Kinetics and Mechanism of the Thermal Decomposition Reaction of 3,3-Bis(azidomethyl)oxetane/Tetrahydrofuran Copolymer

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The thermal behavior, mechanism and kinetic parameters of the exothermic decomposition reaction of 3,3-bis(azidomethyl)oxetane/tetrahydrofuran (BAMO/THF) copolymer in a temperature-programmed mode have been investigated by means of DSC, TG-DTG, fast and lower thermolysis/FTIR and TG-MS. The reaction mechanism was proposed. The apparent activation energy and pre-exponential constant of exothermic decomposition reaction of the compound at 0.1 MPa are 167.04 kJ•mol^{-1} and $10^{14.41}$ s^{-1}, respectively. The corresponding critical temperatures of thermal explosion obtained from the onset temperature T_e and the peak temperature T_p are 223.20 and 245.78 ℃, respectively. The kinetic equation of the exothermic decomposition process of BAMO/THF at 0.1 MPa could be expressed as: $\dfrac{d\alpha}{dT} = 10^{15.19} \left[-\ln\left(1-\alpha\right) \right]^{\frac{2}{3}} e^{-2.009 \times 10^4 / T}$

Keywords   BAMO/THF copolymer, thermal decomposition, kinetic parameter, mechanism

Introduction

3,3-Bis(azidomethyl)oxetane/tetrahydrofuran (BAMO/THF, marked as B/T) copolymer can be used as an azide binder of high energy propellants with the lower signature, and lower sensitivity to improve the mechanical properties at lower temperature and the burning rate characteristics. Its decomposition kinetics and the effects of THF on the decomposition kinetics of BAMO copolymers have been reported.[1,2] In the present work, we report the kinetic model function and kinetic parameters of the exothermic decomposition reaction of BAMO/THF (molar ratio 1∶1) copolymer studied by DSC, TG and DTC, and its decomposition mechanism studied with fast and lower thermolysis/FTIR spectroscopy and TG-MS. This is quite helpful to control the chemical properties and sensitivities of rocket propellants.

Experimental

Material

BAMO/THF copolymer used was prepared by Li-Ming Chemical Material Institute. Its mean molecular weight is 6000. The organic function degree is 2, and the humidity is smaller than 0.5%. The structural formula is as Scheme 1.

Scheme 1
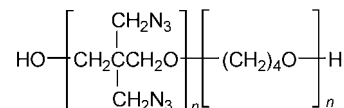
Apparatus and conditions

The DSC data were obtained by a model DSC190S differential scanning calorimeter made in American TA Company. The conditions of DSC were as follows: sample mass, less than 2.00 mg; heating rate, 2, 5, 10 and 20 ℃•min^{-1}; atmosphere, static nitrogen; reference sample, aluminum oxide. The TG/DTG curve was obtained using a model TGA2950 thermobalance. The conditions of TG were as follows: sample mass, less than 1.00 mg; heating rate, 10 ℃•min^{-1}; atmosphere, flowing N$_2$ gas, 50 mL•min^{-1}.

Fast thermolysis/FTIR confirmations were conducted on a Nicolet 60SXR FTIR spectrometer with 1—2 mg of sample spread on the Nichrome ribbon filament. The heating rate (50 ℃•s^{-1}) of the filament was monitored at real-temperature while concurrently detecting the gas products 3 mm above the surface by FTIR spectroscopy. Two scans per second and 5 files per second were corded at a resolution of 8 cm^{-1}. The IR spectra of the condensed phase products for the BAMO/THF copolymer were determined using KBr disc (4000—400

cm^{-1}) on a solid reaction cell of a Nicolet 60SXR FTIR spectrometer. The experimental conditions were as follows: heating rate, 10℃•s^{-1}, 16 scans per file, 8.8 files per second, resolution, 4 cm^{-1}.

The operation conditions for the determination of segment ion of the gas product were: Ar atmosphere, a flowing rate of 25 mL•min^{-1}; heating rate of 10 ℃•min^{-1}. The gas product escaping from the furnace of SETARAM TG92 analyzer entered into BtBalzers Omnistar quadrupole mass spectrometer through a capillary with 150 ℃.

