

Contents lists available at ScienceDirect

**Reactive and Functional Polymers** 



journal homepage: www.elsevier.com/locate/react

**Perspective Article** 

# Polymerization kinetics of adamantane-based dicyanate ester and thermal properties of resulting polymer

Andrey Galukhin<sup>a,\*</sup>, Roman Nosov<sup>a</sup>, Guzel Taimova<sup>a</sup>, Ilya Nikolaev<sup>a</sup>, Daut Islamov<sup>b</sup>, Sergey Vyazovkin<sup>a,c,\*\*</sup>

<sup>a</sup> Alexander Butlerov Institute of Chemistry, Kazan Federal University, 18 Kremlevskaya Street, 420008 Kazan, Russian Federation

<sup>b</sup> Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center, Russian Academy of Sciences, 8 Arbuzov street, Kazan 420088, Russian Federation

<sup>c</sup> Department of Chemistry, University of Alabama at Birmingham, 901 S. 14<sup>th</sup> Street, Birmingham, AL 35294, USA

#### ABSTRACT

The kinetics of liquid-state polymerization of adamantane-based dicyanate ester has been studied for the first time by means of conventional and temperaturemodulated DSC. It has been detected that the later stages of polymerization undergo a transition from kinetic- to diffusion-controlled regime. Detailed analysis of the polymerization kinetics in the reaction-controlled regime has revealed that the process rate can be well described in the frameworks of the presently proposed autocatalytic quasi-one-step model. The proposed model eliminates arbitrarily guessing the value for the initial conversion that provides a reasonable alternative to the broadly used truncated Sestak-Berggren model. The adamantane-based dicyanate ester polymerization product demonstrates markedly higher thermal stability and glass transition temperature compared to those of dicyanate esters with flexible hydrocarbon bridging units. The obtained experimental results confirm our hypothesis about the influence of the rigidity of cyanate ester molecule on its reactivity and thermal properties of the corresponding polymer product.

### 1. Introduction

High-performance thermosets based on cyanate resins play an important role in the electronic, military, and aerospace industries because the resulting materials possess unique mechanical, thermal, and dielectric properties [1–4]. Their irreplaceable practical utility promotes fundamental studies of intrinsic relationships between the structure of cyanate esters and their reactivity, as well as properties of the final polymeric materials. Such studies are essential for directed design of thermosets with desired properties [3,5–7]. The thermal stability and glass transition temperature are the most important thermal properties that determine possible areas and conditions of the application of thermosets.

The influence of the polymer structure on the thermal properties of polymers is generally well studied. It is known that introduction of rigid fragments into the main polymer chain increases both thermal stability and glass transition temperature ( $T_g$ ) of the corresponding polymers [8]. The presence of polar side groups or groups capable of forming hydrogen bonds tends to decrease the segmental mobility of polymer chains and thus results in higher glass transition temperatures of the corresponding polymers [9–12]. The effect of aforementioned groups on thermal stability of polymers is more complex and depends on particular nature of

the group and may either increase or diminish thermal stability [13,14]. The introduction of adamantane groups into polymer structure is of special interest because of their rigidity and high thermodynamic stability. Being introduced into the main chain or as side group, adamantane increases thermal stability of the polymeric material [15,16].

Finding general relationships between the structure of a monomer and its reactivity is a difficult task because of numerous possible mechanisms of polymerization process (cationic, anionic, radical, coordination, etc). For example, electron-withdrawing groups accelerate anionic-polymerization of vinyl monomers, but inhibit its cationic polymerization [17,18]. Also, the process may switch from a kinetic- to diffusion-controlled regime during the polymerization progress that further complicates the task. However, since this switch is usually observed near the glass transition temperature of the reaction mixture one can expect that the structural factors decreasing the segmental mobility (i.e., those increasing T<sub>g</sub>) should promote an earlier transition of the reaction kinetics to diffusion-controlled regime during polymerization. This idea is illustrated schematically in Fig. 1, where two monomers of similar reactivity (similar α-T curves), but with markedly different Tg's (both for monomers and polymers) have significantly different points of intersection of the corresponding  $\alpha$ -T and  $T_{g}$ - $\alpha$  curves. It is seen that polymerization of a monomer that gives rise to a polymer

\* Corresponding author.

https://doi.org/10.1016/j.reactfunctpolym.2021.104956

Received 27 February 2021; Received in revised form 11 May 2021; Accepted 2 June 2021 Available online 10 June 2021 1381-5148/© 2021 Elsevier B.V. All rights reserved.

<sup>\*\*</sup> Corresponding author at: Department of Chemistry, University of Alabama at Birmingham, 901 S. 14<sup>th</sup> Street, Birmingham, AL 35294, USA. *E-mail addresses:* and galuhin@mail.ru (A. Galukhin), vyazovkin@uab.edu (S. Vyazovkin).



**Fig. 1.** Schematic illustration of the effect of the polymer  $T_g$  value on the reactivity of a monomer. Dashed lines represent variation of  $T_g$  with conversion ( $\alpha$ ), solid lines represent  $\alpha$ -*T* plots obtained at the heating rate  $\beta$ . Circles show intersection points of the corresponding  $\alpha$ -*T* and  $T_{g}$ - $\alpha$  curves.

having higher  $T_g$  is more likely to encounter vitrification at earlier stages of the reaction progress.

In all, we hypothesize that incorporation of adamantane into the structure of cyanate resin as a rigid bridging fragment should increase the glass transition temperature and thermal stability of the resulting polymer. Also we expect that the reactivity of the monomer should be affected by vitrification as described above. To explore this hypothesis we have synthesized adamantane-based dicyanate ester, which is subjected to thermal polymerization. We have studied the obtained monomer reactivity by both conventional and temperature-modulated DSC under nonisothermal conditions and parameterized its polymerization kinetics with the aid of isoconversional methodology [19]. We have also applied thermogravimetry to test the thermal stability of the polymerization product and compared it with that of the polymers produced from commercially available dicyanate esters of similar structure. It should be noted that although adamantane-based cyanate esters are known since the middle of the last decade [20,21] the kinetics of their polymerization has never been studied before.

