

Research Article

Preparation and Thermal Decomposition Kinetics of Novel Silane Coupling Agent with Mercapto Group

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Using carbon disulfide and 3-aminopropyltriethoxysilane as raw materials, a novel silane coupling agent with a terminal group was synthesized for the first time. The compound was synthesized in two steps in ethanol water solvent under the action of the catalyst triethylamine and a sulfhydryl-protecting agent. The product was characterized by FT-IR, ¹H NMR, and mass spectra to determine and prove its structure. The best experimental scheme was explored by a single factor experiment: a thiol-protecting agent selected iodomethane, the total reaction time was 2 hours, the two-step reaction temperature was 15°C and 10°C, respectively, and n(carbon disulfide): n(3-aminopropyl three ethoxysilane) = 1.4 : 1. Under these conditions, the product yield was up to 74.28%. Secondly, using the nonisothermal decomposition method, the thermal stability and thermal decomposition enthalpy of a thiohydrazide-iminopropyltriethoxysilane coupling agent were measured by a differential scanning calorimeter (DSC). Thereby, the thermal decomposition kinetic parameters and kinetic equations of the thiohydrazide-iminopropyltriethoxysilane coupling agent were derived.

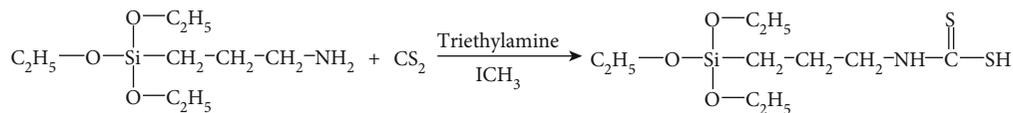
1. Introduction

The mercaptosilane coupling agent is a special kind of organosilicon compound [1]. The structural formula can be represented by OR₃-Si-Y-SH [2], wherein Y represents normally a propyl group and Si-OR₃ represents a siloxy group such as a methoxy or ethoxy group. From this, it was shown that the mercaptosilane coupling agent contains both a carbon functional group reactive with an organic substance and a silicon functional group reactive with an inorganic substance. Due to this special molecular structure, a mercaptosilane coupling agent could be used as a “molecular bridge” [3] between an organic material and an inorganic material to prepare an organic polymer composite having excellent properties. Therefore, mercaptosilane coupling agents are widely used in batteries [4], coatings [5], pollution control [6], composite materials, and other fields.

The mercapto group was oxidized easily. In the presence of free radical-producing substances, sulfhydryl groups could form sulfur radicals through -S atom transfer and ini-

tiate monomer polymerization [7]. Therefore, sulfonium-containing silane coupling agents have attracted the interest of many researchers in the fields of biomedicine [8] and nanoscience [9]. Chen et al. [10] used the two-component initiating system of the mercapto group and benzoyl peroxide (BPO) to initiate the polymerization of HEMA grafted on SiO₂ to study the adsorption of quercetin by SiO₂-g-PHEMA. Motevalizadeh et al. [11] used MPTMS to modify MNP, the mercapto group, and butylactam and formed a two-component initiating system to initiate the copolymerization of St and AL, and studied the rate of drug delivery control. Servant et al. [12] modified organoclay by MPTMS and initiated free radical polymerization on its surface to prepare polystyrene-organoclay composites.

However, in the process of silane coupling and modification of inorganic materials with polymers, many common silane coupling agents require the addition of an initiator to initiate the polymerization of the monomers. If the silane coupling agent has both a polymerization-initiating group and a functional group bonded to the



SCHEME 1: The preparation of thiohydrazide-iminopropyltriethoxysilane coupling agent.

inorganic nanoparticles, the silane coupling agent can initiate polymerization of the monomer while modifying the inorganic nanoparticles, thereby simplifying the reaction step [13].

Therefore, this paper is devoted to the synthesis of a silane coupling agent with both coupling and initiating functions. In this paper, a sulfonyl coupling with a thiol group was prepared by using carbon disulfide and 3-aminopropyltriethoxysilane as raw materials. The structure was confirmed and characterized by FT-IR, ^1H NMR, and mass spectra. Through DSC, the thermal decomposition kinetics of a thiohydrazide-iminopropyltriethoxysilane coupling agent was investigated, including thermal stability, decomposition constants (K_d), and activation energy (E_a), and then the equation of thermal decomposition kinetics was obtained.