Results and discussion

Thermal behavior and decomposition mechanism

The typical TG-DTG and DSC curves for the thermal decomposition of the B/T copolymer at a heating rate of 10 ℃•min^{-1} are shown in Figures 1 and 2. The TG curve consists of two-stage mass loss process without any stable intermediate product formed in which the first-stage began at about 200.0 ℃ and was completed at 299.47 ℃ accompanied with 40.69% mass loss. More studies have pointed out that the first decomposition of the azide material began from the thermolysis of
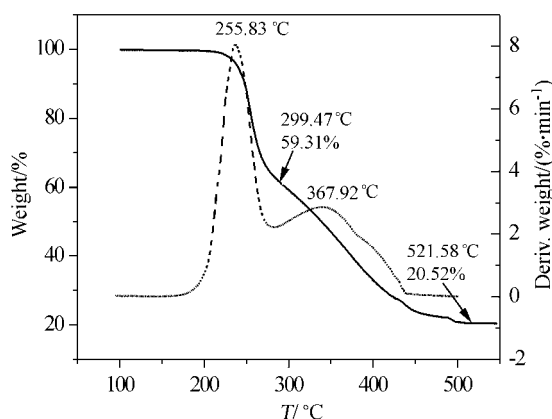
the azide groups.[3,4] Of course, the B/T copolymer also belongs to this kind of material. The second-stage was completed at 521.58 ℃ accompanied with 38.79% mass loss, and the mass percent of the residue was about 20.52%.

Contrasting to TG-DTG curve, DSC curve of the B/T copolymer has only one sharp exothermic peak between 200 ℃ and 300 ℃. The peak temperature T_P and the onset temperature T_e are 258.53 and 236.68 ℃, respectively, and the enthalpy of the exothermic decomposition reaction (ΔH_{dec}) is 2169 J•g^{-1}.

The gas product concentrations of the B/T copolymer are shown in Figures 3—5. It can be seen from them that: (1) the main gas products during the thermal decomposition process of the B/T copolymer are HCN, NH$_3$, CO and N$_2$; (2) poly-THF was observed, which indicates that the THF unit acts as a relatively inert and stable material in the polymer chain and the decomposition of the BAMO unit still dominates the copolymer decomposition over the whole temperature region. The same conclusion is drawn in Ref. 5; (3) with the decomposition being carried out, the gas emersion order can be clearly shown from Figure 5. N$_2$ is mainly released in the first mass loss stage. The concentration of

Figure 1 TG and DTG curves for the B/T copolymer at a heating rate of 10 ℃•min^{-1}.
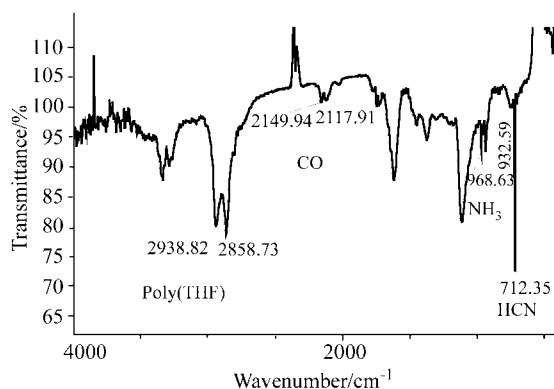
Figure 3 The gas products from the B/T copolymer at about 250 ℃.

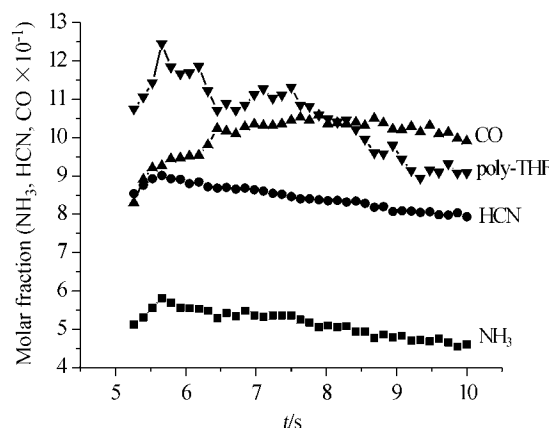**Figure 2** DSC curve for the B/T copolymer at a heating rate of 10 ℃•min^{-1}.

Figure 4 The gas products of the B/T copolymer.

