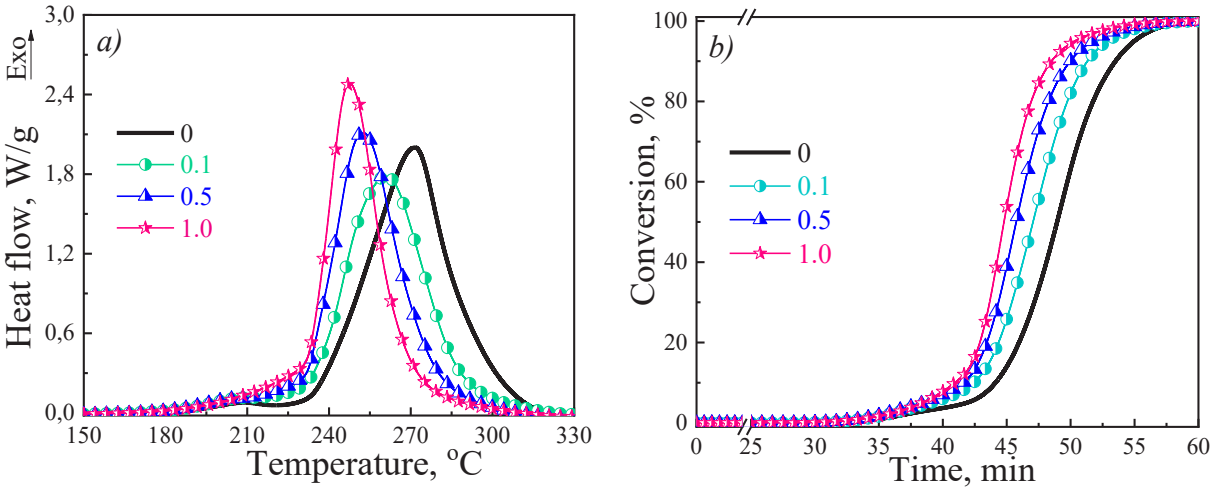

Fig. 5. DSC kinetic profiles (*a*) and time dependencies of conversion (*b*) for the individual DCBE and DCBE/AP-OSS compositions (AP-OSS content is indicated in the plot).

It is clear from the data provided in Tab.2 that the incorporation and increase of the AP-OSS content significantly change the kinetic characteristics of DCBE polycyclotrimerization.This is confirmed by the fact that τ_i and τ_{end} decrease by ~6,5 % and 2–5 %, respectively, $T_{p(max)}$ reduces by 11–24 °C, W_{max} increases by 0,4–6,1 %/min, the ΔH_f value for synthesis of PCN/AP-OSS networks decreases as well compared to pure PCN. As far as primary amino groups exhibit high reactivity towards cyanate groups [30, 31], it is expected that the amino groups on a surface of AP-OSS nanoparticles chemically interact with the –O–C≡N groups of the DCBE molecules during the *in situ* synthesis of the nanocomposite samples. This process results in the covalent embedding of AP-OSS into the forming PCN matrix. The chemistry of the embedding process is schematically shown in Fig.6. Isourea fragments formed are supposed to be a good catalyst for polycyclotrimerization of cyanate ester resins [30].

In addition, the processes of incorporation and conversion occur with the heat release and they are the first kind of phase transition. The thermal effect of the transition is characterized by a non-monotonic dependence of its intensity on the AP-OSS content Fig. 5*a*), whereas the embedding rate of AP-OSS complexes and formation of hybrid composites smoothly increases with growing AP-OSS content. The behavior of thermodynamic parameters indicates that the conversion process has an island character. At a low AP-OSS content, the

formation of the hybrid PCN/AP-OSS network realizes in the vicinities of localization of separated complexes AP-OSS, while with rise of their content the hydride conversion occurs in the entire reaction volume and its speed increases with the value of released heat.

Table 2.

Kinetic parameters of DCBE, DCBE/AP-OSS polymerization and thermal characteristics of synthesized PCN/AP-OSS nanocomposites.

