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Curing of Oligomers with Thermoreactive Norbornene, Chalcone, and Maleimide Groups

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Abstract—Curing of powdered chalcone-containing oligoimides with terminal maleimide or norbornenedicarboxylic acid imide groups was studied by differential scanning calorimetry. The calorimetric characteristics of curing were discussed in relation to the chemical structure and conformational isomerism of the oligomers.

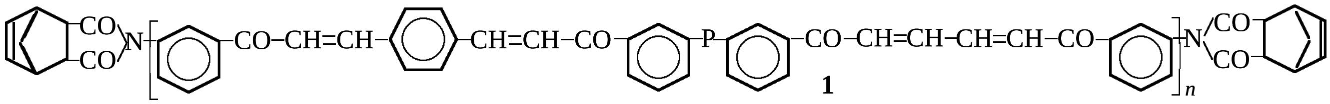
One of urgent problems in preparation of polymeric composites is development of high-heat-resistance reinforced plastics based on polyimides and related compounds, with the characteristics meeting the requirements of modern engineering. In this connection, it becomes necessary to elucidate relationships between curing conditions and structure of oligomers containing various thermoreactive groups, with the aim to find oligomers suitable as binders in high-heat-resistance composites.

In this work, we studied how the phase and aggregation state of a series of monomers and oligomers containing norbornenedicarboxylic acid imide, maleimide, and chalcone functional groups varies in the course of thermal cross-linking.

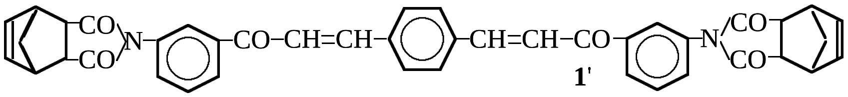
EXPERIMENTAL

The chemical structures of oligomers **1**–**6** and the corresponding monomers **1'**–**6'** are given below:

Series I

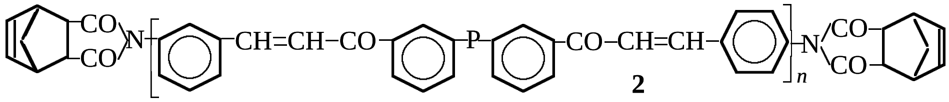


1



1'

Series II



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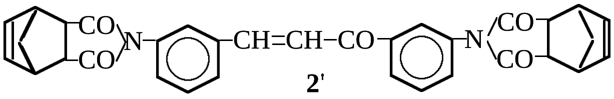
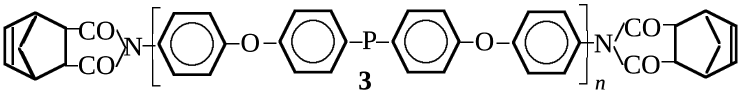
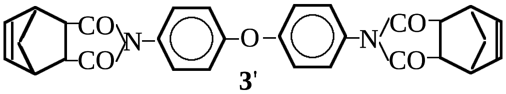


2'

Series III



3



3'

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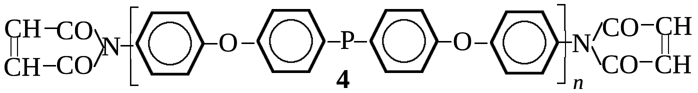
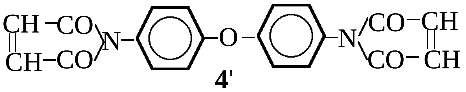
Series IV

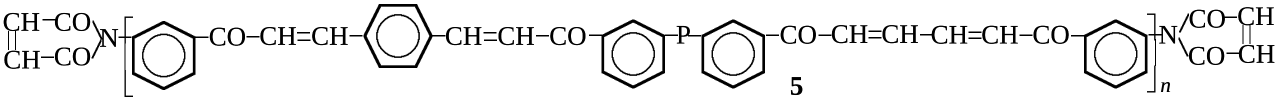


4



4'