Thermal decomposition
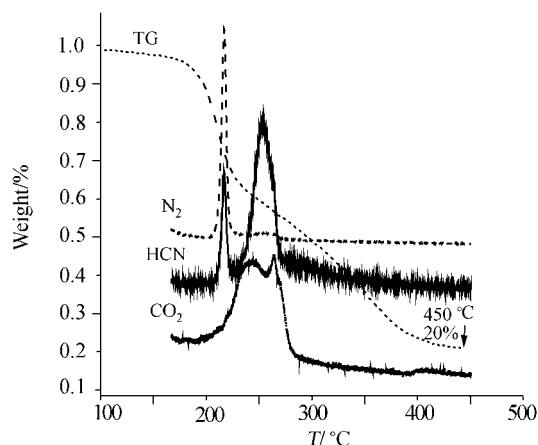
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Figure 5 TG/MS results of the gas products from the B/T copolymer by TG-MS.

HCN gives two high peaks at the first and the second mass loss stages respectively. CO_2 is formed only in the second stage, indicating that the carbon bone is decomposed at the second stage mainly to produce gas product CO_2; (4) the final residue in coacervate phase amounts to about 20%, which is in good agreement with the result in Figure 1.

The typical IR spectra of the condensed phase products at different temperatures during the thermal decomposition process of the B/T copolymer are shown in Figure 6. The corresponding two-dimensional curves for the FTIR relative absorbance intensity vs. time are shown in Figure 7.
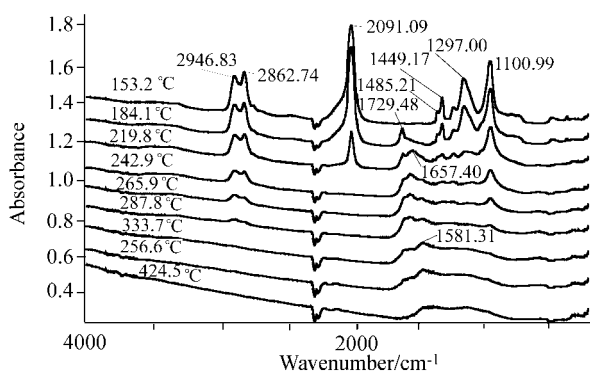

Figure 6 The typical IR spectra of the condensed phase products at different temperatures during the thermal decomposition process of the B/T copolymer (2946.83 cm^{-1}, $v_{as(CH_2)}$; 2862.74 cm^{-1}, $v_{s(CH_2)}$; 2091.09 cm^{-1}, $v_{as(N_3)}$; 1297.00 cm^{-1}, $v_{s(N_3)}$; 1449.17 cm^{-1}, $\delta_{(CH_2-O)}$; 1485.21 cm^{-1}, $\delta_{(CH_2-N_3)}$; 1100.99 cm^{-1}, $v_{as(C-O-C)}$).

It can be seen from Figures 6 and 7 that with increase of temperature, the intensity of characteristic absorption peak of N_3 at 2091.09 cm^{-1} first decreases gradually until disappearance at 242.9 ℃. The intensity of characteristic absorption peak at 100.99 cm^{-1} [$v_{as(C-O-C)}$] also decreases and disappears at 356.6 ℃. This fact shows that the N_3 group is first cleaved from the B/T copolymer at 242.9 ℃. A new weak absorption peak appears at 1729.48 cm^{-1} assigned to C=O, which
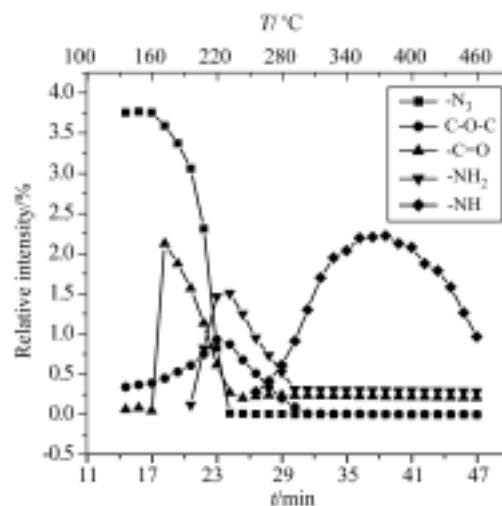

Figure 7 The relative intensity of the characteristic groups of the thermal decomposition products for B/T copolymer vs. time.

may be formed during the bond breaking between the unit of BAMO and that of THF. With increase of temperature, another new absorption peak appears at 1657.40 cm^{-1} along with the characteristic absorption peak at 1729.48 cm^{-1} gradually becoming weak until disappearing. In the same way, following with the peak of 1657.40 cm^{-1}, the characteristic absorption peak at 1581.31 cm^{-1} appears. The peaks at 1657.40 cm^{-1} and 1581.31 cm^{-1} are assigned to δ_{N-H} of the primary amine and the secondary amine, respectively, both of them may be the medium products of the transposition of —CH_2N.

