

# Thermal decomposition behaviour of cobalt(II)-picolyl-terminated poly(dimethylsiloxane)

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**Abstract** A series of coordination polymers, cobalt(II)–[dipicolylamide-propyl poly(dimethylsiloxane)]<sub>s</sub> (Co-DPPDMS), was prepared and studied by thermogravimetry (TG) and double-shot pyrolysis-gas chromatograph-mass spectrometry (Pyro-GC-MS). The TG curves of the Co-DPPDMSs exhibited two events for the mass loss, and the Pyro-GC-MS results suggested that the decomposition reaction of the PDMS chains in the ligand polymer occurred at the second event. The activation energy  $E_a$  and the reaction order  $n$  of each event were estimated by curve fitting based on the order rate equation, and the results were compared with those obtained using the Kissinger method for non-isothermal degradation.

**Keywords** Siloxane · TG · Chain length ·  
Activation energy · Coordination polymer

## Introduction

In recent years, global competition is intensifying for rare metals and energy resources such as oil, natural gas and uranium. Consequently, recycling rare metals has become an important topic [1]. A promising method to recover rare metals from water is to first convert them into coordination polymers and then separate them from the polymers by pyrolysis.

A coordination polymer is attractive not only as a flocculation agent for resource conservation or sewage disposal but also as a material which can design the fine pores of various structures [2]. In general, a coordination

polymer is made of metal ions and low-molar-mass telechelic molecules. For example, it is known that *N,N'*-bis(2-pyridinecarboxamido)-1,4-butane and cobalt(II) form a coordination polymer [3]. Although a variety of characteristic organic ligands can be designed it is expected that the coordination polymer made of these organic ligands will be influenced by temperature. Pyrolysis of coordination polymers proceeds via metal-ligand bond dissociation and ligand decomposition [4]. Therefore, it is very interesting to study how the properties of a coordination polymer are affected by using a macromolecule as a ligand. Due to its superior thermal stability and the easiness of the raw material recovery by pyrolysis, polydimethylsiloxane (PDMS) can be used for diverse applications [5–11]. By using telechelic PDMS as the ligand, the construction of a recycling system can be developed for both the raw material of the ligand polymer and metal [9]. However, it has been reported that the decomposition mechanism of PDMS depends on the terminal groups [6, 11].

Although many investigations have been conducted on the pyrolysis and kinetics of PDMS, only few studies have been reported on its coordination polymers [6, 7, 9]. In this study, a series of coordination polymers Co-DPPDMS was synthesised from dipicolylamide-propyl poly(dimethylsiloxane) (DPPDMS) and cobalt(II) chloride, and their thermal decomposition DPPDMS was studied by TG and pyrolysis-GC-MS.

## Experimental

### Materials

Four different formula mass of Poly(dimethylsiloxane), bis(3-aminopropyl) terminated DAPDMS were used for the

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synthesis of dipicolylamidopropylpoly(dimethylsiloxane) (DPPDMS). DAPDMS with molar masses of 250 (PAM-E), 800 (KF-8010), and 1600 (X-22-161A) were kindly offered by Shin-Etsu Chemical Co., Ltd. DAPDMS with a molar mass of 3200 was purchased from Sigma Aldrich Co. DPPDMS was synthesised from DAPDMS and picolic acid. Cobalt(II)-DPPDMS (Co-DPPDMS) was synthesised from cobalt(II) chloride and DPPDMS in acetonitrile [3]. The number-average molar mass of DAPDMSs and the chemical structure of DPPDMS were determined by  $^1\text{H-NMR}$  in  $\text{CDCl}_3\text{-d}_1$  (Bruker DMX-500).

### Thermal analysis

Thermogravimetry was carried out on a PerkinElmer 7 series/UNIX TGA7 analyser. About 1 mg of a sample was taken in a platinum pan and heated from room temperature to 1173 K at the rates of 1, 2, 5, 10, 20  $\text{K min}^{-1}$  under a nitrogen flow ( $50 \text{ cm}^3 \text{ min}^{-1}$ ). Pyrolysis gas chromatography mass spectroscopy was carried out on a Shimadzu GC-MS-QP2010 gas chromatograph mass spectrometer and a Frontier Laboratory Model PY-2020D double-shot pyrolyser. The pressure of helium gas was set to 50 kPa, total flow quantity  $50 \text{ cm}^3 \text{ min}^{-1}$ . The pyrolysis temperatures were set on the basis of a DTG curve.