Series V



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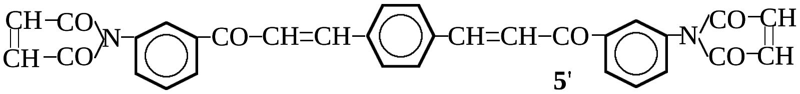
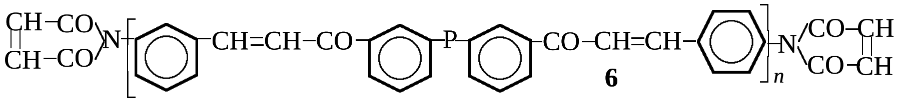
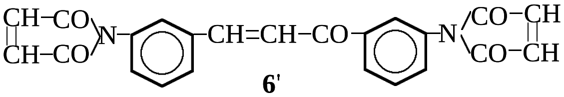


5'

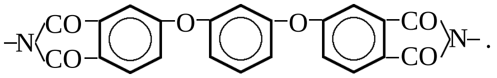
Series VI



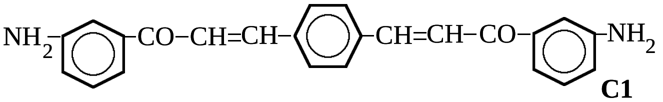
6



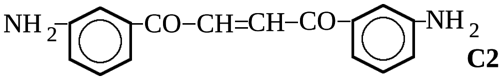
6'

where P = .

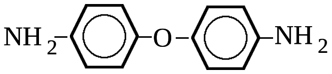
Monomers **1**'–**6**' were prepared by acylation of chalcone-containing diamines **C1** and **C2** with 4,4'-diaminodiphenyl ether (DADPE), maleic anhydride, or 5-norbornene-2,3-dicarboxylic anhydride, respectively:



C1

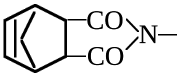


C2

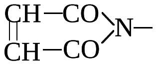


DADPE

Oligomers **1**–**3** and monomers **1**'–**3**' have the terminal norbornenedicarboxylic acid imide group (**a**), and oligomers **4**–**6** and **4**'–**6**', maleimide group (**b**):

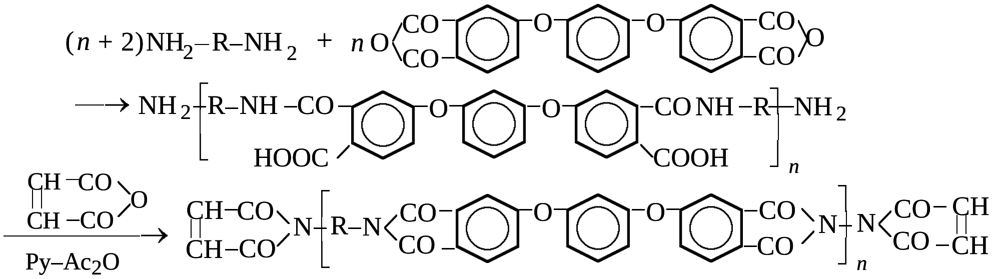


a



b

Oligomers **1**–**6** were prepared from 1,4-bis[3-oxo-3-(3'-aminophenyl)-1-propenyl]benzene [1] (bischalcone **C1**), 1,4-bis(3'-aminophenyl)-2-butene-1,4-dione [2] (chalcone **C2**), DADPE, and 1,3-bis(3',4'-dicarboxyphenoxy)benzene dianhydride (DA-P) by the following scheme:



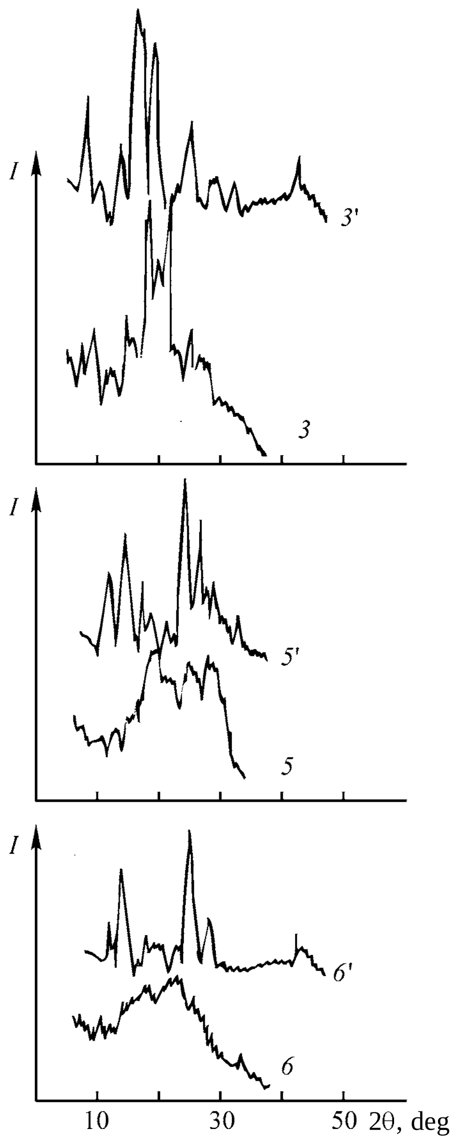
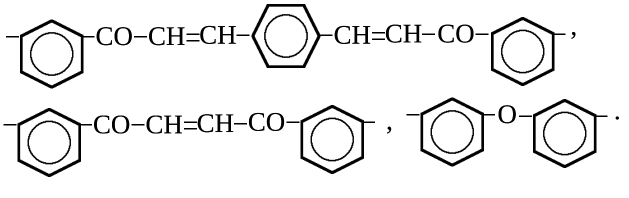


Fig. 1. Diffraction patterns of the monomers and oligomers of series III, V, and VI: (*I*) intensity and (2θ) Bragg angle. Curve numbers are monomer and oligomer numbers; the same for Figs. 2 and 3.

where R =



Dianhydride DA-P was added to a solution of appropriate diamine in dimethylformamide (DMF) at 20°C. The solution was stirred for 3 h, after which maleic or 5-norbornene-2,3-dicarboxylic anhydride was added. The oligomer concentration was 30 wt %. After 2 h, the imidizing mixture of acetic anhydride and pyridine (2 : 1 by volume) was added in a fivefold molar excess relative to the reactive units, and the solution was left overnight. Then the solution was stirred for an additional 2 h at 60–70°C, and the polymer was precipitated with methanol. The powders were vacuum-dried at 50°C. Monomers **1**'–**6**' were prepared similarly but without DA-P.

Compounds **1**–**6** and **1**'–**6**' were characterized by IR and electronic spectra. According to the IR spectra, the degree of imidization was 95–97%. The electronic spectra of **1**, **1**', **5**, and **5**' exhibited absorption with λ_{max} = 360 nm, characteristic of bischalcone **C1**, and those of **2**, **2**', **6**, and **6**', absorption with λ_{max} = 308 nm, characteristic of chalcone **C2**.

Curing of monomers and oligomers was monitored by calorimetric, X-ray diffraction, and thermomechanical methods. Calorimetric measurements were performed in the range 30–400°C with a DSM-2M calorimeter at a scanning rate of 16 deg min^{-1} and theshold sensitivity of 0.04 MW [3].

X-ray diffraction data were obtained with a DRON-2 diffractometer using Ni-filtered CuK_{α} radiation. Thermomechanooptical measurements were performed with a Boetius heating stage; the softening range was evaluated visually from changes in the powder particle shape and in the response on pressing.

In the initial state, powders of monomers **1**'–**6**' were highly crystalline substances; the phase state of oligomers **1**–**6** depended on their chemical structure: oligomers **2** and **4** were crystalline; **5** and **1**, mesomorphic; and the others, amorphous. Figure 1 shows the X-ray diffraction patterns of monomers **3**', **5**', and **6**' and of crystalline (**3**), mesomorphic (**5**), and amorphous (**6**) polymers.