On the basis of above mentioned experimental results, the thermal decomposition mechanism of the B/T copolymer could be shown as Scheme 2.

Analysis of kinetic data

In order to obtain the kinetic parameters (apparent activation energy E_a and pre-exponential constant A) of the exothermic decomposition reaction for the B/T copolymer, a multiple heating method[6] (Kissinger's method) and Ozawa's method[7] were employed. The calculated results (in Table 1) show that E_k was determined to be 158.29 kJ•mol^{-1} and A $10^{13.58}$ s^{-1}. The correlation coefficient r_k is 0.9992. The values of E_o and r_o obtained by Ozawa's method are 155.34 kJ•mol^{-1} and 0.9996, respectively.

The integral Eqs. (1) and (2) are cited to obtain the values of E_a, A and the most probable kinetic model function $G(\alpha)$ from a single non-isothermal DSC curve.[8]

$$\lg G(\alpha) = \lg\left(\frac{AE_a}{\beta R}\right) - 0.4828 E_a^{0.4357} - \frac{0.449 + 0.217 E_a}{0.001} \frac{1}{T}$$

(1)

$$\lg G(\alpha) = \lg\left(\frac{AE_a}{\beta R}\right) - 2.315 - 0.4567 \frac{E_a}{RT}$$

(2)

Scheme 2
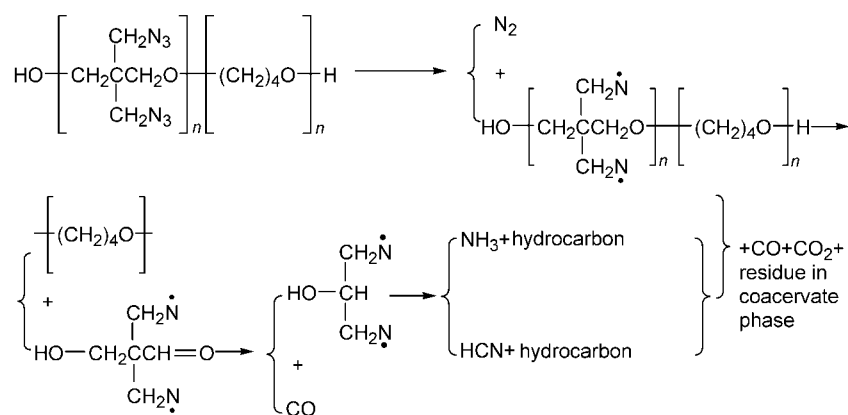
Table 1 Calculated values of the kinetic parameters for the exothermic decomposition reaction of the B/T copolymer determined from the DSC curves at various heating rates [a]

$\beta/(°C•min^{-1})$	$T_e/°C$	$E_o/(kJ•mol^{-1})$	r_o	$T_p/°C$	$E_k/(kJ•mol^{-1})$	$\log A_k$ $(A_k \text{ in } s^{-1})$	r_k	$E_o/(kJ•mol^{-1})$	r_o
2.0	216.38	151.82	0.9996	237.68	158.29	13.58	0.9992	158.85	0.9993
5.0	227.54			249.79					
10.0	236.68			258.53					
20.0	246.97			269.73					

Mean: $E_o = (151.82 + 158.85)/2 = 155.34$ kJ•mol^{-1}

[a] β, Heating rate; T_e, onset temperature in the DSC curve; T_p, maximum peak temperature; E, apparent activation energy; A, pre-exponential constant; r, linear correlation coefficient; subscript k for data obtained by Kissinger's method; subscript o for data obtained by Ozawa's method.

where $G(\alpha)$ is the integral model function, R the gas constant, α the conversion degree ($\alpha = H_t/H_0$), H_0 the total heat effect corresponding to the global area under the DSC curve, H_t the reaction heat at a certain time (corresponding to the partial area under the DSC curve), T the temperature at time t.