### Data analysis

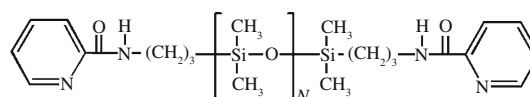
The TG data were analysed in the same manner as that reported by Inoue et al., using the following equation:

$$m = m_1 - (m_1 - m_0) \left( (n-1) (AE_a / \beta R) \times \exp(-5.331 - 1.052E_a / RT) + 1 \right)^{1/(n-1)} \quad (1)$$

where  $m$ ,  $m_1$ ,  $m_0$ ,  $n$ ,  $A$ ,  $E_a$ ,  $\beta$ , and  $R$  are the sample mass at temperature  $T$ , the sample mass at the end of the reaction, the initial mass of the sample, a frequency factor of the reaction, the activation energy for the reaction, the heating rate, and the gas constant, respectively [12]. The values of the activation energy  $E_a$  and the frequency factor  $A$  were obtained using the Ozawa method, and these values were used for curve fitting. After fairly good fitting was obtained, the simulated curve was subtracted from the original TG curve and the resulting curve was analysed by the same method. The reaction order  $n$  of each event was estimated by this method (method 1). The reaction order was also estimated independently by the Kissinger method [13]:

$$n = 1.26S^{1/2} \quad (2)$$

where  $S$  is the absolute value of the ratio of the slopes of tangents drawn to the DTG curve at the inflection point (method 2) (Fig. 1).



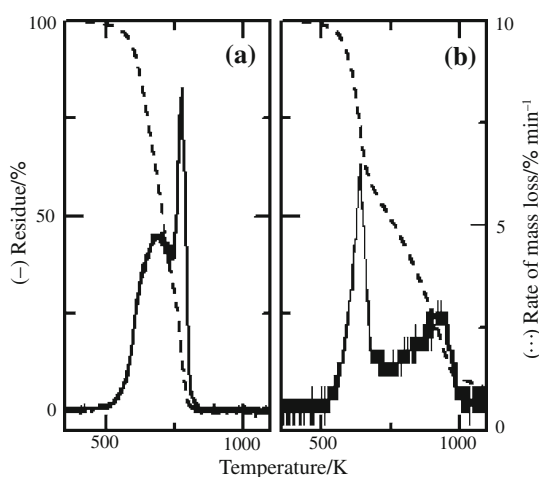
**Fig. 1** Chemical structure of DPPDMS

## Results and discussion

### Thermal degradation behaviour of DPPDMS and Co-DPPDMS

Figure 2 shows the TG curves of the ligand polymer DPPDMS1600 and the coordination polymer Co-DPPDMS1600. These TG curves show that the degradation of the DPPDMS proceeded in one event, whereas that of the Co-DPPDMS proceeded in more than two events. Although the influence of the end-groups on the thermal decomposition behaviours of PDMS has been reported, the structure of the end-groups of a ligand polymer remained unchanged after the synthesis of a coordination polymer [6, 11]. Therefore, from the pyrolysis results, it can be considered that a coordination bond between the end-group of the ligand polymer and the metal ion affects the pyrolysis mechanisms of the ligand polymer.

Table 1 lists each DPPDMS and the corresponding Co-DPPDMS, together with the inherent mass loss temperatures observed on their respective TG curves. The temperature of both, namely, DPPDMS and its Co-DPPDMS increases with the chain length of the PDMS and that of the Co-DPPDMS is slightly higher than that of the ligand, except when the formula mass of the PDMS chain is 250. While the peak temperature of the DTG curve of DPPDMS increases from 608 to 734 K



**Fig. 2** TG/DTG curves of DPPDMS1600 (a) and Co-DPPDMS1600 (b) obtained under nitrogen atmosphere and a heating rate of 10  $\text{K min}^{-1}$

**Table 1** DPPDMS, Co-DPPDMS and the inherent mass loss temperatures

Sample name	$M_n^a$	$N^b$	Onset temperature <sup>c</sup> /K		Temperature <sup>c</sup> for mass loss (5%)/K		Peak temperature <sup>c</sup> /K				Residue at 1173 K <sup>d</sup> /%
							DPPDMS		Co-DPPDMS		
			DPPDMS	Co-DPPDMS	DPPDMS	Co-DPPDMS	1st	2nd	1st	2nd	
DPPDMS250	458	1	564	549	523	539	608	–	573	683	17.8
DPPDMS800	1064	9	554	555	544	572	637	762	636	847	10.5
DPPDMS1600	1962	20	572	592	585	573	681	776	636	928	5.6
DPPDMS3200	3418	42	598	603	542	602	734	928	641	856	5.0