## 2. Experimental section

#### 2.1. Materials

Iron powder ( $\geq$ 99%, Sigma-Aldrich), bromine (99.6%, Acros Organics), adamantane (>99%, Sigma-Aldrich), triethylamine (>99%, Sigma-Aldrich), cyanogen bromide (97%, Acros Organics), phenol (99.5%, Acros Organics), ethanol (95%, RFK), trichloromethane (>99.5%, EKOS-1), dichloromethane (>99.5%, EKOS-1), hexane

(>99.5%, EKOS-1), hydrochloric acid (>35%, Component-Reagent), Na<sub>2</sub>SO<sub>3</sub> (anhydrous, > 99%, Chimmed), Na<sub>2</sub>SO<sub>4</sub> (anhydrous, > 99.5%, Chimmed), SiO<sub>2</sub> (60 Å, 0.04–0.063 mm, Machery-Nagel), P<sub>2</sub>O<sub>5</sub> (>98%, Vekton), and isopropanol (99.8%, REACHEM) were purchased and used as received. Acetone (>98%, TatChemProduct) was purchased and additionally distilled over P<sub>2</sub>O<sub>5</sub>.

Target dicyanate ester **4** was obtained according to the synthetic procedure presented in Fig. 2.

1,3-dibromoadamantane **2** and 1,3-bis(4-hydroxyphenyl)adamantane **3** were synthesized according to known synthetic protocols [22,23].

Synthesis of 1,3-bis(4-cyanatophenyl)adamantane 4. 1,3-bis(4hydroxyphenyl)adamantane 3 (2.0 g, 6 mmol), cyanogen bromide (2.7 g, 25 mmol), and 30 mL of acetone were added to a round bottom flask with a magnetic stirrer. The reaction mixture was cooled to  $-20^{\circ}$ C, and then triethylamine (3.5 mL, 25 mmol) was added dropwise. The synthesis was carried out for an hour under continuous stirring and cooling. Then solvent was removed from reaction mixture under reduced pressure and obtained residue was dissolved in dichloromethane and washed several times with deionized water. Obtained organic solution was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and target compound was separated by column chromatography (dichloromethane as an eluent). The resulting product 4 was purified by recrystallization from the mixture of CH<sub>2</sub>Cl<sub>2</sub> and hexane. The final yield of pure product was 1.8 g (81%). Mp: 122 °C. <sup>1</sup>H NMR, CDCl<sub>3</sub>-d1,  $\delta$  (ppm): 1.83 (s, -CH<sub>2</sub>-, 2H), 1.97-2.00 (m, -CH<sub>2</sub>-, 8H), 2.38 (s, -CH-, 2H), 7.27 (d, ArH, 4H, J = 8.4 Hz), 7.47 (d, ArH, 4H, J = 8.4 Hz). <sup>13</sup>C NMR,  $\delta$  (ppm): 29.32, 35.47, 37.22, 42.11, 49.02, 108.98, 115.02, 126.98, 149.19, 150.97. Crystal **Data.**  $C_{24}H_{22}N_2O_2$ ,  $M_r = 370.43$ , triclinic, P-1 (No. 2), a = 7.3404(3) Å, b = 10.5239(6) Å, c = 12.9183(6) Å,  $\alpha = 107.619(4)^{\circ}$ ,  $\beta = 104.129(4)^{\circ}$ ,  $\gamma = 93.734(4)^{\circ}$ , V = 911.86(8) Å<sup>3</sup>, T = 100.0(2) K, Z = 2, Z' = 1,  $\mu$ (Cu  $K_{\alpha}$ ) = 0.686, 10,248 reflections measured, 3681 unique ( $R_{int} = 0.0297$ ) which were used in all calculations. The final  $wR_2$  was 0.1182 (all data) and *R*<sub>1</sub> was 0.0409 (*I* > 2(I)). CCDC number 2065109.

#### 2.2. Methods

# 2.2.1. Methods for the determination of the structure and purity of target monomer

Data set for single crystal of the monomer was collected on a Rigaku XtaLab Synergy S instrument with a HyPix detector and a PhotonJet microfocus X-ray tube using Cu K<sub> $\alpha$ </sub> (1.54184 Å) radiation at low temperature. Images were indexed and integrated using the CrysAlisPro data reduction package. Data were corrected for systematic errors and absorption using the ABSPACK module: numerical absorption correction based on Gaussian integration over a multifaceted crystal model and empirical absorption correction based on spherical harmonics according to the point group symmetry using equivalent reflections. The GRAL module was used for analysis of systematic absences and space group determination. The structure was solved by direct methods using SHELXT and refined by the full-matrix least-squares on F<sup>2</sup> using SHELXL [24,25]. Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were inserted at the calculated positions and refined as



Fig. 2. Scheme of synthesis of target dicyanate ester.



**Fig. 3.** Single-crystal X-ray crystallographic structure of synthesized tricyanate ester 4 (H atoms – light grey, C atoms – dark grey, N atoms – blue, O atoms – red). – (A). Crystal packing of dicyanate ester view along a axes – (B). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

riding atoms. The figures were generated using Mercury 4.1 program [26]. Crystals of the target cyanate ester were obtained by crystallization from the mixture of CH<sub>2</sub>Cl<sub>2</sub> and hexane. The HPLC analysis was carried out with a Dionex Ultimate 3000 chromatograph equipped with a UV detector (254 nm) and Dionex Acclaim 120 chromatographic column (C18-bonded silica, 5  $\mu$ m, 120 Å, 4.6  $\times$  250 mm). Mixture of 85% of acetonitrile and 15% of deionized water (by volume) was used as an eluent at a flow rate of 1 mL min<sup>-1</sup>. The <sup>1</sup>H and <sup>13</sup>C NMR experiments were carried on a Bruker AVANCE III NMR spectrometer operating at 600.13 MHz. IR spectra were recorded with Bruker Vertex 70 FTIR spectrometer.