Characteristics	AP-OSS content, wt.%			
Reactive DCBE/AP-OSSblends	0	0.1	0.5	1.0
Induction period, τ_i, min	30.7	28.8	28.4	28.5
Reaction end time, τ_{end}, min	59.0	57.8	56.6	56.0
Maximum reaction rate, W_{max}, %/min	12.3	12.7	14.5	18.4
Time to reach W_{max}, τ_{max}, min	49.4	47.3	45.5	44.5
Total time of reaction, τ_{tot}, min	28	29	28	28
Temperature at W_{max}, $T_{p(max)}$, °C	272	261	253	248
Conversion of cyanate groups at W_{max}, α, %	56.2	53.1	47.3	45.3
Total enthalpy of reaction, ΔH_{tot}, J/g	984	842	873	818
PCN/AP-OSS nanocomposites				
T_g, °C	285,6	286,6	282,6	281,8
$T_{g(onset)}/T_{g(end)}$, °C/°C	278/293	279/294	276/290	274/289
ΔT_g, °C	15	15	14	15
ΔC_p, J/g·°C	0.245	0.227	0.240	0.156

Using DSC method (Fig.7) it was found out that, as for the individual PCN, high values of T_g are observed for the synthesized PCN/AP-OSS nanocomposites (Tab.2). However, with an increase in the AP-OSS content by 10 times (from 0.1 wt.% to 1.0 wt.%), the T_g value slightly decreases from T_g = 286.6°C to T_g = 281.8°C, respectively. One can suppose that the nanoparticles of AP-OSS embedded into the PCN network structure play the role of the additional inorganic network junctions. This phenomenon should limit the relaxation of the kinetic segments of the polymer chains in the hybrid PCN/AP-OSS network that leads to increasing T_g value and decreasing the ΔC_p. However, at the same time, the presence of a significant number of flexible linear organic fragments out of cage of AP-OSS nanoparticles can facilitate the relaxation of the kinetic segments of the hybrid network formed and lead to a decreasing T_g value. The total effect of these two competitive processes provides the close values of T_g for individual PCN and PCN/AP-OSS nanocomposites. It is worth noting that for the

sample with the highest content of nanofiller (1.0 wt.%), a significant decrease (~1.6 times) of the ΔC_p value is observed compared to the unfilled PCN matrix. It is known that this is a manifestation of an increase in the density of network junctions for crosslinked polymers [32]. It can be concluded that the PCN/AP-OSS nanocomposite sample with 1.0 wt.% of AP-OSS demonstrates the highest crosslinked density.

