Short Communication

Thermal degradation kinetics of polyketone based on styrene and carbon monoxide

Jiali Mu, Wenjun Fan, Shaoyun Shan, Hongying Su, Shuisheng Wu, Qingming Jia*

Faculty of Chemical Engineering, Kunming University of Science and Technology, Kunming 650500, PR China

ABSTRACT

Copolymerization of styrene with carbon monoxide to give polyketones (PK) was carried out under homogeneous palladium catalyst and polyaniline (PANI) supported palladium(II) catalyst, respectively. The copolymers were characterized by ^{1}H NMR, ^{13}C NMR and GPC. The results indicated that the PK catalyzed by the supported catalyst has narrow molecular weight distribution (PDI = 1.18). For comparison purpose of thermal behaviors of PK prepared by the homogeneous and the supported catalyst, thermogravimetric (TG) analysis and derivative thermogravimetric (DTG) were conducted at different heating rates. The peak temperatures (396–402 °C) for PK prepared by the supported catalyst are higher than those (387–395 °C) of PK prepared by the homogeneous catalyst. The degradation activation energy (E_k) values were estimated by Flynn–Wall–Ozawa method and Kissinger method, respectively. The E_k values, as determined by two methods, were found to be in the range 270.72 ± 0.03–297.55 ± 0.10 kJ mol^{-1}. Structures analysis and thermal degradation analysis revealed that the supported catalyst changed the microstructures of PK, resulting in improving thermal stability of PK.

Crown Copyright © 2014 Published by Elsevier B.V. All rights reserved.

1. Introduction

Polyketones (PK) obtained by alternating copolymerization of carbon monoxide (CO) with styrene, first reported by Drent [1,2], have attracted great attentions (Fig. 1) [3–5]. Synthesis, properties and applications of PK have turned into an important subject in polymer science [6]. Owing to their unique properties, such as the regular and ordered structures and high crystallinity, PK is endowed with reasonably good mechanical strength and thermal stability. These polymers are used in wide variety of applications, for instance, film coatings, fire-resistance materials, packing materials, and fibers [7]. Moreover, the carbonyl groups containing in PK backbone abundantly enable the materials to be chemically modified to other functional polymers and possess photo-degradation properties [8,9]. As the thermal stability of PK can determine final properties of the material, such as the upper temperature limit, the mechanism of the solid-state process, and the life time, it is significant to investigate the thermal decomposition kinetics of PK.

In order to improve the thermal stability of PK, a series of different methods were employed. Thermal stability of the copolymer can be finely tailored via changing the olefinic comonomers. Thus far, monosubstituted alkenes such as ethylene, propylene and styrene have been well documented as comonomers for copolymerization with CO [10–12]. However, PK formed of various olefins possess a low glass temperature or a high melting point, which limits their industrial applications. Introducing other olefins (e.g. 7-methylenebicyclo [4,1,0] heptane, acrylates, bornadiene, *p*-ethylstyrene etc.) to copolymerization and modifying the structure of α-olefins would greatly improve the polymer properties of PK [13–16]. By contrast, the resulting copolymers would possess functional groups directly attached to the polymer main chain and their properties are expected to be quite different from copolymers. Besides, a great number of researchers are involved to find new cheap and effective catalysts or modify palladium catalysts, which also can affect the microstructures and the properties of PK [17–19].

So far, many papers and patents have focused on effective catalysts [20–22]. Nevertheless, there is no paper can be found detailed studies on the effects of the homogeneous catalyst and the supported catalyst on thermal stability of PK. In order to investigate the thermal degradation behavior of PK, improve the thermal stabilities of PK, and reuse of the catalyst, in this paper, we report on the synthesis of the polyaniline (PANI) supported palladium catalyst in the copolymerization of CO with styrene. Besides, the degradation activation energies and the thermal properties of PK were also investigated.

2. Experimental

2.1. Materials and apparatus

Palladium chloride; 2, 2′-dipyridyl (bipy); ammonium persulphate; *p*-benzoquinone; styrene; *o*-chlorophenol and
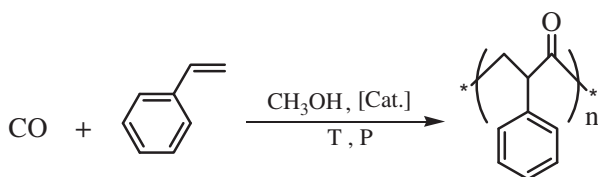
Fig. 1. Copolymerization of monoxide and styrene.

trifluoromethanesulfonic acid were purchased from Acros and used as received. Aniline was distilled twice under reduced pressure prior to use. ^{1}H and ^{13}C NMR spectra were recorded on Mercury 500 MHz VX type (^{1}H, 500 MHz; ^{13}C, 500 MHz) spectrometer (Bruker, America) using D-chloroform (CDCl$_3$) as the solvent. The molecular weights (M_n and M_w) and molecular weight distribution (PDI) of PK were determined by gel permeation chromatography versus polystyrene standards. The analysis were recorded on Bruker HPLC (model LC-22) with an Altech macrosphere GPC 60 Å column and chloroform as solvent (flow rate 0.6 ml/min). The thermal degradation analysis and differential scanning calorimetry (DSC) of the copolymer was carried out with a STA 449 F3 (Netzsch, Germany) thermogravimetric analyzer from 30 to 700 °C. The mass of samples was fixed as 8 mg and the heating rates employed were 10, 15 and 20 K min^{-1} in aluminum oxide crucibles under constant flow of nitrogen (50 ml min^{-1}).