The thermograms of oligomers and monomers of series I–VI are compared in Fig. 2. The monomers exhibit thermal effects in two ranges, with different signs of the effects: endothermic (melting of crystals) and exothermic (curing due to cross-linking of thermoreactive groups). The oligomers exhibit thermal effects in three ranges. The effects manifested at low and moderate temperatures are endothermic, and the high-temperature effects are exothermic. The low-temperature range, 50–150°C, is similar for all the oligomers; it corresponds to removal of residual solvents used in the synthesis of the oligomers. As it has no relation to the structure of the oligomers, it is not discussed further. The medium- and high-temperature ranges are different for different oligomers. The DSC curves of some oligomers, recorded on heating to 400°C , do not return to zero (baseline), suggesting

Temperature ranges of endo- and exothermic effects, ΔT_{endo} and ΔT_{exo}, of monomers and oligomers; softening ranges, ΔT_{s}, of oligomers

Monomers			Oligomers			
no.	ΔT_{endo}, °C	ΔT_{exo}, °C	no.	ΔT_{endo}, °C	ΔT_{exo}, °C	ΔT_{s},* °C
1'	220–260	230–340	**1**	150–240	230–390	200–265
2'	240–280	250–380	**2**	130–240	250–390	190–250
3'	240–330	310–380	**3**	190–270	280–380	220–270
4'	150–200	230–360	**4**	160–250	230–390	–
5'	250–280	280–350	**5**	140–230	230–400	230 with partial fusion, onset of cross-linking
6'	140–220	215–310	**6**	130–220	215–370	100–210

* Determined by a thermomechanooptical method.

incompleteness of double bond opening or instability of the process. Repeated scanning to a higher temperature (450°C) revealed no exothermic effects. Hence, curing that occurred in these monomers in the course of the first scanning to 400°C went to completion, and a new equilibrium state was formed.

The temperature ranges of the endothermic (ΔT_{endo}) and exothermic (ΔT_{exo}) effects exhibited by the monomers and oligomers, and also the softening ranges (ΔT_{s}) evaluated by a thermomechanooptical method are listed in the table. The lower boundary of the softening range corresponds to the onset of fusion of powder particles, followed by spreading and passing to the hyperelastic state at the upper boundary of this range.

Oligomer **5**, in contrast to the other oligomers, showed no softening range; caking and darkening of the powder started without fusion.

Comparison of the ranges ΔT_{endo} for monomers **1'**–**6'** and oligomers **1**–**6** shows that, in going from monomers to the corresponding oligomers, ΔT_{endo} shifts to lower temperatures in the case of **1**–**3** and **5**, remains virtually the same in the case of **6**, and shifts to higher temperatures in the case of **4**. Comparison of the temperature ranges in which the monomers exhibit endothermic effects (melting) with the softening ranges of the oligomers shows that softening of the oligomers occurs at lower temperatures than melting of the monomers. For example, softening of **3** is complete at 270°C, and melting of **3'**, at 330°C. These differences in the ranges of the endo- and exothermic effects are due to the influence of structural conformational isomerism: Oligomers have a larger number of rotational isomers than the corresponding monomers. In the case of oligomers, the softening range depends on both the chemical structure and the rotational isomerism (number of rotational isomers). Crystallization of oligomers **3** and **4** is due to greater, compared to the other oligomers, conformational freedom because of the presence of the DADPE fragment containing no thermoreactive double bonds, and mesomorphic structure of **1** and **5** is due to specific conformational features of the **C1** fragment, compared to **C2** in amor-