Forty-one types of kinetic model functions[9] and DSC data at various heating rates of 2, 5, 10 and 20 °C•min^{-1} such as DSC data listed in Table 2, are put into Eqs. (1) and (2) for calculation, respectively. The values of E_a, A, linear correlation coefficient r, standard mean square deviation Q and believable factor d [where $d = (1-\alpha)Q$] were obtained by the linear least-squares method. The probable kinetic model function of two methods selected by the better values of r, Q and d and satisfying ordinary range of the thermal decomposition kinetic parameters for energetic materials ($E = 80$—250 kJ•mol^{-1} and $\log A = 7$—30) is $G(\alpha) = \frac{3}{2}(1-\alpha)\cdot[-\ln(1-\alpha)]^{\frac{1}{3}}$ and $f(\alpha) = [-\ln(1-\alpha)]^{\frac{2}{3}}$, which indicates that the reaction mechanism of the exothermic decomposition process of the B/T copolymer is classified as nucleation and growth, and the mechanism function is the Avrami-Erofeev equation with $n = 2/3$. Substituting

Table 2 Basic data of the exothermal process of the B/T copolymer determined by DSC[a] at 0.1 MPa [a]

T_i/K	α_i	$(dH/dt)_i/$ $(mJ•s^{-1})$	$(d\alpha/dT)_i$ $\times 10^3/K^{-1}$
461.15	0.0002	0.0429	0.26
463.15	0.0006	0.0641	0.39
465.15	0.0013	0.0936	0.57
467.15	0.0024	0.1251	0.76
469.15	0.0039	0.1696	1.03
471.15	0.0059	0.2233	1.36
473.15	0.0089	0.2856	1.74
475.15	0.0126	0.3663	2.23
477.15	0.0174	0.4598	2.80
479.15	0.0234	0.5686	3.46
481.15	0.0307	0.7009	4.27
483.15	0.0399	0.8594	5.23
485.15	0.0512	1.0455	6.37
487.15	0.0650	1.2660	7.71
489.15	0.0813	1.5223	9.27
491.15	0.1009	1.8282	11.14
493.15	0.1249	2.1873	13.32
495.15	0.1545	2.6013	15.85

Thermal decomposition

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Continued

T_i/K	α_i	$(\mathrm{d}H/\mathrm{d}t)_i$/ $(\mathrm{mJ \cdot s^{-1}})$	$(\mathrm{d}\alpha/\mathrm{d}T)_i$ $\times 10^3/\mathrm{K}^{-1}$
497.15	0.1874	3.0896	18.82
499.15	0.2275	3.6534	22.25
501.15	0.2742	4.2876	26.12
503.15	0.3284	4.9949	30.43
505.15	0.3928	5.7205	34.85
507.15	0.4645	6.4017	38.99
509.15	0.5437	6.9211	42.16
511.15	0.6256	7.1195	43.37
513.15	0.7106	6.7984	41.41
515.15	0.7887	5.9450	36.21
517.15	0.8577	4.6165	28.12
519.15	0.9070	3.3219	20.23
521.15	0.9417	2.2351	13.61
523.15	0.9636	1.4571	8.88
525.15	0.9782	0.9040	5.51
527.15	0.9870	0.5592	3.41
529.15	0.9924	0.3395	2.07
531.15	0.9957	0.2040	1.24
533.15	0.9976	0.1230	0.75
535.15	0.9988	0.0068	0.41
537.15	0.9995	0.0369	0.22
539.15	0.9999	0.0142	0.09

[a] $T_0 = 453.15$ K; $H_0 = 4925.07$ mJ; $\beta = 0.0333$ K$\cdot$s^{-1}.

$f(\alpha)$ with $[-\ln(1-\alpha)]^{\frac{2}{3}}$, E with 167.04 kJ$\cdot$mol^{-1}, β with 0.1667 K$\cdot$s^{-1} and A with $10^{14.41}$ s^{-1} in Eq. (3),

$$\mathrm{d}\alpha/\mathrm{d}T = \frac{A}{\beta} f(\alpha) e^{-E/RT} \tag{3}$$

we can now establish the kinetic equation of the exothermic decomposition process of the B/T copolymer as follows:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = 10^{15.19} [-\ln(1-\alpha)]^{\frac{2}{3}} e^{-2.009 \times 10^4/T}$$

The corresponding kinetic parameters are summarized in Table 3.