#### 2.2.2. Thermal analysis

Calorimetric measurements were carried out using a heat flux DSC 3+ (Mettler-Toledo). Indium and zinc standards were used to perform temperature, heat flow, and tau-lag calibrations. The experiments were performed in the atmosphere of argon flow (80 mL min $^{-1}$ ) at the heating rates of 2.0, 4.0, 6.0, 8.0 and 10.0  $^{\circ}$ C min<sup>-1</sup> in 40  $\mu$ L aluminum pans sealed in argon atmosphere as well. Because moisture could potentially affect polymerization, before sealing the monomer samples placed in 40 µL aluminum pans were kept in a vacuum desiccator containing a beaker filled with P2O5 for 1 day to remove traces of water before measurements. The mass of the cyanate ester sample for each run was  $\sim 1$  mg. For temperature modulated DSC (TMDSC), the samples were heated from 25 to 400 °C at the heating rate of 1 °C min<sup>-1</sup> superimposed with stochastic temperature pulses of 0.5 °C amplitude and pulse time that ranged from 15 to 30 s. For the glass transition measurements 10 mg of cvanate ester monomer in 40 µL aluminum pans were polymerized directly in DSC instrument (25 to 400 °C at the heating rate of 4 °C min<sup>-1</sup>) and then studied by TMDSC. Thermogravimetric analysis was carried out with Netzsch STA 449 F1 Jupiter thermal analyzer. The sample of  $\sim 10$  mg was heated from 40 to 1000 °C under argon flow of 75 mL min<sup>-1</sup>.

#### 3. Computations

The recommendations of the ICTAC Kinetic Committee were followed to evaluate the activation energy and preexponential factor dependencies [27]. The extent of conversion,  $\alpha$ , values were determined as the partial areas of the DSC peaks associated with polymerization of the cyanate ester. The effective activation energy,  $E_{\alpha}$ , was evaluated as a function of conversion with the aid of the flexible integral isoconversional method of Vyazovkin [28–30]. The method allows one to eliminate a systematic error in  $E_{\alpha}$  when it varies with  $\alpha$ . The error is eliminated via flexible integration that assumes the constancy of  $E_{\alpha}$ within a very narrow integration range,  $\Delta \alpha$ . The value of  $\Delta \alpha$  was taken as 0.01. Within each  $\Delta \alpha$ ,  $E_{\alpha}$  is determined by finding a minimum of the function:

$$\Psi(E_{\alpha}) = \sum_{i=1}^{n} \sum_{j \neq i}^{n} \frac{J[E_{\alpha}, T_{i}(t_{\alpha})]}{J[E_{\alpha}, T_{j}(t_{\alpha})]}$$
(1)

where

$$I[E_{\alpha}, T_{i}(t_{\alpha})] \equiv \int_{t_{\alpha-\Delta\alpha}}^{t_{\alpha}} exp\left[\frac{-E_{\alpha}}{RT_{i}(t)}\right] dt$$
<sup>(2)</sup>

and *n* is the number of the temperature programs. The trapezoid rule was employed to compute the integral. The COBYLA non-gradient method from the NLopt library was utilized to determine a minimum of Eq. (1). The uncertainties in the  $E_{\alpha}$  values were evaluated according to procedure described elsewhere [31].

The preexponential factor values were estimated by substituting the values of  $E_{\alpha}$  into the equation of the compensation effect

$$lnA_a = a + bE_a \tag{3}$$

The parameters *a* and *b* were determined by fitting the pairs of  $lnA_i$  and  $E_i$  into Eq. (3). The respective pairs were found by substituting the reaction models  $f_i(a)$ , into the linear form of the basic rate equation:

$$ln\left(\frac{d\alpha}{dt}\right) - ln[f_i(\alpha)] = lnA_i - \frac{E_i}{RT}$$
(4)

For each reaction model,  $lnA_i$  and  $E_i$  values were evaluated respectively from the slope and intercept of the linear plot of left-hand side of Eq. (4) vs the reciprocal temperature. Five pairs of  $lnA_i$  and  $E_i$  were evaluated by the model

$$f(\alpha) = \alpha^m (1 - \alpha)^n \tag{5}$$

with five different combinations of *m* and *n* (m = 1, n = 1; m = 0.5, n = 1; m = 1, n = 0.5; m = 2, n = 1, m = 1, n = 2). This model was selected because of its ability to imitate the autocatalytic reaction kinetics, which is typical of cyanate esters polymerization [3]. In addition, this  $f(\alpha)$  model is a part of a more complex reaction model by Kamal [32] that has been used successfully for describing the kinetics of cyanate ester polymerization [33,34].

The experimentally estimated values of  $E_{\alpha}$  and  $A_{\alpha}$  have been used to establish the integral reaction model in the numerical form:

$$g(\alpha) = \sum_{\alpha} A_{\alpha} J[E_{\alpha}, T_i(t_{\alpha})]$$
(6)

#### 4. Results and discussion

The structure of the synthesized monomer was confirmed by single



Fig. 4. Scheme of cyclotrimerization of cyanate ester.



Fig. 5. Non-reversing heat flow and heat capacity curves for cyanate ester polymerization measured at 1  $^\circ$ C min $^{-1}$  with stochastic modulation.

crystal X-ray diffraction analysis, which suggests the absence of both intra- and intermolecular interactions between cyanate groups (Fig. 3).

Polymerization of cyanate esters produces significant amounts of heat due to the formation of highly stable aromatic 1,3,5-triazine fragments as cross-links (Fig. 4). Thus, the reaction progress is conveniently followed by DSC.

The kinetics of cross-linking polymerization, especially at later stages of the process can be complicated by a transition from a kinetic- to diffusion-controlled regime [19]. This transition occurs when rising viscosity of the reaction mixture slows down translational motion of the polymer chains so that the characteristic time of diffusion exceeds the characteristic time of the reaction. This phenomenon is usually associated with vitrification of the forming polymer, which is observed when its glass transition temperature rises above the temperature of the reacting system (Fig. 1). Because vitrification decelerates dramatically the polymerization process, its occurrence is an unequivocal sign of the process transitioning into a diffusion-controlled regime.