2. Experimental

2.1. Materials. 3-Aminopropyltriethoxysilane (KH550), carbon disulfide, and triethylamine were purchased from Aladdin Industrial Corporation (Shanghai, China). Ethanol was purchased from Tianjin Fuyu Chemical Co. Ltd. (Tianjin, China). Methyl iodide was purchased from Shanghai Tanghao Chemical Technology Co. Ltd. (Shanghai, China). n-Hexane was purchased from Tianjin Kemiou Chemical Reagent Co. Ltd. (Tianjin, China). All of the chemicals were AR grade and were used as received without any purification. H_2O used for laboratory experiments was obtained after distillation.

2.2. Preparation of Thiohydrazide-Iminopropyltriethoxysilane Coupling Agent. KH550 (1 g), 5 ml ethanol aqueous solution (water : ethanol = 1 : 17), and 20 ml triethylamine were added into a three-neck flask, stirred at 10°C under a purified N_2 atmosphere. After 20 minutes, carbon disulfide (0.1 g) and methyl iodide (1 g) were added into the three-neck flask. The reaction was continued also at 10°C for several hours. The primary product was obtained by cooled to room temperature.

Finally, n-hexane was used to extract and wash the primary product, and then the final product was collected after drying in vacuum under 60°C for over 24 hours. The final product was a liquid. This part of the experiment process is shown in Scheme 1.

2.3. Characterization. The samples which were compressed with KBr were analyzed by an FT-IR spectrometer (Spectrum Two, PerkinElmer, USA) at room temperature, at a spectral range of $450\text{--}4000\text{ cm}^{-1}$, and at a spectral resolution of 4 cm^{-1} . A Bruker AV600 ^1H -NMR spectrometer (Bruker Technology Co., Ltd., Germany) was used to record the ^1H -NMR spectra. Mass spectra was recorded

using a mass spectrometer (Waters Xevo G2 QTof, Waters Corporation, USA).

5-10 mg sample was added into a crucible and protected by a high-purity N_2 atmosphere. The thermal stability and thermal decomposition dynamics of the product were measured using a DSC 204-F1 (NETZSCH, Germany), ranging from 20 to 350°C at a heating rate of 5°C min^{-1} . The isothermal thermodynamic method was used to obtain the relationship between heat flow and time under constant temperature. Thereby, the thermal decomposition kinetics of the thiohydrazide-iminopropyltriethoxysilane coupling agent was investigated, including thermal stability, decomposition constants (K_d), and activation energy (E_a), and then the equation of thermal decomposition kinetics was obtained [14].

3. Results and Discussion

3.1. Effects of Reaction Conditions on Product Yield

3.1.1. Selection of Mercapto Protective Agent. The sulfhydryl-protective agents mainly include methyl iodide and benzyl chloride [15]. Between them, methyl iodide can be reused. The price of methyl iodide is relatively high, but the actual reaction yield is high, and it can be industrially applied. Although benzyl chloride is inexpensive, according to the method described in the literature, it is necessary to carry out the reaction in a solution of tetrahydrofuran. It has been found that tetrahydrofuran cannot be miscible with the reaction raw materials required for the experiment, and the entire experiment cannot be carried out. Therefore, methyl iodide, a highly effective protective agent, is selected as a sulfhydryl-protective agent.

3.1.2. Effects of Reaction Temperature on Product Yield. According to the single-variable method, a chemical reaction is carried out under the same conditions in addition to reaction temperatures. As could be seen from Figure 1, the yield reaches the highest at 15°C when different reaction temperatures were increased. When the temperature exceeded 15°C , the rate of decrease in yield increased as the temperature increases. When the temperature was lower than 15°C , the radical substitution reaction in the system was inhibited and the product yield was affected. Since the hydrolysis of the alkoxy group attached to the silicon atom (Si-OR) of KH550 made it an unstable group, the silicon atom could be partially broken as the reaction temperature was increased, so that the product was reduced and the product yield was also lowered.