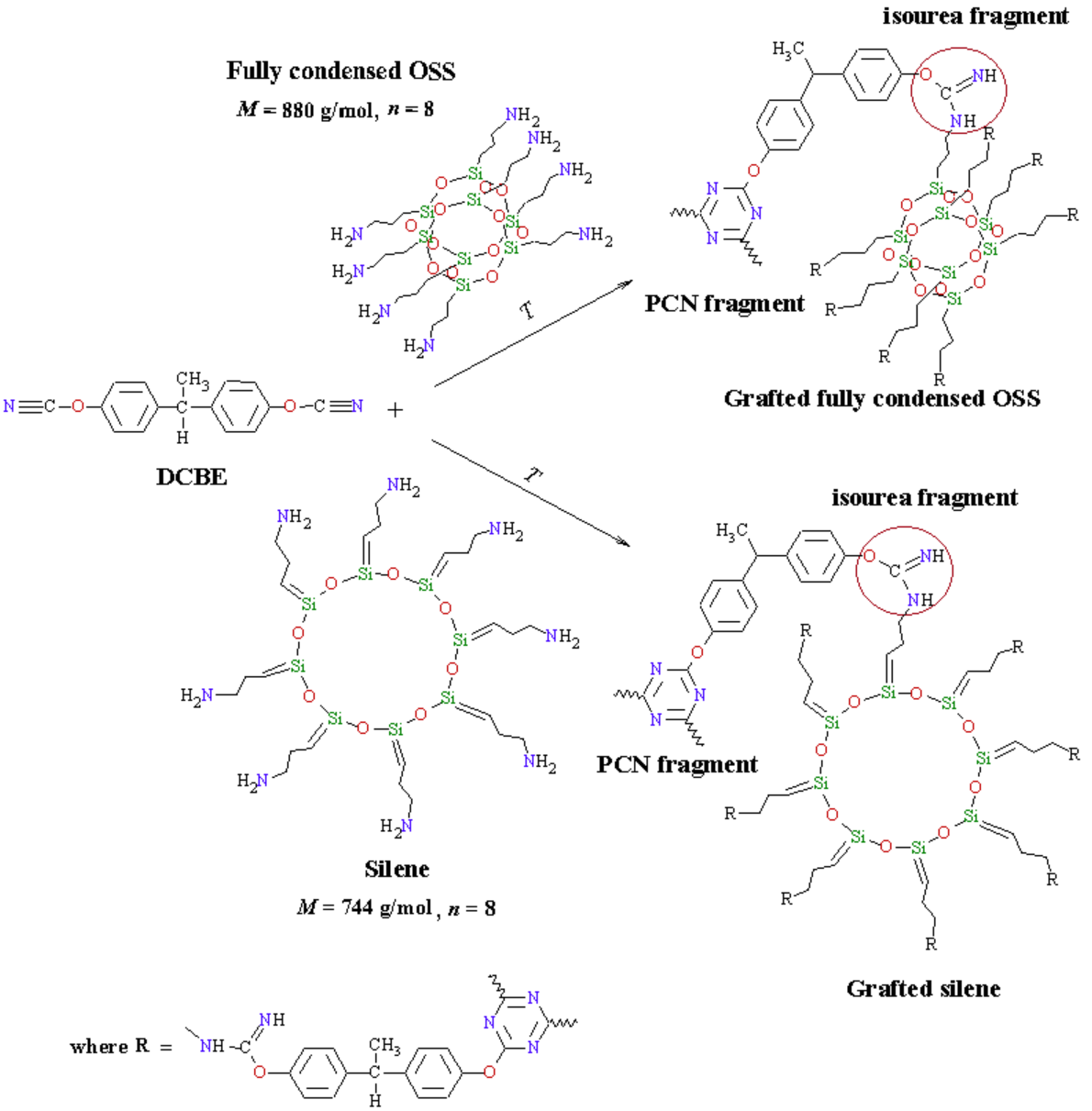

Fig. 6. Schematic presentation of the initial stage of chemical incorporation of AP-OSS particles into the growing PCN network (example for n = 8).

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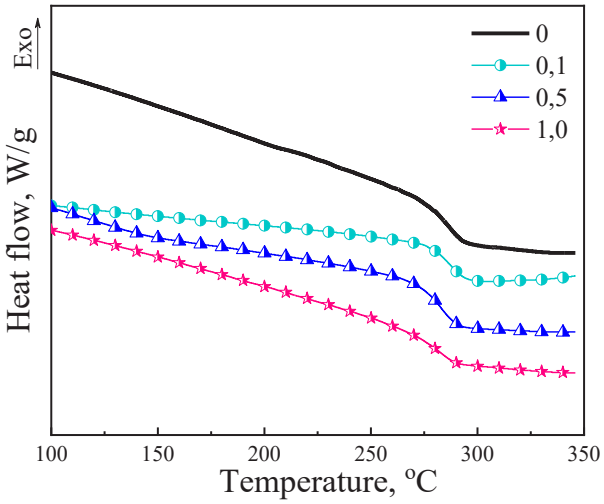

Fig. 7. DSC thermograms (2nd scan) for the neat PCN and PCN/AP-OSS nanocomposites formed.

