Thermochimica Acta 639 (2016) 14–19

Contents lists available at ScienceDirect

Thermochimica Acta

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

Thermal degradation kinetics of functional polysiloxanes containing chloromethyl groups

Fuying Dong[a,b,1], Xingrong Sun[a,1], Shengyu Feng[a,*]

[a] *Key Laboratory of Special Functional Aggregated Materials & Key Laboratory of Colloid and Interface Chemistry (Shandong University), Ministry of Education, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, Shandong Province, PR China*
[b] *Shandong Jiaotong University, Jinan 250357, PR China*

ARTICLE INFO

Article history:
Received 24 April 2016
Received in revised form 6 July 2016
Accepted 10 July 2016
Available online 12 July 2016

Keywords:
Functional polysiloxane
Chloromethyl
Thermal degradation
Kinetics
Activation energy

ABSTRACT

Functional polysiloxanes containing chloromethyl groups, namely, α, ω-Trimethylsiloxy-poly(methylchloromethyl)siloxane (PCMS) and α, ω-Trimethylsiloxy-poly(dimethyl-methylchloromethyl) siloxane (PDCMS), were synthesized in this work. The thermal degradation behaviors of the two functional polysiloxanes were investigated through thermogravimetric analysis (TGA) in nitrogen atmosphere. The two functional polysiloxanes exhibited more than two degradation stages in the temperature range of 30 °C–800 °C. The kinetic parameters of the thermal degradation of PCMS and PDCMS were determined with isoconversional methods, including Friedman and modified Kissinger–Akahira–Sunose (KAS) proposed by Starink.

1. Introduction

Functional polysiloxanes play an important role in organosilicon chemistry and have been utilized in various fields. The incorporation of functional groups can change the structure and property of the original polysiloxanes [1,2]. Notably, some functional groups are highly reactive; thus, functional polysiloxanes could be developed into various organosilicon materials [3–5].

Polysiloxane containing chloromethyl groups has elicited much attention because of the activity of chloromethyl groups. Chloromethyl groups could react with most nucleophilic reagents, such as ammonia [6], amines [7–9], organometallic compounds [10,11], carboxylates [12,13], coordination compounds [14], and thioacetate [15]. Thus, novel functional polysiloxanes and relevant polymer materials with new structures and properties can be easily prepared via the reaction between chloromethyl groups and nucleophilic reagents [16,17]. Organosilicon materials possess unique characteristics, such as resistance to high temperatures and chemical stability. Therefore, investigating the thermal stability of functional polysiloxanes containing chloromethyl groups has important scientific and practical significance. From the point of view of science, such an investigation could provide an insight into the molecular structure of polysiloxane and useful suggestions to prepare novel types of organosilicon materials. From the point of view of practicality, such an investigation can provide useful information to predict the organosilicon materials used in a specific application. However, to the best of our knowledge, no research has focused on the thermal properties of polysiloxane containing chloromethyl groups.

Among all thermal analysis techniques, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) are commonly utilized to study the thermal degradation, kinetics, and degradation mechanisms of materials. Recently, many kinetic methods have been applied to analyze and interpret thermal analysis data obtained from TGA or DSC [18–22]. Kinetic methods can be classified into single-heating and multi-heating rate methods. A general review for the implementation of these analysis methods have been provided by the International Confederation for Thermal Analysis and Calorimetry (ICTAC) [23].

In this study, we synthesized polysiloxanes with pendent chloromethyl groups and studied their thermal degradation, kinetics, and degradation mechanism through TGA. Two isoconversional methods, including modified Kissinger-Akahira-Sunose (KAS) by Starink and Friedman, were applied to investigate the degradation kinetics of the functional polysiloxane containing chloromethyl groups. The effect of the introduced chloromethyl units on the thermal degradation behaviors of the polysiloxane was discussed.

---

[*] Corresponding author.
E-mail address: fsy@sdu.edu.cn (S. Feng).
[1] These authors are co-first authors and they contributed equally to this work.

http://dx.doi.org/10.1016/j.tca.2016.07.007
0040-6031/

2. Experimental

2.1. Materials

Toluene and tetrahydrofuran (THF) were dried over sodium and distilled before use. Dichlorodimethylsilane, chloromethyldichloromethylsilane, chlorotrimethylsilane, and octamethylcyclotetrasiloxane (D_4) were utilized without further purification; these materials were supplied by Zhejiang Xinan Chemical Industrial Group Co., Ltd. Purlite CT-175 (a cation exchanger) was supplied by Purlite Company. All other reagents were of analytical grade.

2.2. Techniques

^{1}H NMR spectra were obtained with a Bruker AVANCE 400 spectrometer at 25 °C with $CDCl_3$ as the solvent. Fourier transform infrared spectroscopy (FT-IR) analysis was conducted with a Bruker Tensor 27 with a frequency range between 400 and 4000 cm^{-1}. The molecular weight distribution (MWD) was measured through gel permeation chromatography (GPC) with polystyrene as a standard sample and THF as the eluent. The samples were dried for 24 h in a vacuum oven at 50 °C before TGA measurement. TGA was performed in the temperature range of 30 °C–800 °C in nitrogen atmosphere at different heating rates of 5, 10, 15, and 25 °C/min with a TGA/DSC 1 thermal analyzer (Mettler).