3.1.3. Effects of Reaction Time on Product Yield. Also according to the single-variable method, the chemical reaction was carried out under different reaction times. As could be seen from Figure 2, as the reaction time reached 2 hours, the product yield was the highest. As the reaction time exceeded 2

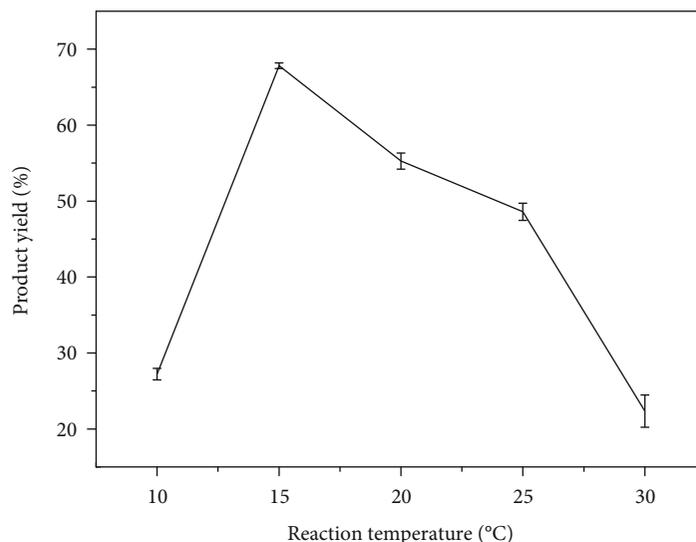


FIGURE 1: Effect of different reaction temperatures on yield.

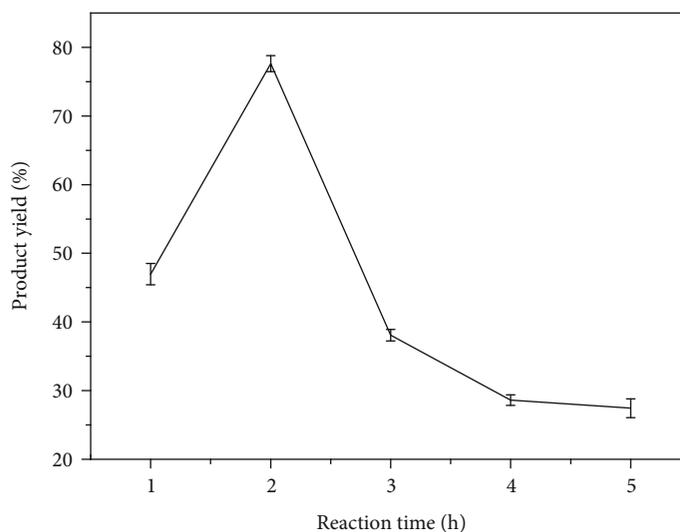


FIGURE 2: Effect of different reaction times on yield.

hours, the product yield also decreased. The radical replacement reaction was required to be carried out at a certain time, and an excessively long reaction time caused the bond between the mercapto group and the carbonyl group to be broken, resulting in the decomposition of the product, which greatly reduced the product yield.

3.1.4. Effects of Material Ratio on Product Yield. The chemical reaction was carried out under different material ratios, as could be seen from Figure 3.

3.2. Confirmation on the Chemical Structure of Thiohydrazide-Iminopropyltriethoxysilane Coupling Agent

3.2.1. $^1\text{H-NMR}$ Analysis. All the functional groups of the product were obtained by $^1\text{H-NMR}$ test, and the results are presented in Figure 4. $^1\text{H NMR}$ (600 MHz, DMSO, TMS): δ 1.10 (m, 9H, OCH_2CH_3), 3.43 (m, 6H, OCH_2CH_3), 0.60

(t, 2H, $\text{Si-CH}_2\text{CH}_2\text{CH}_2$), 1.62 (m, 2H, $\text{Si-CH}_2\text{CH}_2\text{CH}_2$), 2.78 (m, $\text{Si-CH}_2\text{CH}_2\text{CH}_2$), 8.70 (t, 1H, NH), and 9.60 (s, 1H, SH).

