Thermal behavior of the products of 2-chloro-2-propen-1-ol oligomerization

Joanna Drzeżdżon¹ · Barbara Gawdzik² · Przemysław Rybiński² · Jacek Malinowski¹ · Dagmara Jacewicz¹

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Abstract

The thermal stability of the oligomers obtained by using 2-chloro-2-propen-1-ol as the monomer has been studied. The oligomers were synthesized using chromium(III) and oxovanadium(IV) complexes as the catalysts after activation by modified methylaluminoxane (MMAO-12). The complexes used as the catalysts were polycarboxylate complex compounds of oxovanadium(IV) and chromium(III). The studies have been conducted by two methods: thermal gravimetry and differential scanning calorimetry. The obtained results allow to determine the glass transition temperatures and thermal stability of the oligomers depending on the central catalyst cation Cr^{3+} and V^{4+} .

Keywords Catalyst · Oligomers · Glass transition temperature · Chromium(III) · Oxidovanadium(IV) · Complexes

Introduction

The complexes of chromium(III) and vanadium(IV) are an important group of catalysts in the polymerization of olefins [1]. Among these catalysts are metallocene and non-metallocene compounds. Chronologically, metallocene catalysts were first designed and used in the polymerization. However, in subsequent years, it was found that metallocene catalysts have several disadvantages, and among others, they are unstable at high temperatures, which are cognizable in the technological process on the industrial scale of polymer production [2].

The characterization of oligomers in terms of morphological and chemical properties is very important to use oligomeric materials in industry [3]. The formation of different conformations of the oligomer chain, as well as the crystallization capacity and generally understood thermal stability of the oligomer, is tested to determine the suitability of oligomers for a given technological process [4]. Among the methods allowing to study the behavior of polymers and oligomers under the influence of heat, thermal analysis and

differential scanning calorimetry (DSC) occupy an important place [5]. The temperature of glass transition, the melting temperature, the heat capacity, and the crystallization temperature are parameters characterizing the thermal stability of oligomers and polymers.

The chlorine derivative of allyl alcohol, i.e., 2-chloro-2-propen-1-ol, is commonly used to obtain oligomers [6–8]. 2-Chloro-2-propen-1-ol forms the oligomers with chains containing from 4 to 15 monomers in the case of using chromium(III) complexes as catalysts. So far, the physicochemical properties of oligomers of poly(2-chloro-allyl alcohol) obtained using chromium(III) complexes: $[\text{Cr}(\text{dipic})_2]\text{Hdmbipy} \cdot 2.5\text{H}_2\text{O}$, $[\text{Cr}(2\text{-pic})_2(\text{H}_2\text{O})_2]\text{NO}_3$, $[\text{Cr}(\text{dipic})_2][\text{Cr}(\text{bipy})(\text{dipic})\text{H}_2\text{O}] \cdot 2\text{H}_2\text{O}$, $[\text{Cr}(\text{dipic})(\text{H}_2\text{O})_3]\text{Cl}$, *cis*- $\text{K}[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$, and *trans*- $\text{K}[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ (dipic denotes dipicolinate, dmbipy = 4,4'-dimethoxy-2,2'-bipyridine, 2-pic = picolinate) have been investigated by the following methods: MALDI-TOF MS, ^1H and ^{13}C NMR, IR, and UV–VIS [6–9]. The dipicolinate complexes, i.e., $[\text{Cr}(\text{dipic})_2][\text{Cr}(\text{bipy})(\text{dipic})\text{H}_2\text{O}] \cdot 2\text{H}_2\text{O}$ and $[\text{Cr}(\text{dipic})_2]\text{Hdmbipy} \cdot 2.5\text{H}_2\text{O}$, have the catalytic activities equal to 2609.86 and 2254.57 $\text{g mmol}^{-1} \text{h}^{-1}$, respectively [6]. The picolinate complexes $[\text{Cr}(2\text{-pic})_2(\text{H}_2\text{O})_2]\text{NO}_3$ and $[\text{Cr}(\text{dipic})(\text{H}_2\text{O})_3]\text{Cl}$ exhibit the catalytic activities equal to 1434.33 and 632.5 $\text{g mmol}^{-1} \text{h}^{-1}$, respectively [7, 8], whereas the oxalate complexes: *cis*- $\text{K}[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$ and *trans*- $\text{K}[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$, have very high values of catalytic activities. These values are 2163.25 and

✉ Dagmara Jacewicz
dagmara.jacewicz@ug.edu.pl

¹ Faculty of Chemistry, University of Gdańsk, Wita Stwosza 63, 80-308 Gdańsk, Poland

² Institute of Chemistry, Jan Kochanowski University, Świętokrzyska 15 G, 25-406 Kielce, Poland

3479.15 g mmol⁻¹ h⁻¹ for *cis*-K[Cr(C₂O₄)₂(OH₂)₂] and *trans*-K[Cr(C₂O₄)₂(OH₂)₂·3H₂O] [9], but attention need to be paid to the fact that there is no literature data on the thermal stability of oligomers obtained using the mentioned catalysts, i.e., poly(2-chloroallyl alcohol). The thermal stability of oligomers such as amorphous styrene oligomers, poly(3-hydroxybutyrate), polyethylene terephthalate, oligo[(ε-caprolactone)-co-δ-gluconolactone], poly(2-hexyl-ethylacrylate), and poly(n-butyl acrylate) was investigated recently [10–13]. The temperature drift rate was determined in the vicinity of the glass transition temperature for styrene oligomers [10].

In this reports, we show the results of the studies on the thermal stability of oligomers of 2-chloroallyl alcohol. In particular, we focused on determining the glass transition temperatures of oligomers obtained using catalysts that are polycarboxylate complex compounds of oxovanadium(IV) and chromium(III). These studies have been conducted by two methods: thermal gravimetry (TG) and differential scanning calorimetry (DSC).