2.3. Preparation of polysiloxanes

2.3.1. α, ω-Trimethylsiloxy-poly(methylchloromethyl)siloxane (PCMS)

PCMS was synthesized through hydrolysis and polycondensation reaction [16,17]. A glass reactor fitted with a reflux condenser, a mechanical stirrer, and a thermometer was charged with a mixture of toluene (40 ml) and distilled water (20 ml). A mixture of chlorotrimethylsilane (0.346 g, 0.003 mol) and chloromethyldichloromethylsilane (21.53 g, 0.132 mol) was added dropwise to the solution under stirring at 20 °C. The reaction mixture was stirred for another 1 h at room temperature. Afterward, the organic layer was separated. The organic layer was washed with 5 wt% Na_2CO_3 aqueous solution and distilled water, dried over $CaCl_2$, and filtered. The solvent was removed via distillation, and then 12.38 g of transparent oil (PCMS) was obtained (yield: 86%).

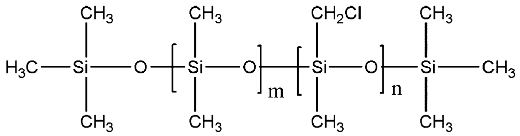
$$^1\text{H NMR}\,(\text{CDCl}_3): \delta = 0.15\,\text{ppm}\,(\text{s},\ \text{C}H_3\text{Si}),\ \delta = 2.71\,\text{ppm}\,(\text{s},\ \text{C}H_2\text{Cl});$$

$$\text{FT-IR}\,(\text{cm}^{-1}):\ 2962,\ 2906\,(\upsilon(\text{CH}_3),\ \upsilon(\text{CH}_2));\ 1261,\ 787\,(\delta(\text{Si-CH}_3));\ 1076\,(\upsilon(\text{Si—O—Si}));\ 1186(\upsilon(\text{CH}_2\text{-Cl}));$$

$$\text{GPC}:\ \overline{M}n = 21300,\quad \overline{M}w/\overline{M}n = 1.25.$$

2.3.2. α, ω-Trimethylsiloxy-poly(dimethyl-methylchloromethyl)siloxane (PDCMS)

PDCMS was prepared through acid equilibration of PCMS and D_4 [16,17]. Copolymerization equilibration was performed at 90 °C for 8 h–10 h. Purlite CT-175 was utilized as the catalyst (2.5 wt%–4 wt% of the reactant) and removed by filtration after the reaction was completed. Transparent oil (PDCMS) was obtained after the reaction mixture was devolatilized by heating at 150 °C/7 mmHg. The yield was 85%.



$$H_3C-\underset{CH_3}{\overset{CH_3}{Si}}-O-\left[\underset{CH_3}{\overset{CH_3}{Si}}-O\right]_m\left[\underset{CH_3}{\overset{CH_2Cl}{Si}}-O\right]_n\underset{CH_3}{\overset{CH_3}{Si}}-CH_3$$

Scheme 1. Structures of PCMS (m = 0, n ≠ 0), PDCMS (m ≠ 0, n ≠ 0), PDMS (m ≠ 0, n = 0).

$$^1\text{H NMR}\,(\text{CDCl}_3): \delta = 0.15\,\text{ppm}\,(\text{s},\ \text{C}H_3\text{Si}),\ \delta = 2.71\,\text{ppm}\,(\text{s},\ \text{C}H_2\text{Cl});$$

$$\text{FT-IR}\,(\text{cm}^{-1}):\ 2962,\ 2905\,(\upsilon(\text{CH}_3),\ \upsilon(\text{CH}_2));\ 1261,\ 787\,(\delta(\text{Si-CH}_3));\ 1075\,(\upsilon(\text{Si—O—Si}));\ 1186\,(\upsilon(\text{CH}_2\text{-Cl}));$$

$$\text{GPC}:\ \overline{M}n = 16600,\quad \overline{M}w/\overline{M}n = 1.35.$$

2.3.3. α, ω-Trimethylsiloxy-polydimethylsiloxane (PDMS)

PDMS was prepared through ring-opening polymerization of D_4 and the process was similar to that of PDCMS [16,17].

$$^1\text{H NMR}\,(\text{CDCl}_3): \delta = 0.07\,\text{ppm}\,(\text{s},\ \text{C}H_3\text{Si}).$$

$$\text{FT-IR}\,(\text{cm}^{-1}):\ 2962,\ 2906\,(\upsilon(\text{CH}_3),\ \upsilon(\text{CH}_2));\ 1261,\ 787\,(\delta(\text{Si-CH}_3));\ 1076\,(\upsilon(\text{Si—O—Si})).$$

$$\text{GPC}:\ \overline{M}n = 18500,\quad \overline{M}w/\overline{M}n = 1.33\,.$$

The structures of the above three polysiloxanes are shown in Scheme 1.

3. Results and discussion

3.1. Thermal degradation

The thermal degradation behaviors of polysiloxanes containing chloromethyl groups were investigated through TGA in nitrogen atmosphere at heating rate of 10 °C/min. For comparison, the thermal degradation behavior of PDMS was also measured through TGA.

The TG and DTG curves of PCMS, PDCMS, and PDMS are shown in Figs. 1 and 2, respectively. More than two degradation stages were observed in the thermal degradation behaviors of PCMS and PDCMS in the temperature range of 30 °C–800 °C in nitrogen atmosphere, as shown in Fig. 2. Particularly, PDCMS exhibited more degradation shoulder peaks than PDMS, indicating that the degradation mechanism of PDCMS is more complicated than that of PDMS. Fig. 2 shows that PCMS decomposed rapidly at temperatures ranging from 180 °C to 360 °C in the first degradation stage, in which the highest rate of degradation occurred and the largest amount of mass loss (60%) was observed. This thermal behavior was different from that of PDCMS and PDMS in this degradation stage, which is attributed to the thermal rearrangement reactions induced