3.2.2. FT-IR Analysis. All the functional groups of the product were obtained by FT-IR test, and the results are presented in Figure 5. The peaks that could be seen at 2930 and 2886 cm^{-1} are attributed to the stretching vibration of $-\text{CH}_2-$, the peak at 2586 cm^{-1} is attributed to $-\text{SH}$, the peak at 1443 cm^{-1} is attributed to the hydrocarbon bending vibration of $-\text{CH}_3$, the peak at 1390 cm^{-1} is attributed to the stretching vibration of $-\text{C-C-}$, the peak at 1073 cm^{-1} is attributed to the antisymmetric stretching vibration peak of C-H , the peak at 1067 cm^{-1} is attributed to the stretching vibration peak of C=S , and the peak at 798 cm^{-1} is attributed to the stretching vibration peak of Si-O-CH_3 . From curve (a) and curve (b), the peaks at 2586 cm^{-1} and 1067 cm^{-1} were only attributed to curve (b). This indicated that

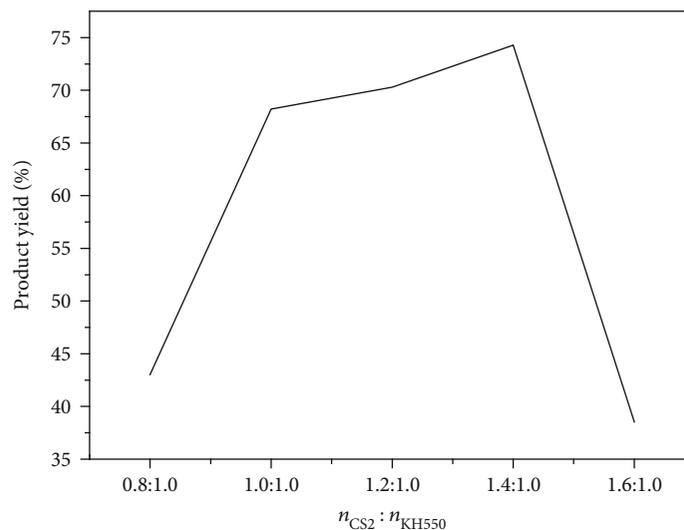


FIGURE 3: Effect of reaction raw material ratio on yield.

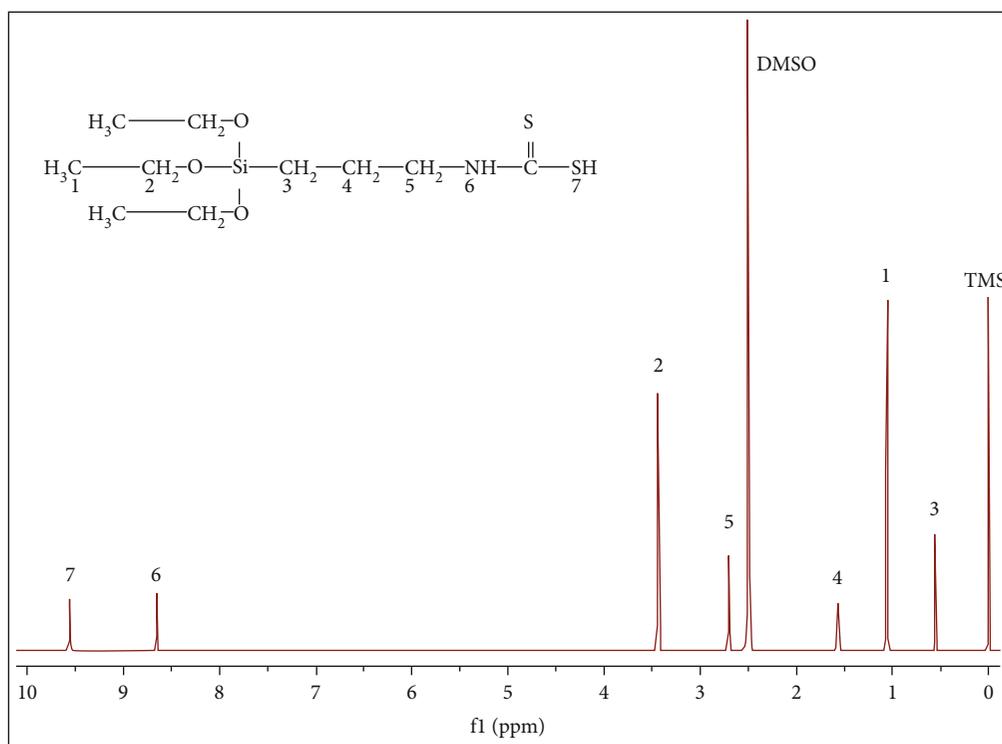


FIGURE 4: ¹H-NMR spectra of the thiohydrazide-iminopropyltriethoxysilane coupling agent.

the thiohydrazide-iminopropyltriethoxysilane coupling agent was successfully synthesized by carbon disulfide and 3-aminopropyltriethoxysilane in a radical substitution reaction.