<sup>a</sup>  $M_n$ : Molecular mass of DPPDMS

<sup>b</sup>  $N$ : Number of the dimethylsiloxane unit

<sup>c</sup> Under a nitrogen atmosphere and a heating rate of 10 K/min

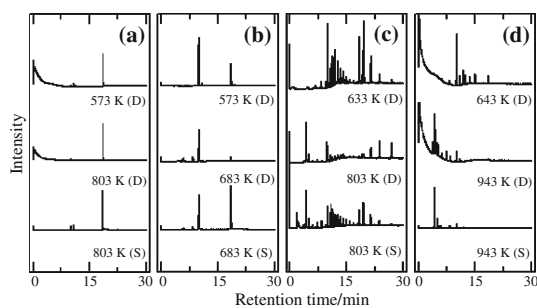
<sup>d</sup> Mixture of PDMS pyrolysis products and cobalt compounds

(at the first peak) and from 762 to 928 K (at the second peak) depending on the chain length, that of the corresponding Co-DPPDMS hardly changes (636–641 K, at the first peak) or changes inconsistently (847–928 K, at the second peak) expect for Co-DPPDMS250. In addition, black residue remained after pyrolysis of the Co-DPPDMS at 1173 K. These results indicate that the pyrolysis of DPPDMS proceeds through complicated volatilisation process that depends on the molecular weight, whereas that of the corresponding Co-DPPDMS proceeds through independent two-step process that is independent of the molecular weight.

#### Pyro-GCMS

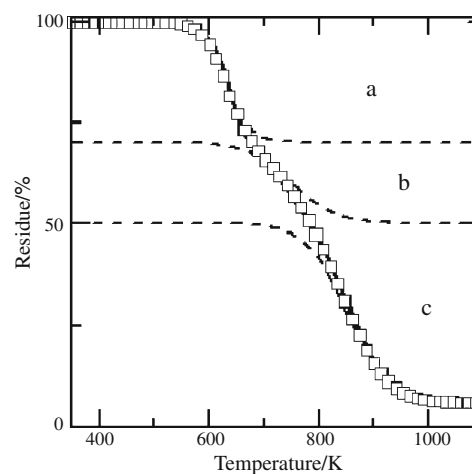
Figure 3 shows the pyrograms of DPPDMS250 and 800 and Co-DPPDMS250 and 800. The pyrograms of DPPDMS1600 and DPPDMS3200 were similar to that of DPPDMS800, but that of DPPDMS250 was clearly different. The pyrogram of Co-DPPDMS250 was also clearly different from that of the other Co-DPPDMSs.

For DPPDMS250, its mass spectrum indicated that its pyrolysis product at 10 min comprises picolyl-substituted



**Fig. 3** Pyrograms of DPPDMS250 (a), Co-DPPDMS250 (b), DPPDMS800 (c), and Co-DPPDMS800 (d) obtained by single- and double-shot pyrolysis. (S) and (D) denote single- and double-shot pyrolysis, respectively

compounds and that the pyrolysis product at 18 min is DPPDMS250 itself. On the other hand, several pyrolysis products occur in DPPDMS800 (c); however, only few pyrolysis products are formed in the case of Co-DPPDMS800 (d). Although an intense peak of picolyl-substituted compounds was observed on the pyrogram of Co-DPPDMS800 obtained at 633 K in double-shot pyrolysis experiment, it decreased the intensity and the peak of hexamethylcyclotrisiloxane was observed instead on the pyrogram at 943 K. The single-shot pyrolysis of the Co-DPPDMS800 at 943 K showed the similar results. These single- and double-shot Pyro-GC-MS results revealed that the depolymerisation of poly(dimethylsiloxane) chain in the coordination polymer does not occur below about 900 K, while the decomposition of DPPDMS starts and yields a random depolymerisation product, including hexamethylcyclotrisiloxane.