To check whether vitrification occurs during the polymerization we have performed temperature modulated DSC measurements (TMDSC). The technique permits separation of the reversing (vitrification) and non-reversing (chemical reaction) contributions to the measured total heat flow [35]. Since the liquid and glass states possess different heat capacities, vitrification manifests itself as a step change in the measured value of the heat capacity. As seen from Fig. 5, such a step is clearly observed in the quasistatic heat capacity,  $C_{p,0}$  determined from the reversing heat flow component of the TMDSC measurement. The midpoint of the heat capacity step is found at 273 °C, which corresponds to conversion of 0.95. Thus, one can expect that the kinetics of polymerization of the present monomer may demonstrate a transition to a diffusion-controlled regime in the later stages of the process.

The kinetics of polymerization process was studied by conventional DSC. Heat flow curves for polymerization of the cyanate ester at different heating rates are presented in Fig. 6. Average heat of polymerization is 480  $\pm$  20 J g<sup>-1</sup> or 180  $\pm$  8 kJ mol<sup>-1</sup>. This corresponds to



Fig. 6. Heat flow curves for cyanate ester polymerization (numbers denote heating rates in  $^{\circ}C$  min<sup>-1</sup>).

90 kJ per 1 mol of OCN groups, which agrees well with the known reaction heat values for dicyanate esters (80–110 kJ per 1 mol of OCN groups) [2].

To quantify the reactivity of the synthesized cyanate ester DSC data were treated by isoconversional kinetic analysis. The isoconversional values of the activation energy  $E_{\alpha}$  and preexponential factor  $A_{\alpha}$  for polymerization process are displayed in Fig. 7. Fig. 7A shows that polymerization of cyanate ester demonstrates insignificant variation of the activation energy with conversion in a range of 0.10–0.75 of  $\alpha$ (variation of  $E_{\alpha}$  does not exceed 10% of average  $E_{\alpha}$  in that range of conversions), which equals to  $93 \pm 3$  kJ mol<sup>-1</sup>. The subsequent rise of the activation energy to 114 kJ mol<sup>-1</sup> is likely related to the transition of the polymerization kinetics to a diffusion-controlled regime. The preexponential factor values demonstrate similar variation (Fig. 7B) with average  $lnA_{\alpha}$  value of  $15.7 \pm 0.6$  in the same aforementioned conversion range.

The constancy of the activation energy at conversions below 0.75 signifies that polymerization process is controlled by a single reaction step, which is uncommon for non-catalyzed polymerization of cyanate esters. Because the process occurs via a complex mechanism involving the formation of several intermediates [5], one should rather expect to encounter a variation in the effective activation energy with conversion, as observed in previous work [34,36]. The kinetics of cyanate esters polymerization is usually described by a reaction model that involves two steps (eq. (7)), one of which has auto-catalytic nature [6,33,37–43], however attempts to describe the kinetics of polymerization as a single n<sup>th</sup>-order [44] or auto-catalytic [45] reaction have also been reported.

$$\frac{d\alpha}{dt} = k_1 \alpha^m (1-\alpha)^n + k_2 (1-\alpha)^n \tag{7}$$

However it should be noted that the occurrence of single-step kinetics is not the only reason of constant activation energy. The latter would be constant when a process involves two or more steps having the same (or reasonably close) values of the activation energy. To make eq. (7) more convenient for description of such situation let us factor out  $(1 - \alpha)^n$  and  $k_1$ , and replace  $k_2/k_1$  by B:

$$\frac{d\alpha}{dt} = k_1 (B + \alpha^m) (1 - \alpha)^n, \tag{8}$$

The rate equation of a similar form (with m = 1, n = 1 or 2, and *B* as a constant) was semi-empirically derived by Simon and Gillham [6,41] for mono- and dicyanate esters polymerization. In these studies, the



Fig. 7. Dependencies of activation energy (A, left panel) and preexponential factor (B, right panel) as a function of conversion for polymerization of cyanate ester.

constant *B* was linked to the amount of impurities, which catalyze reaction initially. Of course, eq. (8), as derived here, is quite different not only because it contains the exponents *m* and *n*, but also because it assigns entirely different meaning to the parameter *B*. In general, eq. (8) can be reduced to four different cases:

1. 
$$E_1 \neq E_2$$
,  $A_1 \neq A_2$ , then  $B = \frac{A_2}{A_1} exp\left[\frac{E_1 - E_2}{RT}\right]$   
2.  $E_1 \neq E_2$ ,  $A_1 \approx A_2$ , then  $B \approx exp\left[\frac{E_1 - E_2}{RT}\right]$   
3.  $E_1 \approx E_2$ ,  $A_1 \neq A_2$ , then  $B \approx \frac{A_2}{A_1}$   
4.  $E_1 \approx E_2$ ,  $A_1 \approx A_2$ , then  $B \approx 1$ 

The first and second cases  $(E_1 \neq E_2)$  result in *B* being a function of temperature, whereas third and fourth cases  $(E_1 \approx E_2)$  provide constant *B* values. Thus, both eqs. (7) and (8) can be used for description of polymerization of cyanate esters involving one or two steps. For the sake of clarity, we propose to use eq. (7) explicitly involving two kinetic triplets for the processes with variable activation energy, whereas eq. (8) involving one kinetic triplet for the processes demonstrating constant or insignificantly variable activation energy. The reaction model in the rate eq. (8) presented by the function:

$$f(\alpha) = (B + \alpha^m)(1 - \alpha)^n \tag{9}$$

where B is a constant, can be considered as a reasonable alternative to the autocatalytic model expressed by eq. (5) (aka the truncated Sestak-Berggren or expanded Prout-Tompkins model), widely used for description of autocatalytic processes. An alternative is needed because eq. (5) cannot be used for kinetic simulations without making an illogical assumption that a reaction has to start at a nonzero value of  $\alpha$  [46]. This problem is aggravated by the fact that the resulting simulations are affected significantly by the specific choice of this initial nonzero value of  $\alpha$ . The proposed model (eq. (9)) does not have this problem that provides an important advantage over autocatalytic model expressed by eq. (5). It should be noted, that the constant B in the proposed model being a ratio of preexponential factors of two competing reactions with similar activation energies indicates how many times the n<sup>th</sup>-order reaction rate constant exceeds the autocatalytic reaction rate constant. In case of  $B \le 0.1$  or  $B \ge 10$ , the contribution of one of the reactions to the effective reaction rate constant is less than 10%, which is close to the error of its calculation, therefore such reactions might be considered as a quasi-one-step processes.