In summary, a new reagent has been synthesized, and the structural formula is shown in Figure (6)

3.2.3. Mass Analysis. As shown in Figure 6, when the product was broken into pieces by the mass spectrometer, many molecular ion peaks appeared; however, there were stable and symmetrical structures, such as the imino group, the mercapto group, and the ethoxy group. The m/z of 320 was for the thiohydrazide-iminopropyltriethoxysilane coupling

agent. The results generated from the mass-to-charge ratio and possible fragments are shown in Table 1. The characteristic fragment that contained the ethoxy group was identified, which has an m/z of 163.

3.3. Isothermal Thermodynamic Analysis of Thiohydrazide-Iminopropyltriethoxysilane Coupling Agent

3.3.1. Thermal Stability. Figure 7 shows the nonisothermal decomposition curve of a thiohydrazide-iminopropyltriethoxysilane coupling agent. From Figure 7, since the product structure contains a mercapto group, the mercapto group

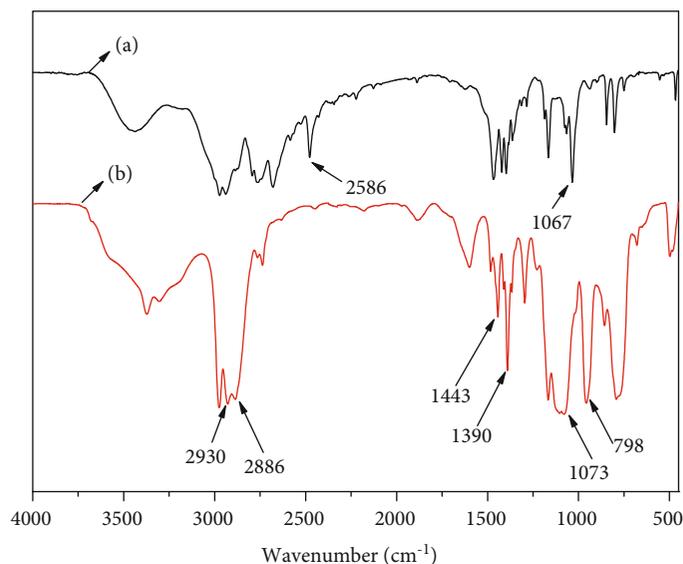


FIGURE 5: FT-IR spectra of products: (a) thiohydrazide-iminopropyltriethoxysilane coupling agent; (b) KH550.

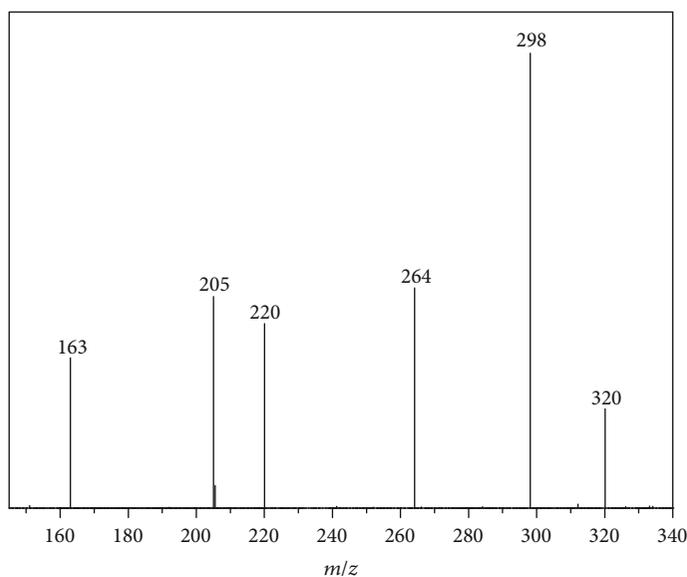


FIGURE 6: Mass spectrum of the product.

TABLE 1: The main fragment of the product analysis.