2.2. Synthesis of polyaniline supported palladium catalyst and polyketone

Freshly distilled aniline (3.06 g, 23 mmol) and ammonium persulfate (7.30 g, 32 mmol) were dissolved in 200 ml (1 M) nitric acid solution, respectively. The two solutions were mixed and then stirred for 30 min. The reaction was allowed to react under unstirred condition for 4 h. Finally, the emeraldine precipitates were collected by filtration and washed with copious amount of distilled water followed by acetone. Then obtained PANI-nitrate salts were stirred for 24 h at room temperature with sodium hydroxide solution (1 M, 400 ml). Thus the deprotonated PANI were filtered and dried at 60 °C for 24 h in a vacuum oven.

In a typical synthesis, 0.3 g of potassium permanganate was added to 30 ml distilled water, stirring until it dissolves. Then 0.7 g deprotonated polyaniline was dissolved into the above solution. The mixtures were allowed to stand for 2 h at room temperature. Finally, the products were washed and dried at 60 °C for 24 h in a vacuum oven to obtain the partial oxidation state PANI.

PANI (0.4 g) was charged into a diluted solution of palladium chloride (PdCl$_2$) [a certain amount of PdCl$_2$ in hydrochloric acid (HCl) was mixed with 30 ml of water, the pH value of the mixture solution (include PANI and PdCl$_2$) is 9.0]. The mole ratio of PANI to PdCl$_2$ was 1.0. The solution was ultrasonic oscillated for 2 h and allowed to stand for 1 h under static condition. The solid was isolated by filtration followed by washing with distilled water and ethanol for several times, then dried at 60 °C under vacuum to obtain the supported PANI/Pd(II) catalyst.

Styrene (20 ml) was transferred into a stainless steel autoclave (500 ml) containing o-chlorophenol (30 ml), methyl alcohol (8 ml) and stirrer. Then catalysts mixture consists of precursor catalyst (0.22 g), bipy (1 mmol), p-benzoquinone (6 mmol) and trifluoromethanesulfonic acid (0.4 mmol) was added to the autoclave. The system was then charged with N$_2$ at 0.5 MPa and CO at 1.0 MPa three times, respectively. The reaction mixture was stirred at 600 rpm under various temperatures (55–85 °C), pressures (2.0–3.5 MPa), and time (1.0–2.5 h). After a period of time, the autoclave was cooled with running tap water, the gas was vented in a fume hood, and then the reaction mixture was quenched

with ethanol. Finally, the catalysts were filtered off and the crude product was purified in CH$_2$Cl$_2$/ethanol several times and the white polyketone (PK) was dried under vacuum overnight at 60 °C.

2.3. Kinetic analysis of the decomposition process

Thermogravimetry (TG) is the most common experiment technique which was employed to study the thermal degradation kinetics of solid. For the kinetics analysis [23–26], it is assumed that a solid to gas phase transformation during the degradation process can be accordance with the following formula:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where α is the conversion degree defined as the ratio of the actual mass loss to the total mass loss, $k(T)$ is the reaction rate constant, $f(\alpha)$ is the kinetics model function that can take various mathematical forms depending on the physical mechanism [27,28].

When the reaction rate constant is expressed by the Arrhenius equation and β as the heating rate, the reaction rate can be defined as Eq. (2),

$$\frac{d\alpha}{dT} = \left(\frac{A}{\beta}\right) e^{-(E_k/RT)} f(\alpha) \tag{2}$$

2.3.1. Flynn–Wall–Ozawa method

Flynn–Wall–Ozawa method (FWO) is a simple method to determine the activation energy value directly from TGA thermal curves [29].

By separating the variables, integrating, Eq. (2) becomes:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T e^{-(E_k/RT)} dT \tag{3}$$

After intergrating the right-hand side of Eq. (3) and taking logarithms, we obtain

$$\ln \beta = \lg \frac{AE_k}{Rg(\alpha)} + \lg p(x) \tag{4}$$

where $x = E_k/RT$, $x = \frac{E_k}{RT}$ $p(x) = \left(\frac{e^{-1}}{x^2}\right) \sum_{n=1}(-1)^{n-1}\left(\frac{n!}{x^{n-1}}\right)$

This method is based on the Doyle's approximation, when $20 \leq x \leq 60$, $\lg p(x)$ may be closely approximated by Eq. (5),

$$\lg p(x) \cong -2.135 - 0.4567 \frac{E_K}{RT} \tag{5}$$

Then, Eq. (4) becomes

$$\lg \beta = \lg \frac{AE_k}{Rg_{(\alpha)}} - 2.135 - 0.4567 \frac{E_k}{RT} \tag{6}$$

Therefore, the apparent activation energy (E_k) can be obtained from the plot of $\lg \beta$ against $1/T$ for a fixed degree of conversion ($\alpha = \text{const}$).

2.3.2. Kinssinger method

Kinssinger method has a correlation between the peak temperature (T_p) and the heating rate (β) [30]. If we assume the order of reaction, then the kinetic function $f(\alpha)$ is shown as follows:

$$f(\alpha) = (1-\alpha)^n \tag{7}$$

where n is the empirical order of reaction.

Substituting Eq. (7) into Eq. (2), we obtain

$$\frac{d\alpha}{dT} = \left(\frac{A}{\beta}\right) e^{-(E_k/RT)}(1-\alpha)^n \tag{8}$$