To show the ability of the proposed model (eq. (9)) to describe experimental data we have fitted the numerical  $g(\alpha)$  data obtained via



Fig. 8. Experimental  $g(\alpha)$  data for polymerization of dicyanate ester.

Table 1

Estimated kinetic	parameters for	polymerization	of dicvanate	ester 4.
Louinated kinetie	parameters ior	porymenzation	or uncyamate.	Colur 4.

Fit to	$E_1/kJ$ mol <sup>-1</sup>	$ln(A_1/s^{-1})$	m	n	В	ln(A <sub>2</sub> / s <sup>-1</sup> )
Eq. (10)	-	-	$\begin{array}{c} 1.16 \ \pm \\ 0.01 \end{array}$	$\begin{array}{c} 1.15 \ \pm \\ 0.01 \end{array}$	$\begin{array}{c} \textbf{0.024} \pm \\ \textbf{0.001} \end{array}$	-
Eq. (8) (way 1)	$*93\pm3$	$\begin{array}{c} 15.5 \pm \\ 0.1 \end{array}$	$\begin{array}{c} 1.3 \pm \\ 0.1 \end{array}$	$\begin{array}{c} 0.9 \pm \\ 0.1 \end{array}$	$\begin{array}{c} \textbf{0.09} \pm \\ \textbf{0.02} \end{array}$	**13.1
Eq. <mark>(8)</mark> (way 2)	$*93\pm3$	$\begin{array}{c} 15.2 \pm \\ 0.2 \end{array}$	$\begin{array}{c} 0.8 \pm \\ 0.1 \end{array}$	0.7 ± 0.1	$^{*0.024} \pm 0.001$	**11.5

Symbol \* denotes values used as constants during fitting; Symbol \*\* denotes the  $lnA_2$  values estmated from the values of *B* and  $lnA_1$ 

eq. (6) to the integral form of eq. (9) as follows:

$$g(\alpha) = \int_{0}^{\alpha} \frac{d\alpha}{(B+\alpha^{m})(1-\alpha)^{n}}$$
(10)

The results of the fit are presented in Fig. 8. It is seen that the proposed model allows for a good quality fit. The estimated values of *B*, *m*,



**Fig. 9.** The diffusion factor  $f_d(\alpha)$  values averaged over all heating rates (diamonds) calculated with kinetic parameters from Table 1 (second line) and the best fit by eq. (12) (dashed line).

and *n* are shown in Table 1. The results indicate that the *m* and *n* values are close to 1 and from the value of *B* we can conclude that  $A_2$  is about 40 times larger than  $A_1$ .

Alternatively, we have used the rate data for  $\alpha < 0.75$  to fit to eq. (8) to estimate the parameters of the kinetically-controlled polymerization. This has been done in two different ways (denoted in Table 1 as "way 1" and "way 2"). First, the fitting has been performed by using A<sub>1</sub>, m, n, and *B* as the fit parameters. Second, only *A*<sub>1</sub>, *m*, and *n* have been used as the fit parameters, while keeping *B* as a constant determined by fitting eq. (10). In both cases,  $k_1$  in eq. (8) has been replaced with the Arrhenius equation, in which the  $E_1$  value taken as a constant (93  $\pm$  3 kJ mol<sup>-1</sup>), as determined by the advanced isoconversional method. The resulting values of the obtained kinetic parameters are presented in Table 1 (uncertainties are given in as the standard deviations). Using *B* as a fit parameter yields about 4 times larger value than the one determined from eq. (10). However, the parameters *m* and *n* remain close to 1. When using *B* obtained from fitting eq. (10), the parameters *m* and *n* drop to smaller values. Yet, the value of  $\ln A_1$  remains practically the same in both cases. Combining the  $A_1$  and B values, it is also possible to estimate the  $\ln A_2$  values, which differ by less than 2 units on the natural log scale (Table 1). More precisely, the respective  $A_2$  values differ by about 5 times. To sum up, all the obtained fitting parameters seem reasonably consistent with each other regardless of the way used for fitting. Since fitted B parameter values are below 0.1 regardless of fitting procedure, the polymerization in reaction-controlled regime might be considered as a quasi-one-step processes according to the aforementioned reasons.

To account for diffusion that controls the later stages ( $\alpha > 0.75$ ) of polymerization, we have employed a simple and convenient approach, which parameterizes the total polymerization rate as the product of reaction-controlled reaction rate  $[d\alpha/dt]_r$  and conversion-dependent diffusion factor  $f_d(\alpha)$  [47,48]:

$$\frac{d\alpha}{dt} = \left[\frac{d\alpha}{dt}\right]_r f_d(\alpha) \tag{11}$$

 $f_d(\alpha)$  is close to unity when reaction proceeds in a reaction-controled regime, and decreases when it switches to diffusion control. Knowing the parameters of the reaction-controlled process (Table 1) one can easily calculate the corresponding reaction rate using the experimental  $\alpha$  and T values in eq. (7). In accord with eq. (11) the ratio of the experimental rate to the reaction controlled rate gives the diffusion factor



**Fig. 10.** Comparison of the experimental polymerization rate curves (triangles) with the ones estimated with (solid line) and without (dashed line) account of diffusion control.