CONCLUSIONS. In this work, the reactive amino-functionalized AP-OSS has been synthesized and characterized, the effect of the AP-OSS content (0.1–1.0 wt.%) on the kinetics of polycyclotrimerization of DCBE was studied by using dynamic DSC method. AP-OSS was prepared in high yield by hydrolysis and polycondensation of $H_2NCH_2CH_2CH_2Si(OCH_3)_3$ monomer in the mixture of acetonitrile and ethanol, with tetrabutyl ammonium hydroxide (But_4NOH) as the catalyst.The chemical structure of the synthesized AP-OSS was confirmed by the results of FTIR and ^1H NMR spectroscopy, as well as by MALDI-TOF methods. The predominantly singly charged protonated ions, indicating that the degree of oligomerization within this silsesquioxane ranges from n = 3 to 10 were found by MALDI-TOF method. It was found that AP-OSS accelerated the polycyclotrimerization of DCBE allowing decreasing the final temperature and time of PCN network synthesis, the higher content of the AP-OSS the higher acceleration effect has been observed. As far as during the *in situ* synthesis of the PCN/AP-OSS nanocomposites, the amino groups on a surface of AP-OSS nanoparticles can chemically interact with –O–C≡N-groups of DCBE with formation of isourea fragments, the covalent embedding of AP-OSS into the growing PCN matrix with formation of the hybrid PCN/AP-OSS network occurs. It was found also that all synthesized PCN/AP-OSS nanocomposites have high T_g values (T_g > 280 °C) similar to individual PCN. A slight decrease in T_g (from 286.6 °C to 281.8 °C, respectively) and ΔC_p (by 1.6 times compared to PCN) at increasing amount of the AP-OSS used was observed. It was explained by the competition of two factors: 1) the presence of a number of flexible linear fragments of AP-OSS in the hybrid crosslinked matrix promotes the relaxation of the kinetic segments of the hybrid network and leads to a decrease in the T_g value; 2) incorporation into the PCN network of the inorganic nanoparticles, which act as the additional network junctions increases a crosslink density of the network hindering relaxation and increasing T_g value of the hybrid network. The synthesized and investigated PCN/AP-OSS nanocomposites belong to the class of high-performance thermostable polymer materials with controlled structure and properties suitable for application in extreme conditions.

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КАТАЛІТИЧНИЙ ВПЛИВ 3-АМІНОПРОПІЛОЛІГОМЕРНОГО СИЛСЕСКВІОКСАНУ НА КІНЕТИКУ ФОРМУВАННЯ ТЕРМОСТІЙКИХ ГІБРИДНИХ НАНОКОМПОЗИТІВ НА ОСНОВІ ПОЛІЦІАНУРАТНОЇ СІТКИ

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У цій роботі було синтезовано і досліджено реакційно здатний 3-амінопропілолігомерний силсесквіоксан (AP-OSS) та визначено вплив AP-OSS залежно від його вмісту (0,1–1,0 мас.%) на кінетику поліциклотримеризації диціанового естеру бісфенолу Е (ДЦБЕ) з використанням методу динамічної ДСК. AP-OSS був отриманий шляхом гідролізу та поліконденсації 3-амінопропілтриметоксисилану з суміші ацетонітрилу та етанолу, з гідроксидом тетрабутиламонію (But_4NOH) як каталізатором. Хімічну структуру синтезованого AP-OSS було підтверджено результатами ФТІЧ та ^{1}H ЯМР-спектроскопії, а також методом MALDI-TOF. На ФТІЧ-спектрах виявлено широкі та інтенсивні смуги поглинань валентних коливань із максимумами за ν≈3431 см$^{-1}$і ν≈3378 см$^{-1}$ та смуги поглинань деформаційних коливань із максимумами заδ≈1638 см$^{-1}$ та δ≈1599 см$^{-1}$ зв'язку N–H у групах NH_2, а також смуги поглинань за ν≈1027 та δ≈859 см$^{-1}$, які відносять до характерних вібрацій сил сесквіоксанового ядра Si–O–Si. Методом MALDI-TOF було виявлено переважно однозарядні протоновані іони, що вказує на те, що ступінь олігомеризації в цьому силсесквіоксані коливається від n = 3 до 10. Було виявлено, що AP-OSS прискорює поліциклотримеризацію ДЦБЕ, що зумовлює зменшення кінцевої температури та часу синтезу поліціануратної сітки (ПЦС), при цьому що вищий вміст AP-OSS, то вищий ефект прискорення реакції. Вважаємо, що під час *in situ* синтезу гібридних ПЦС/AP-OSS нанокомпозитів аміногрупи на поверхні наночастинок AP-OSS хімічно взаємодіють з ціанатними групами ДЦБЕ з утворенням фрагментів ізосечовини, що забезпечує ковалентне вбудовування AP-OSS у ПЦС-матрицю, що формується. Методом ДСК встановлено, що всі синтезовані гібридні ПЦС/AP-OSS-нанокомпозити мають високі температури склування ($T_{ск}$> 280°C), що дозволяє їх класифікувати як термостійкі полімерні матеріали.

Ключові слова: ціанатестерні смоли, олігомерний силсесквіоксан, поліціанурат, кінетика синтезу, ефект прискорення.

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