Mass-to-charge ratio	Possible fragments
163	$(OC_2H_5)_3Si+$
205	$(OC_2H_5)_3Si+C_3H_6$
220	$(OC_2H_5)_3Si+C_3H_6NH$
264	$(OC_2H_5)_3Si+C_3H_6NHSC$
298	$(OC_2H_5)_3Si+C_3H_6NHSCSH$

was thermally decomposed at a certain temperature to generate a radical which could initiate radical polymerization. The decomposition temperature and peak temperature are shown in Table 2. As could be seen from Table 2, the

thiohydrazide-iminopropyltriethoxysilane coupling agent was relatively stable before the temperature was 181.6°C, but as the temperature increases, a significant exothermal appeared. It was due to the decomposition of the thiol group. When the temperature reaches 183.7°C, the thermal decomposition of the thiol group reaches the maximum extent, and the decomposition rate was the fastest at this time. When the temperature continues to rise, the DSC curve could see that its enthalpy value begins to decrease, the thiol group contained in the product gradually decomposes completely, and the heat was in a lost state. Because the temperature was too high, the thiohydrazide-iminopropyltriethoxysilane coupling agent was completely decomposed, so a temperature that was too high was not

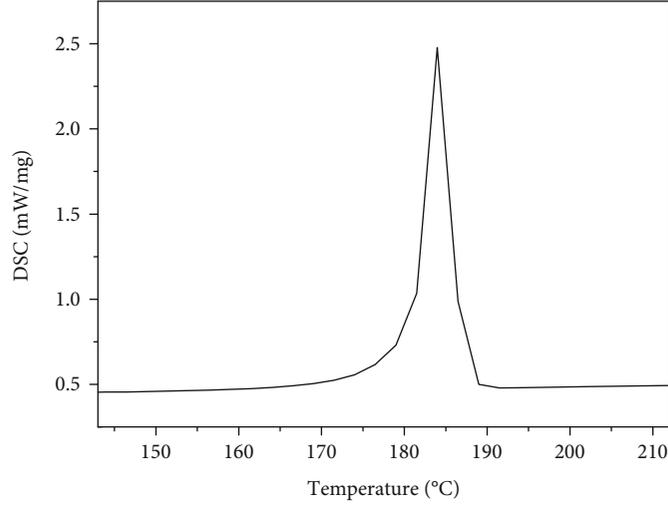


FIGURE 7: Thermal decomposition curve of the thiohydrazide-iminopropyltriethoxysilane coupling agent.

TABLE 2: Thermal decomposition temperature and peak temperature of the thiohydrazide-iminopropyltriethoxysilane coupling agent.

	Decomposition temperature (°C)	Peak temperature (°C)
Thiohydrazide- iminopropyltriethoxysilane coupling agent	181.6	183.7

meaningful for us to study its thermodynamic properties. When the temperature reaches 181.6°C, the heat provided by the entire environment was sufficient for the thiohydrazide-iminopropyltriethoxysilane coupling agent to react rapidly. Therefore, the product was a sulfhydryl-based initiator having thermal initiation properties.

3.3.2. Isothermal Decomposition Kinetic Analysis of Thiohydrazide-Iminopropyltriethoxysilane Coupling Agent. The decomposition rate constant of the reaction product during thermal decomposition is an important parameter for measuring the reaction rate, which can be obtained by changing the concentration of the reactant with time. By calculating the decomposition rate constant, the amount of change in the concentration of the reactant can be obtained, and further, the relative data such as the half-life of the reactant can be obtained by calculation.

(1) *Decomposition Constant (K_d)*. Based on the isothermal decomposing data, K_d could be calculated through the ΔH of decomposition [16]. The reaction is a first-order reaction expressed as follows:

$$R_d = \frac{-dC}{dt}. \quad (1)$$

In the DSC isothermal decomposition mode [17], the change in reactant concentration was unknown and the conversion calculation was performed using thermal enthalpy:

$$\frac{-dC}{dt} = \frac{d\Delta H \cdot C_0}{\Delta H_0 \cdot dt}, \quad (2)$$

$$dC = \frac{d\Delta H \cdot C_0}{\Delta H_0}, \quad (3)$$

$$\frac{C_0}{C} = \frac{\Delta H_0}{\Delta H_0 - \Delta H_{re}}, \quad (4)$$

$$\ln \frac{C_0}{C} = K_d \cdot t. \quad (5)$$

Combining equation (5) with the decomposition equation (4), a new equation (equation (6)) was developed as follows:

$$\ln \frac{\Delta H_0}{\Delta H_0 - \Delta H_{re}} = K_d \cdot t. \quad (6)$$

The half-life and reaction activation energy [18] were determined by a DSC isothermal decomposition mode. It could be seen from Figure 8 that the decomposition rate was the fastest at the initial stage of the isothermal reaction, the heat release was rapidly increased, and then the heat release tended to be stable. At different temperatures, the thiohydrazide-iminopropyltriethoxysilane coupling agent is decomposed for 10 min, 30 min, and 40 min, and the corresponding ΔH is shown in Table 3.