values at the corresponding  $\alpha$  values. As expected, the values of  $f_d(\alpha)$  stay close to unity up to conversion of 0.75 then drop quickly to  $\sim$ 0.3–0.4 after the reaction swithes to diffusion-control regime (Fig. 9). Fournier et al. proposed the following empirical equation [47] to describe a dependence of diffusion factor on conversion:

$$f_d(\alpha) = 2\left(1 + exp\left[\frac{\alpha - \alpha_f}{b}\right]\right)^{-1} - 1,$$
(12)

where  $\alpha_f$  is the final conversion and *b* is an empirical parameter. The use of empirical models, such as eq. (12), remains the most efficient way for accounting the effect of diffusion on the crosslinking kinetics. The application of more advanced phenomenological models is obstructed by the need in nontrivial and extensive experimental studies to obain such data as the diffusion rate constant and its dependence on viscosity and temperature of the reaction medium as well as of viscosity of the medium and its dependence on the polymerization degree and temperature [49].

Eq. (12) has been fitted to the  $f_d(\alpha)$  values obtained as the ratio of the experimental rate to the reaction-controlled rate data. The latter have been determined by substituting the  $A_1$ , m, n, and B (second line in Table 1) into eq. (8). The  $\alpha_f$  has been set as 1 because a FTIR spectrum of the polymerization product does not show the presence of unreacted cyanate groups at 2265 and 2360 cm<sup>-1</sup>, i.e., polymerization can be considered as complete. The resulting  $f_d(\alpha)$  data are presented in Fig. 9.

Fig. 10 illustrates how the rate equations with and without the diffusion factor (i.e., eq. (8) and eq. (13)) describe the experimental data in the whole range of conversions. Expectedly eq. (8) fails to describe the experimental data outside of the kinetically-controlled conversion range, whereas eq. (13) matches well the experimental plots in the whole conversion range. The overall rate equation with account of diffusion takes the following form:

$$\frac{d\alpha}{dt} = k_1 (1-\alpha)^n (B+\alpha^m) \left( 2 \left( 1 + exp \left[ \frac{\alpha - 1}{0.068} \right] \right)^{-1} - 1 \right)$$
(13)

It is instructive to compare the reactivity of the presently studied monomer containing the rigid adamantane bridging fragment with other dicyanate esters containing flexible hydrocarbon bridging units. The switching of the polymerization from reaction- to diffusioncontrolled regime is of particular interest. As already mentioned, the polymerization of presently studied dicyanate ester with rigid



Fig. 11. Heat capacity curve for fully cured polymer sample measured at 1  $^\circ C$  min $^{-1}$  with stochastic modulation.



Fig. 12. TG and derivative TG curves of thermal decomposition of polymer at 10  $^\circ C$  min  $^{-1}.$ 

adamantane bridging fragment swithes to diffusion-controlled regime at  $\alpha = 0.75$ . Studies of the uncatalyzed polymerization kinetics of dicyanate esters with flexible bridging units in non-isothermal conditions show that reaction proceeds in a reaction-controlled regime in a whole conversion range [36,38,50].

To measure the glass transition temperature of the resulting polymer we have employed TMDSC. Fig. 11 presents the results of the  $T_g$  measurements at the heating rate of 1 °C min<sup>-1</sup>. As one can see, the synthesized adamantane-based polymer possesses very high glass transition temperature of 345 °C. It should be noted that dicyanate esters with flexible hydrocarbon bridging fragments (namely, based on bisphenols A, E, F, and M or dimer of p-*tert*-butylphenol) in general give rise to polymers that feature much lower glass transition temperatures than that of the presently studied polymer (192–289 °C vs 345 °C) [3,50,51]. Thus, the obtained results are consistent with our initial hypothesis that the factors increasing  $T_g$  must favor earlier transition of the polymerization to diffusion control.

Thermal stability of the polymerization product of the adamantanebased monomer in inert atmosphere was evaluated by thermogravimetry (TG). Complexity of thermal decomposition process is revealed in the presence of two peaks (448 and 540  $^{\circ}$ C) on derivative TG (DTG) curve (Fig. 12). The two-step mass loss is typical for cyanate polymers [51].

It is also informative to compare the thermal stability of the present polymer product against above-mentioned polymers containing flexible hydrocarbon bridging fragments. The 5% mass loss temperature of our adamantane-based polymer is 446 °C, which is comparable to that of the aforementioned polymers (439–455 °C) [51]. However, the maximum mass loss rate temperature of the presently obtained polymer (540 °C) is significantly higher that of the polymers obtained from the commercially available monomers (468–482 °C) [51]. Such difference is related to the fact that the polymers from commercial monomers lose most of their mass during the first step of decomposition, whereas the adamantane-based polymer during the second step of decomposition.

### 5. Conclusions

We have synthesized adamantane-based dicvanate ester and confirmed its structure by X-ray analysis. The synthesized monomer undergoes thermally-stimulated polymerization in the liquid state. The polymerization process has been studied by conventional and temperature-modulated DSC, which show that the reaction switches to diffusion-controlled regime at the later stages of polymerization. Detailed analysis of the polymerization kinetics in the reaction-control regime has revealed that the process rate might be described as a quasi-one-step process. The reaction is found to be auto-catalytic. A new autocatalytic model has been proposed as an alternative to the broadly used truncated Sestak-Berggren model. Unlike the latter, the proposed model avoids arbitrarily guessing the value for the initial conversion. The polymerization product has demonstrated the thermal stability and glass transition temperature that are higher than those for dicyanate esters with flexible hydrocarbon bridging units. Overall, the obtained experimental results confirm our hypothesis about the effect of the rigid adamantane fragment on the reactivity of the monomer and thermal properties of the corresponding polymer product.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgments

This work was supported by the Russian Foundation of Basic Research (RFBR) (Project N $^{\circ}$  20-33-70174). AG acknowledges the Assigned Spectral-Analytical Center of FRC Kazan Scientific Center of RAS for the opportunity of conducting the NMR experiments.