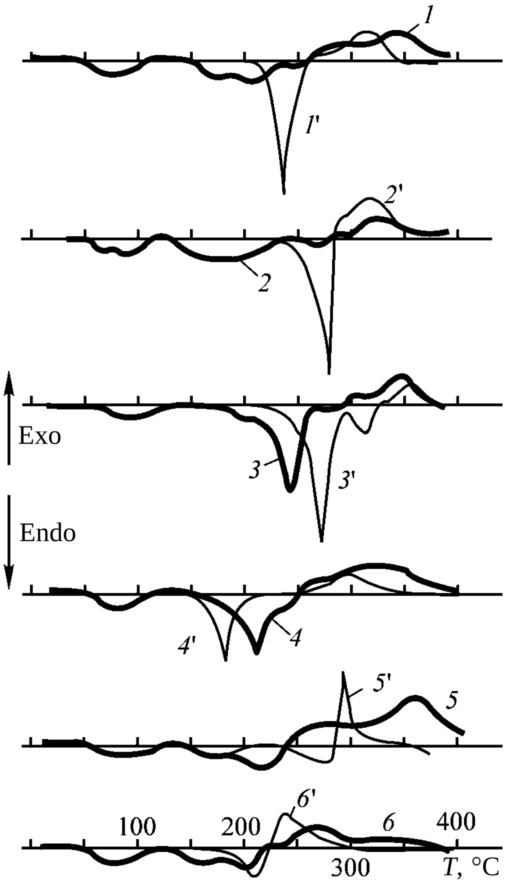


Fig. 2. Thermograms of monomers and oligomers of series I–VI. (*T*) Temperature; the same for Fig. 3.

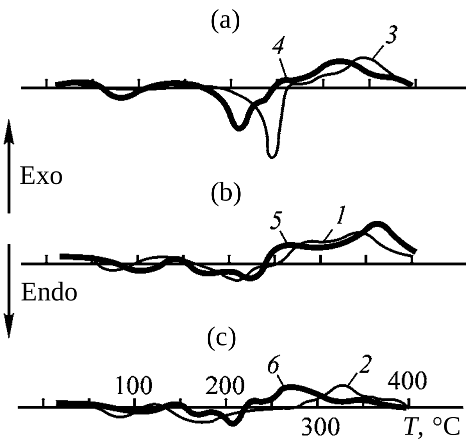


Fig. 3. Thermograms of oligomers (a) **3** and **4**, (b) **1** and **5**, and (c) **2** and **6**.

phous oligomers **2** and **6**. The maximum of the melting peak in the DSC curve of oligomer **3** (Fig. 2) is lower, compared to the corresponding monomer **3**', by 40°C, whereas in the case of **4** it is 25°C higher.

Crystalline oligomer **3** has the lattice similar to that of the monomer, as suggested by coincidence of several reflections, but more defective, as indicated by lower intensity of reflections. The lattice of **4** differs from that of **4**'.

Figure 3 shows the thermograms of the oligomers grouped with respect to the phase state: crystalline (**3**, **4**, Fig. 3a), mesomorphic (**1**, **5**, Fig. 3b), and amorphous (**2**, **6**, Fig. 3c). It is clearly seen that the energy characteristics of the curing transitions correlate with the phase state. The heats of endothermic transitions regularly decrease in going from crystalline (**3**, **4**; 42 kJ kg^{-1}) to mesomorphic (**1**, **5**; 26 kJ kg^{-1}) and amorphous (**2**, **6**; 21 kJ kg^{-1}) oligomers. The respective heats of exothermic transitions are 78, 161, and 51 kJ kg^{-1}. The considerably larger heat of the exothermic transition (curing) in the case of **1** and **5**, with the transition extending to 400°C, is due to the more pronounced conformational isomerism, compared to **2** and **6**.

Within each pair in Fig. 3, the oligomers differ only in the structure of the terminal group. Comparison of the thermograms of **3** and **4**, **1** and **5**, or **2** and **6** reveals the effect of the terminal group on curing. In the case of oligomers **3** and **4** containing the diphenyl oxide unit and no chalcone units, replacement of the terminal norbornenedicarboxylic acid imide group (Fig. 3a, curve *3*) by maleimide group (Fig. 3a, curve *4*) shifts the melting range, curing range, and maximum of the exothermic effect to lower temperatures by 50, 25, and 30°C, respectively.