As in equation (6), the data of Table 3 was substituted into this equation. The thermal decomposition rate constant of the thiohydrazide-iminopropyltriethoxysilane coupling agent at different temperatures and different times, respectively, is shown in Table 4.

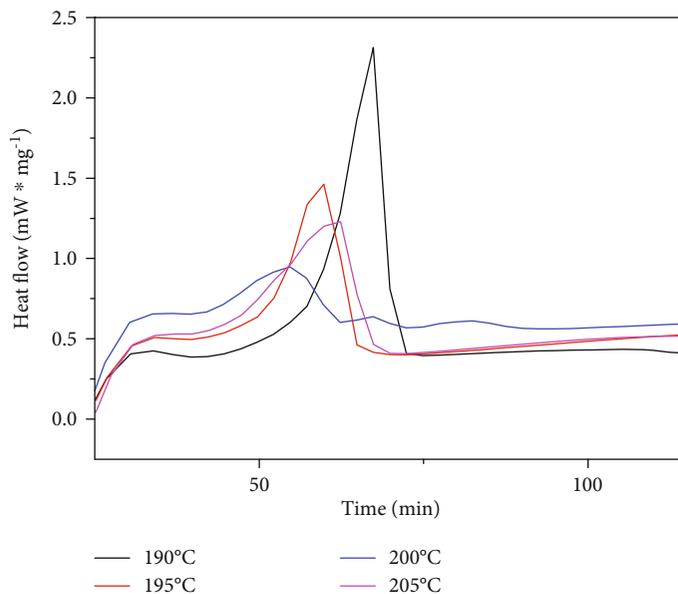


FIGURE 8: Isothermal decomposition curves of products at different temperatures.

TABLE 3: Isothermal decomposition kinetics DSC data of the thiohydrazide-iminopropyltriethoxysilane coupling agent.

	ΔH_0	ΔH_{10} (10 min)	ΔH_{30} (30 min)	ΔH_{40} (40 min)
190°C	290.9 J/g	37.6 J/g	104.6 J/g	135.9 J/g
195°C	299.9 J/g	38.4 J/g	107.1 J/g	139.3 J/g
200°C	315.7 J/g	45.8 J/g	136.3 J/g	173.9 J/g
205°C	327.0 J/g	75.0 J/g	213.9 J/g	281.6 J/g

TABLE 4: The thermal decomposition rate constant of the product at different temperatures.

	$\Delta K_{d10 \text{ min}}$	$\Delta K_{d30 \text{ min}}$	$\Delta K_{d40 \text{ min}}$	Average K_d
190°C	0.0138	0.0149	0.0157	0.0148
195°C	0.0137	0.0147	0.0156	0.0147
200°C	0.0157	0.0188	0.0200	0.0182
205°C	0.0260	0.0353	0.0494	0.0369

The Arrhenius equation equation (7) is as follows:

$$\ln K_d = -\frac{E_d}{RT} + \ln A_d. \quad (7)$$

By plotting $1/T$ and $\ln K_d$, as shown in Figure 9, it could be seen that these points were discrete, and the applied Arrhenius empirical formula is a linear function, so these data points are idealized by linear regression [19].

(2) *Linear Equation Fitting*. In the obtained equation, the intercept [20] represents the logarithm value $\ln A_d$ of the pre-factor in the Arrhenius empirical formula, and the slope represents the negative ratio of the decomposition activation

energy to the gas molar constant $-E_d/R$ in the Arrhenius empirical formula. Therefore, the activation energy of the decomposition reaction is $E_d = 108.155$ kJ/mol, and the preexponential factor is $A_d = 4.773 \times 10^8$. The thermal decomposition kinetic equation of the final thiohydrazide-iminopropyltriethoxysilane coupling agent is as follows:

$$\ln K_d = \frac{-108.155}{RT} + \ln (1.998 \times 10^{10}). \quad (8)$$

4. Conclusion

The thiohydrazide-iminopropyltriethoxysilane coupling agent was synthesized by using carbon disulfide and KH550. The optimal scheme was obtained by a single-factor experiment: the sulfhydryl-protecting agent was methyl iodide, the reaction time was 2 hours, the reaction temperature was 15°C, and $n(\text{carbon disulfide}) : n(\text{KH550}) = 1 : 1$. Under these conditions, the product yield was up to 74.28%. The product was characterized by infrared absorption spectroscopy, ^1H NMR nuclear magnetic resonance spectroscopy, and mass spectrometry. The product was identified as a novel silane coupling agent with the mercapto group.