#### References

- [1] D.N. Burrows, J.E. Hill, J.A. Nousek, J.A. Kennea, A. Wells, J.P. Osborne, A. F. Abbey, A. Beardmore, K. Mukerjee, A.D.T. Short, G. Chincarini, S. Campana, O. Citterio, A. Moretti, C. Pagani, G. Tagliaferri, P. Giommi, M. Capalbi, F. Tamburelli, L. Angelini, G. Cusumano, H.W. Bräuninger, W. Burkert, G. D. Hartner, The swift X-ray telescope. Space Sci. Rev, 120 (3) (2005) 165–195.
- [2] Chemistry and Technology of Cyanate Ester Resins, Springer Netherlands, 1994.
- [3] T. Fang, D.A. Shimp, Polycyanate esters: science and applications, Prog. Polym. Sci. 20 (1) (1995) 61–118.
- [4] 13 Polymers for aerospace structures, in: A.P. Mouritz (Ed.), Introduction to Aerospace Materials, Woodhead Publishing, 2012, pp. 268–302.
- [5] M.-F. Grenier-Loustalot, C. Lartigau, F. Metras, P. Grenier, Mechanism of thermal polymerization of cyanate ester systems: chromatographic and spectroscopic studies, J. Polym. Sci. A Polym. Chem. 34 (14) (1996) 2955–2966.
- [6] S.L. Simon, J.K. Gillham, Cure kinetics of a thermosetting liquid dicyanate ester monomer/high-Tg polycyanurate material, J. Appl. Polym. Sci. 47 (3) (1993) 461–485.
- [7] C.A. Fyfe, J. Niu, S.J. Rettig, N.E. Burlinson, High-resolution carbon-13 and nitrogen-15 NMR investigations of the mechanism of the curing reactions of

#### A. Galukhin et al.

cyanate-based polymer resins in solution and the solid state, Macromolecules 25 (23, 1992) 6289–6301.

- [8] S.S. Stivala, L. Reich, Structure vs stability in polymer degradation, Polym. Eng. Sci. 20 (10, 1980) 654–661.
- [9] W. Xia, J. Song, D.D. Hsu, S. Keten, Side-group size effects on interfaces and glass formation in supported polymer thin films, J. Chem. Phys. 146 (20, 2017) 203311.
- [10] A. Singh, N.R. Krogman, S. Sethuraman, L.S. Nair, J.L. Sturgeon, P.W. Brown, C. T. Laurencin, H.R. Allcock, Effect of side group chemistry on the properties of biodegradable l-alanine Cosubstituted Polyphosphazenes, Biomacromolecules 7 (3) (2006) 914–918.
- [11] A.L. Agapov, Y. Wang, K. Kunal, C.G. Robertson, A.P. Sokolov, Effect of polar interactions on polymer dynamics, Macromolecules 45 (20, 2012) 8430–8437.
- [12] Q. Liu, C. Wang, Y. Guo, C. Peng, A. Narayanan, S. Kaur, Y. Xu, R.A. Weiss, A. Joy, Opposing effects of side-chain flexibility and hydrogen bonding on the thermal, mechanical, and rheological properties of Supramolecularly cross-linked polyesters, Macromolecules 51 (22, 2018) 9294–9305.
- [13] V.V. Korshak, S.V. Vinogradova, Dependence of thermal stability of polymers on their chemical structure, Russ. Chem. Rev. 37 (11, 1968) 885–906.
- [14] A. Witkowski, A.A. Stec, T.R. Hull, Thermal decomposition of polymeric materials, in: M.J. Hurley, D. Gottuk, J.R. Hall, K. Harada, E. Kuligowski, M. Puchovsky, C. Wieczorek (Eds.), SFPE Handbook of Fire Protection Engineering, Springer New York, New York, NY, 2016, pp. 167–254.
- [15] T. Ishizone, R. Goseki, Synthesis of polymers carrying adamantyl substituents in side chain, Polym. J. 50 (9) (2018) 805–819.
- [16] A.S. Mathews, I. Kim, C.-S. Ha, Fully aliphatic polyimides from adamantane-based diamines for enhanced thermal stability, solubility, transparency, and low dielectric constant, J. Appl. Polym. Sci. 102 (4) (2006) 3316–3326.
- [17] D. Baskaran, A.H.E. Müller, Anionic Vinyl Polymerization, Controlled and Living Polymerizations, 2009, pp. 1–56.
- [18] M. Sawamoto, Modern cationic vinyl polymerization, Prog. Polym. Sci. 16 (1) (1991) 111–172.
- [19] S. Vyazovkin, Isoconversional Kinetics of Thermally Stimulated Processes, Springer International Publishing, 2015.
- [20] C. Shen, H. Yu, Z. Wang, Synthesis of 1,3,5,7-tetrakis(4-cyanatophenyl)adamantane and its microporous polycyanurate network for adsorption of organic vapors, hydrogen and carbon dioxide, Chem. Commun. 50 (76) (2014) 11238–11241.
- [21] K.T.M. Katagiri, M. Tsubuku, T. Tsujimoto, K. Arii, T. Kobayashi, M. Sogame, Y. Mabuchi, S. Hiramatsu, Aromatic Cyanate Esters Having Adamantyl Groups with Good Solvent Solubility, Curable Compositions Containing them, and Cured Products from them, World Intellectual Property Organization, Japan, 2015.
- [22] A.S. Degtyarenko, M. Handke, K.W. Krämer, S.-X. Liu, S. Decurtins, E.B. Rusanov, L.K. Thompson, H. Krautscheid, K.V. Domasevitch, Mixed-ligand hydroxocopper (ii)/pyridazine clusters embedded into 3D framework lattices, Dalton Trans. 43 (22, 2014) 8530–8542.
- [23] B.J. Cha, S. Kim, K. Char, J.-K. Lee, D.Y. Yoon, H.-W. Rhee, Nanoporous organosilicate thin films prepared with covalently bonded adamantylphenol pore generators, Chem. Mater. 18 (2) (2006) 378–385.
- [24] G.M. Sheldrick, SHELXT integrated space-group and crystal-structure determination, Acta crystallographica, Sec A Found. Advances 71 (Pt 1) (2015) 3–8.
- [25] G. Sheldrick, A short history of SHELX, Acta Crystallographica Sec. A 64 (1) (2008) 112–122.
- [26] C.F. Macrae, P.R. Edgington, P. McCabe, E. Pidcock, G.P. Shields, R. Taylor, M. Towler, J. van de Streek, Mercury: visualization and analysis of crystal structures, J. Appl. Crystallogr. 39 (3) (2006) 453–457.
- [27] S. Vyazovkin, A.K. Burnham, J.M. Criado, L.A. Pérez-Maqueda, C. Popescu, N. Sbirrazzuoli, ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data, Thermochim. Acta 520 (1) (2011) 1–19.