In the compound with the bischalcone (**C1**) fragment, replacement of the norbornenedicarboxylic acid imide group (Fig. 3b, curve *1*) by the maleimide group (Fig. 3b, curve *5*) affects the melting range of the mesophase insignificantly, but considerably extends the curing range: Curing is not complete even at 400°C, whereas in the case of **1** (Fig. 3b, curve *1*) it is virtually complete at 400°C. In oligomers with the chalcone (**C2**) fragment, the norbornenedicarboxylic acid imide group (Fig. 3c, curve *2*), compared to the maleimide group (Fig. 3c, curve *6*), does not alter the range of transition from the amorphous to softened state but noticeably (by 50 – 60°C) shifts the exothermic effect to higher temperatures. Compound **6** with the maleimide group (Fig. 3c, curve *6*) exhibits the narrowest curing range and the lowest temperature in the maximum of the exothermic effect, 270°C.

The thermograms in Fig. 3 show that the temperature ranges of the exothermic effects of the oligomers with the norbornenedicarboxylic acid imide terminal groups (curves *1–3*) differ to a lesser extent compared to the oligomers with the maleimide terminal groups (curves *4 – 6*). For example, in the case of **4** the exothermic effect is complete at 400°C; in the case of **5**, it is not complete at this temperature; and in the case of **6**, it is complete even at 370°C, which is more favorable for using the oligomer as a binder. Therefore, we chose **6** for further experiments aimed to determine the activation energy of curing. For this purpose, we heated samples of **6** to 523, 533, 543, and 573 K at a rate of 32 deg min^{-1} and obtained the isotherms of heat release capacity Qt. The isotherms plotted in the coordinates Qt–t (Fig. 4a) and $\ln(Qt)$–t (Fig. 4b) show that curing at 523, 533, 543, and 573 K is a first-order reaction; its rate constant is $k = -d[\ln(Qt)]/dt$. Fig. 4c shows a plot of $\ln k$ vs. reciprocal temperature $1/T$. From this plot, we determined the activation energy $E_a = 8.314\, d(\ln k)/d(1/T) =$ 79 kJ mol^{-1}. For cross-linking of bisbornenimide, Liu *et al.* report a somewhat higher value, 94 kJ mol^{-1}. This fact is consistent with our DSC data that oligomers **1** and **3** with the norbornenedicarboxylic acid imide terminal groups exhibit higher temperatures of the onset and end of the exothermic effect and higher heat of curing, compared to **6**.

We found that the course of cross-linking is influenced by preliminary pressing of oligomer powders: The exothermic effect starts at lower temperatures. We performed experiments with samples of oligomer powders compacted before curing at a pressure of 50 atm in a mold with a punch diameter of 10 mm. Upon pressing, the initially weakly colored powders became yellow, dark yellow, and brown, and in some places even dark brown. The temperature of the onset of the exothermic effect decreased after pressing by the following values ΔT_{exo}:

Oligomer	ΔT_{exo}, °C
4	8
1	12
2	17
3	17
5	22
6	36

It is seen that, for **6**, ΔT_{exo} is as large as 36°C, whereas for **4** it only slightly exceeds the measurement error.

The dependence of ΔT_{exo} on the oligomer structure can also be explained by the influence of the concentration of thermoreactive bonds and by conformational features. As in the case of nonpressed powders, the conditions for cross-linking are optimal in **6**.