The thermal decomposition kinetics of the thiohydrazide-iminopropyltriethoxysilane coupling agent was investigated. The thermal stability and thermodynamic parameters were analyzed and calculated by the isothermal decomposition mode. It was found that the decomposition temperature of the thiohydrazide-iminopropyltriethoxysilane coupling agent was between 181.6°C and 187.2°C. Combining the first-order reaction equation and the thermodynamic kinetic equation, the data of the thiohydrazide-iminopropyltriethoxysilane coupling agent under a constant temperature were analyzed, and the calculated decomposition rate constant and temperature value were calculated by the linear fitting method. The decomposition reaction was activated with $E_d = 108.155$

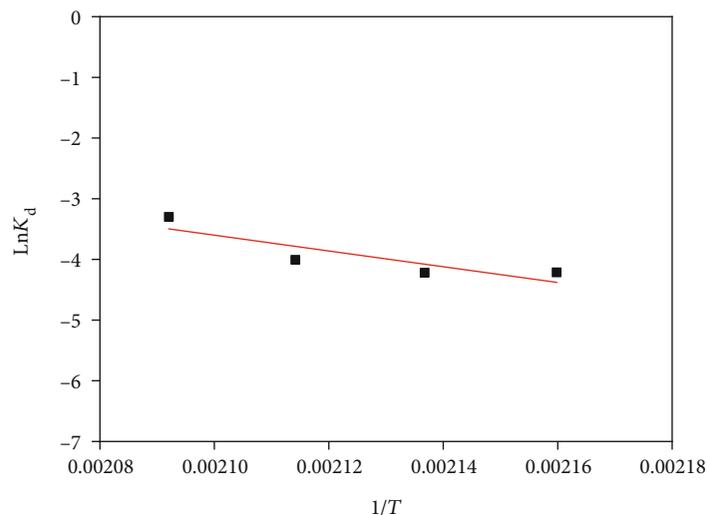


FIGURE 9: Arrhenius equation curve for thermal decomposition data of the thiohydrazide-iminopropyltriethoxysilane coupling agent.

kJ/mol, and the preexponential factor was $A_d = 1.998 \times 10^{10}$. The thermal decomposition kinetic equation of the thiohydrazide-iminopropyltriethoxysilane coupling agent was $\ln K_d = -108.155/RT + \ln (1.998 \times 10^{10})$.

4.1. The Potential of Thiohydrazide-Iminopropyltriethoxysilane Coupling Agent. We named the thiohydrazide-iminopropyltriethoxysilane coupling agent as TIPTS. Modification of Fe_3O_4 nanoparticles by TIPTS obtained Fe_3O_4 -TIPTS. Among fixed-point modifying groups, the site-nucleophilic activity of the thiol group had higher activity than the carboxyl group, the hydroxyl group, the disulfide bond, and so on. Moreover, when Fe_3O_4 nanoparticles were modified by a fixed-point modifying group for the carboxyl group and the hydroxyl group, the disulfide bond could destroy site-nucleophilic activity and the thiol group could retain the site-nucleophilic activity. Then, grafting Fe_3O_4 -TIPTS by polyether-imide (PEI) and polyethylene glycol (PEG) obtained Fe_3O_4 -TIPTS-g-(PEI-co-PEG). Inside, magnetic nanoparticles (MNPs) were used as magnetically responsive carriers, PEG was the surface-modifying agent, and PEI was the drug-loading site with which primary amine reacts with doxorubicin (DOX). Targeting nanoparticles were quite stable in various physiological solutions and exhibited a pH-sensitive property in drug release. Therefore, Fe_3O_4 -TIPTS-g-(PEI-co-PEG) is a promising nanocarrier for targeting tumor therapy in vivo.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

No potential conflict of interest was reported by the authors.

Acknowledgments

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