- Reactive and Functional Polymers 165 (2021) 104956
- [28] S. Vyazovkin, Modification of the integral isoconversional method to account for variation in the activation energy, J. Comput. Chem. 22 (2) (2001) 178–183.
- [29] S. Vyazovkin, Evaluation of activation energy of thermally stimulated solid-state reactions under arbitrary variation of temperature, J. Comput. Chem. 18 (3) (1997) 393–402.
- [30] S. Vyazovkin, D. Dollimore, Linear and nonlinear procedures in Isoconversional computations of the activation energy of nonisothermal reactions in solids, J. Chem. Inf. Comput. Sci. 36 (1) (1996) 42–45.
- [31] S. Vyazovkin, C.A. Wight, Estimating realistic confidence intervals for the activation energy determined from thermoanalytical measurements, Anal. Chem. 72 (14, 2000) 3171–3175.
- [32] M.R. Kamal, Thermoset characterization for moldability analysis, Polym. Eng. Sci. 14 (3) (1974) 231–239.
- [33] C.-C. Chen, T.-M. Don, T.-H. Lin, L.-P. Cheng, A kinetic study on the autocatalytic cure reaction of a cyanate ester resin, J. Appl. Polym. Sci. 92 (5) (2004) 3067–3079.
- [34] A. Galukhin, G. Taimova, R. Nosov, T. Liavitskaya, S. Vyazovkin, Polymerization kinetics of Cyanate Ester confined to hydrophilic nanopores of silica colloidal crystals with different surface-grafted groups, Polymers 12 (10, 2020) 2329.
- [35] J.E.K. Schawe, T. Hütter, C. Heitz, I. Alig, D. Lellinger, Stochastic temperature modulation: a new technique in temperature-modulated DSC, Thermochim. Acta 446 (1) (2006) 147–155.
- [36] A. Galukhin, T. Liavitskaya, S. Vyazovkin, Kinetic and mechanistic insights into thermally initiated polymerization of Cyanate esters with different bridging groups, Macromol. Chem. Phys. 220 (13, 2019) 1900141.
- [37] I. Harismendy, C.M. Gómez, M.D. Río, I. Mondragon, Cure monitoring of catalysed cyanate ester resins, Polym. Int. 49 (7) (2000) 735–742.
- [38] R.H. Lin, A.C. Su, J.L. Hong, Kinetics of polycyclotrimerization of aromatic dicyanates, J. Polym. Res. 4 (4) (1997) 191–202.
- [39] A. Osei-Owusu, G.C. Martin, J.T. Gotro, Catalysis and kinetics of cyclotrimerization of cyanate ester resin systems, Polym. Eng. Sci. 32 (8) (1992) 535–541.
- [40] W. Li, G. Liang, W. Xin, Triazine reaction of cyanate ester resin systems catalyzed by organic tin compound: kinetics and mechanism, Polym. Int. 53 (7) (2004) 869–876.
- [41] Y.P. Koh, S.L. Simon, Kinetic study of trimerization of monocyanate ester in nanopores, J. Phys. Chem. B 115 (5) (2011) 925–932.
- [42] S.L. Simon Li, Curing of bisphenol M dicyanate ester under nanoscale constraint, Macromolecules 41 (4) (2008) 1310–1317.
- [43] Y.P. Koh, S.L. Simon, Trimerization of monocyanate ester in nanopores, J. Phys. Chem. B 114 (23, 2010) 7727–7734.
- [44] K.-F. Lin, J.-Y. Shyu, Early cure behavior of a liquid dicyanate ester resin, J. Polym. Sci. A Polym. Chem. 39 (18, 2001) 3085–3092.
- [45] X. Sheng, M. Akinc, M.R. Kessler, Cure kinetics of thermosetting bisphenol E cyanate ester, J. Therm. Anal. Calorim. 93 (1) (2008) 77–85.
   [46] A.K. Burnham, Response to statements by professor Šesták concerning logistic
- equations in kinetics, J. Therm. Anal. Calorim. 127 (1) (2017) 1127–1129.
   [47] J. Fournier, G. Williams, C. Duch, G.A. Aldridge, Changes in molecular dynamics
- [47] J. Fournier, G. Williams, C. Duch, G.A. Aldridge, Changes in molecular dynamics during bulk polymerization of an epoxide–amine system as studied by dielectric relaxation spectroscopy, Macromolecules 29 (22, 1996) 7097–7107.
- [48] J.E.K. Schawe, A description of chemical and diffusion control in isothermal kinetics of cure kinetics, Thermochim. Acta 388 (1) (2002) 299–312.
- [49] K. Dušek, Diffusion control in the kinetics of cross-linking, Polymer Gels Net. 4 (5) (1996) 383–404.
- [50] A. Galukhin, R. Nosov, G. Taimova, D. Islamov, S. Vyazovkin, Synthesis and polymerization kinetics of novel dicyanate ester based on dimer of 4-tertbutylphenol, Macromol. Chem. Phys. 222 (5) (2021) 2000410.
- [51] M.L. Ramirez, R. Walters, R.E. Lyon, E.P. Savitski, Thermal decomposition of cyanate ester resins, Polym. Degrad. Stab. 78 (1) (2002) 73–82.