It should be noted that the influence of pressure on chemical processes was examined in numerous studies. Analysis of their results allows us to interpret the decrease in the temperature of the exothermic effect upon pressing as follows. It is well known that polymerization of many unsaturated organic compounds (olefins, dienes, organosilicon compounds, etc.) accelerates at high pressures. Many monomers that do not polymerize at atmospheric pressure (in particular, tri- and tetrasubstituted ethylenes, aliphatic aldehydes) polymerize at high pressure [5]. Application of a high pressure accelerates polymerization both in liquids and in powders. Furthermore, polymers prepared in the liquid phase at high pressures usually have higher molecular weight [6–8]. The pressure in the course of plastic deformation plays an initiating role in solid-phase polymerization of powders of acrylamide [9] and various heteroarylenes [10]. Solid-phase reactions are accelerate at high pressures also without plastic flow. For example, application of a high pressure considerably accelerated synthesis of the double salt syngenite–schoenite, which allowed its preparation at room temperature [11]. Acceleration of solid-phase reactions at high pressure is due to increase in the number of contacts between particles in the powder. The same factor is apparently responsible for a change in the powder color upon pressing and for a decrease in the curing temperature. In our case, the pressure was insufficient to initiate the reaction, but it decreased the reaction onset temperature.

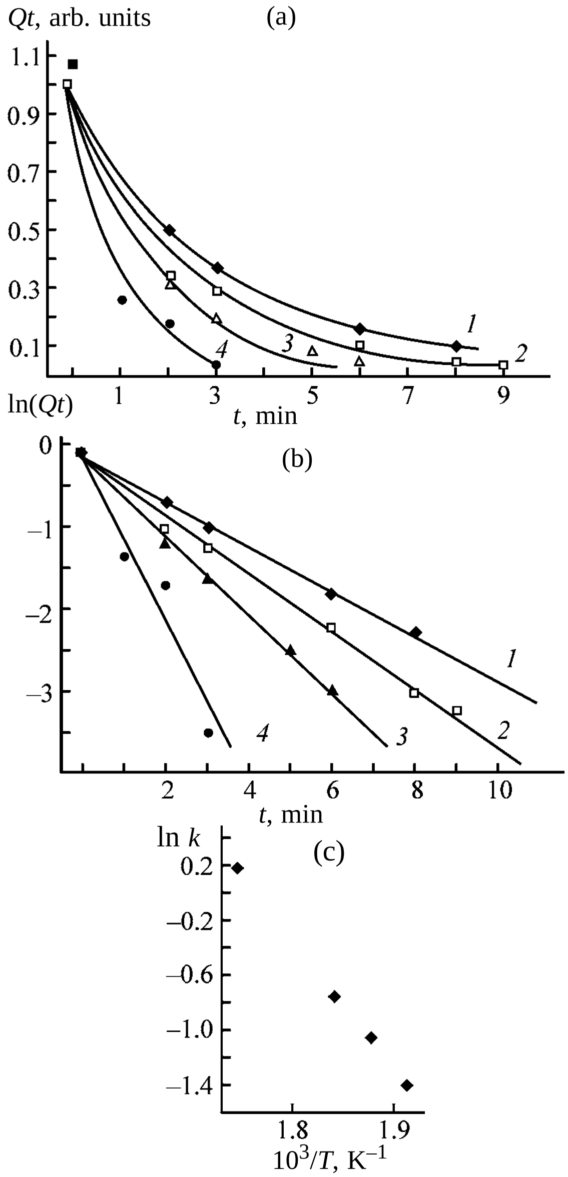


Fig. 4. Thermal and kinetic characteristics of curing of **6**: (a, b) isotherms of the heat release capacity Qt, plotted in the coordinates Qt–time t and $\ln(Qt)$–t; (c) temperature dependence of the reaction rate constant k in the Arrhenius coordinates. T, K: (*1*) 523, (*2*) 533, (*3*) 543, and (*4*) 573.

CONCLUSIONS

(1) Curing of oligomers containing thermoreactive chalcone fragments with norbornenedicarboxylic acid imide and maleimide terminal units was studied. The formula of the oligomer exhibiting the best curing characteristics and showing promise as a binder was suggested, and the activation energy of curing of this oligomer was determined.

(2) Preliminary pressing of oligomers decreases the temperature of the exothermic effect of curing.

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