**Fig. 4** TG curve of Co-DPPDMS3200 (full line) and calculated curve (open square). The kinetic parameters of the pyrolysis of the coordination polymer were obtained by dividing its TG curve into multiple events: event 1 (region a), event 2 (region b), and event 3 (region c)

**Table 2** Activation energies, frequency factor and reaction order for the pyrolysis of DPPDMS and Co-DPPDMS

Sample name	Method 1 <sup>a</sup>									Method 2 <sup>a</sup>		
	Event 1			Event 2			Event 3			Event 1	Event 2	
	$E_a/\text{kJ mol}^{-1}$	A	n	$E_a/\text{kJ mol}^{-1}$	A	n	$E_a/\text{kJ mol}^{-1}$	A	n	n	n	
DPPDMS250	92	$3.60 \times 10^5$	0.0	–	–	–	–	–	–	–	0.2	–
DPPDMS800	77	$1.05 \times 10^4$	1.0	–	–	–	–	–	–	–	1.4	–
DPPDMS1600	101	$1.94 \times 10^6$	1.0	125	$2.26 \times 10^7$	1.0	173	$2.23 \times 10^9$	0.7	2.5	0.9	0.9
DPPDMS3200	71	$2.48 \times 10^3$	2.0	120	$2.32 \times 10^6$	0.0	169	$5.09 \times 10^7$	2.0	0.3	0.9	0.9
Co-DPPDMS250	118	$2.77 \times 10^8$	2.0	203	$1.40 \times 10^{13}$	1.6	–	–	–	1.8	1.5	1.5
Co-DPPDMS800	138	$9.27 \times 10^8$	1.8	146	$3.09 \times 10^7$	1.7	–	–	–	1.4	1.5	1.5
Co-DPPDMS1600	139	$1.05 \times 10^9$	1.8	149	$1.62 \times 10^7$	1.7	196	$5.10 \times 10^8$	1.3	0.9	0.6	0.6
Co-DPPDMS3200	140	$2.92 \times 10^9$	1.8	92	$1.38 \times 10^4$	1.5	132	$5.40 \times 10^5$	1.5	0.9	0.9	0.9

<sup>a</sup> Method 1 is the same manner that was reported by Inoue et al. and Method 2 is the Kissinger method

### Kinetic approach

The experimental and simulated TG curves of Co-DPPDMS S3200 are shown in Fig. 4. The simulated curve fairly fits with the experimental TG curve. Table 2 lists the estimated parameters of the pyrolysis with the reaction order estimated from the DTG curve using the Kissinger method. When the degree of polymerisation of the ligand molecule was up to 9, the simulation curve was well fitted to the experimentally obtained curve by assuming that the number of events was equal to the number of peaks on the DTG curve. The obtained reaction order was comparatively in good agreement with the value estimated by the Kissinger method. However, the number of peaks on the DTG curve was not appropriate to estimate the number of events in the pyrolysis of the ligand polymer whose degree of polymerisation exceeded 20. The DTG curve calculated from the simulated curve exhibited a good fit to the experimentally obtained DTG curve. Therefore, this simulation is considered to be appropriate to estimate the pyrolysis parameters.

The activation energy for the pyrolysis of the macromonomer is 71–125 kJ mol<sup>-1</sup> at the first stage and about 170 kJ mol<sup>-1</sup> at the second stage. The value of 92 kJ mol<sup>-1</sup> for DPPDMS250 corresponds to its diffusion enthalpy. On the other hand, the value for its coordination polymer is 118–134 kJ mol<sup>-1</sup> at the first stage and 92–203 kJ mol<sup>-1</sup> at the second stage. Since all the kinetic parameters of the first event in pyrolysis of the coordination polymers are almost identical, the activation energy at the first event is attributed to the vaporisation of the pyrolysis products that have picolyl substituent in their structures. Camino and co-workers reported that the activation energy for the pyrolysis of PDMS was 213–256 kJ mol<sup>-1</sup>, which is larger than activation energy estimated for the 2nd event of the coordination polymers

[7]. This may be explained by a catalytic action of cobalt complex in the polymer.

### Conclusions

The thermal decomposition mechanism of the coordination polymer Co-DPPDMS differs from that of the ligand DPPDMS. The onset temperature of the first mass loss depends on the chain length. In most cases, the onset temperature of Co-DPPDMS is higher than that of DPPDMS. The pyrolysis of DPPDMS occurs apparently in one step, and yields various products. On the other hand, the pyrolysis of Co-DPPDMS occurs apparently in two steps, and the PDMS chain is not decomposed in the 1st step. Unless the temperature of the reaction system rises by further 100°, the pyrolysis of this residual does not start. The simulated TG curves fairly fit with the corresponding experimental TG curves. The number of events in a TG curve depends on the chain length of DPPDMS.

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