Critical temperature of thermal explosive

In order to obtain the critical temperature of thermal explosion for T_b the B/T copolymer, Eqs. (4) and (5) were used.

$$T_{(e \text{ or } p)_i} = T_{e0 \text{ or } p0} + b\beta_i + c\beta_i^2, \quad i = 1-4 \tag{4}$$

$$T_b = \frac{E_o - \sqrt{E_o^2 - 4E_o RT_{e0 \text{ or } p0}}}{2R} \tag{5}$$

where b and c are coefficients, R is the gas constant (8.314 J$\cdot$mol$^{-1}\cdot$K^{-1}), E_o is the value of E obtained by Kissiger's method.

Table 3 Calculated values of kinetic parameters of the exothermal decomposition reaction for the B/T copolymer

β/℃	$G(\alpha)$	$f(\alpha)$	Eq. (1)		Eq. (2)	
			E_a/ (kJ$\cdot$mol^{-1})	$\log A$ (A in s^{-1})	E_a/ (kJ$\cdot$mol^{-1})	$\log A$ (A in s^{-1})
10	$[-\ln(1-\alpha)]^{\frac{2}{3}}$	$\frac{3}{2}(1-\alpha)[-\ln(1-\alpha)]^{\frac{1}{3}}$	170.84[a]	14.80[a]	169.48[b]	14.69[b]
20	$[-\ln(1-\alpha)]^{\frac{2}{3}}$	$\frac{3}{2}(1-\alpha)[-\ln(1-\alpha)]^{\frac{1}{3}}$	149.10[c]	12.58[c]	148.96[d]	12.60[d]
30	$[-\ln(1-\alpha)]^{\frac{2}{3}}$	$\frac{3}{2}(1-\alpha)[-\ln(1-\alpha)]^{\frac{1}{3}}$	175.78[e]	15.31[e]	174.15[f]	15.17[f]
40	$[-\ln(1-\alpha)]^{\frac{2}{3}}$	$\frac{3}{2}(1-\alpha)[-\ln(1-\alpha)]^{\frac{1}{3}}$	174.78[g]	15.13[g]	173.20[h]	14.99[h]

Mean $E_a = 167.04$ kJ$\cdot$mol^{-1}, $\log A = 14.41$

[a] $r = 0.9708$, $Q = 1.9785$, $d = 0.058$; [b] $r = 0.9708$, $Q = 1.9785$, $d = 0.058$; [c] $r = 0.9988$, $Q = 0.0374$; $d = 0.000046$;
[d] $r = 0.9988$, $Q = 0.0374$, $d = 0.00005$; [e] $r = 0.9635$, $Q = 3.7674$, $d = 0.1373$; [f] $r = 0.9635$, $Q = 3.7674$, $d = 0.1373$;
[g] $r = 0.9730$, $Q = 2.1812$, $d = 0.0589$; [h] $r = 0.9730$, $Q = 2.1812$, $d = 0.0589$.

The values T_{e0} and T_{p0} of the onset temperature T_e and the peak temperature T_p corresponding to $\beta \rightarrow 0$ obtained by Eq. (5) taken from Ref. 10 using the data of T_e, T_p and β in Table 1 are 210.25 and 231.64 ℃, respectively.

The values of the critical temperature of thermal explosion (T_b) obtained from Eq. (5) taken from Ref. 10 using the above-mentioned values of T_{e0} and T_{p0}, and the value of E_o in Table 1 are 223.20 and 245.78 ℃, respectively.

Conclusions

The mechanism of thermal decomposition of the B/T copolymer can be expressed as Scheme 1 in the text. The apparent activation energy and pre-exponential constant of the major exothermic decomposition reaction of the copolymer, at 0.1 MPa, are 167.04 kJ•mol^{-1} and $10^{14.41}$ s^{-1}, respectively. The kinetic equation of the exothermic decomposition process of the B/T copolymer at 0.1 MPa can be expressed as

$$\frac{d\alpha}{dT} = 10^{15.19} \left[-\ln(1-\alpha) \right]^{\frac{2}{3}} e^{-2.009 \times 10^4 / T}$$

The critical temperatures of thermal explosion obtained from the onset temperature T_e and the peak temperature T_p are 223.20 and 245.78 ℃, respectively.

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