Materials and methods

Syntheses

The following complexes: [Cr(dipic)₂]Hdmbipy·2.5H₂O [6], [Cr(2-pic)₂(H₂O)₂]NO₃ [7], [Cr(dipic)₂][Cr(bipy)(dipic)H₂O]·2H₂O [6], [Cr(dipic)(H₂O)₃]Cl [8], *cis*-K[Cr(C₂O₄)₂(H₂O)₂] [9], *trans*-K[Cr(C₂O₄)₂(H₂O)₂·3H₂O] [9], [VO(ida)(H₂O)]H₂O [14], [VO(ida)(bipy)]·2H₂O [14], [VO(ida)(phen)]·2H₂O [15], [VO(oda)(bipy)]·2H₂O [16], [VO(oda)(H₂O)₂] [16, 17], and [VO(oda)(phen)]·1.5H₂O [16, 17] (oda = oxydiacetate, ida = iminodiacetate, bipy = 2,2'-bipyridine, phen = 1,10-phenantroline) were synthesized according to the description available in the literature [14–17].

The composition of the all synthesized complexes was determined using an analyzer CARBO ERBA type CHNS–O 1108. Anal. Calcd for [Cr(dipic)₂][Cr(bipy)(dipic)H₂O]·2H₂O (%): C, 45.95, H, 2.84, N, 8.65. Found: C, 45.88, H, 2.75, N, 8.42. Anal. Calcd for [Cr(dipic)₂]Hdmbipy·2.5H₂O (%): C, 48.41, H, 3.72, N, 8.69. Found: C, 48.25, H, 3.56, N, 8.57. Anal. Calcd for [Cr(dipic)(H₂O)₃]Cl (%): C, 24.52, H, 3.79, N, 4.09. Found: C, 26.64, H, 3.82, N, 4.31. Anal. Calcd for [Cr(2-pic)₂(OH₂)₂]NO₃ (%): C, 36.54, H, 3.07, N, 10.67. Found: C, 36.53, H, 3.07, N, 10.55. Anal. Calcd for *trans*-K[Cr(C₂O₄)₂(OH₂)₂·3H₂O] (%): C, 13.66; H, 2.85; and for *cis*-K[Cr(C₂O₄)₂(OH₂)₂] (%): C, 15.91; H, 1.95. Found for *trans*-K[Cr(C₂O₄)₂(OH₂)₂·3H₂O]: C, 13.41; H, 2.82, and for *cis*-K[Cr(C₂O₄)₂(OH₂)₂]: C, 15.19; H, 1.80. Anal. Calcd for [VO(oda)(H₂O)₂] (%): C, 20.44, H, 3.44. Found: C, 20.42, H, 3.45. Anal. Calcd for [VO(oda)(phen)]·1.5H₂O (%): C, 47.27, H, 3.69. Found: C, 47.17, H,

3.64. Anal. Calcd for [VO(oda)(bipy)]·2H₂O (%): C, 42.94, H, 4.09. Found: C, 42.04, H, 3.32. Anal. Calcd for [VO(ida)(H₂O)]·H₂O (%): C, 20.51, H, 3.84, N, 5.98. Found: C, 21.01, H, 3.57, N, 6.23. Anal. Calcd for [VO(ida)(bipy)]·2H₂O (%): C, 43.08, H, 4.36, N, 10.77. Found: C, 43.08, H, 4.36, N, 10.74. Anal. Calcd for [VO(ida)(phen)]·2H₂O (%): C, 46.38, H, 4.11, N, 10.14. Found: C, 46.47, H, 4.09, N, 10.17.

The oligomerization process

The oligomerization was carried out at atmospheric pressure and under nitrogen atmosphere [6, 7]. The complexes of chromium(III) and oxovanadium(IV) were catalysts after activation by MMAO-12. In the first step, 3 μmol of the complex was dissolved in toluene (2 mL). The exception was [Cr(dipic)₂][Cr(bipy)(dipic)H₂O]·2H₂O, which was used in quantity 1.5 μmol. The prepared solution containing toluene with the complex was poured into a glass tube with a stopper. The solution was constantly mixed using a magnetic stirrer. Then, MMAO-12 (3 mL) was added to the prepared toluene solution. After that the monomer solution 2-chloro-2-propen-1-ol was added dropwise (2-chloro-2-propen-1-ol was purchased from Sigma-Aldrich). All the mixture was stirred for an hour until a gel was obtained. The product was filtered off, dried, and weighed.

TG and DSC tests

The TG studies were performed using the apparatus Jupiter STA 446 F3 purchased from Netzsch Company. The measurements in the range of low temperatures – 140 ÷ 0 °C were performed in helium atmosphere. Thermal analysis in the temperature range of 25 ÷ 550 °C was carried out in air atmosphere. The each sample mass was equal 5 g. The heating rate applied to studies equal to 10 °C min⁻¹.

The differential scanning calorimetry studies were performed using the equipment from Mettler Toledo. The calibration was carried out based on standards of thermal analysis (ind, n-octane). The measurements were conducted in the range from – 150 to 500 °C with the heating rate of 10 °C min⁻¹ in the inert atmosphere. The sample of the oligomer to the measurements was about 5 mg. The liquid nitrogen was used to cooling.

Results and discussion

The chromium(III) and oxovanadium(IV) complexes (Fig. 1) were used as the catalysts to oligomerization 2-chloro-2-propen-1-ol, and the obtained products were investigated by TG and DSC methods. The TG analysis showed that 75% of the oligomer is undergoing thermal decomposition up to 90 °C in the case of [Cr(dipic)₂]Hdmbipy·2.5H₂O and up to 100 °C

Fig. 1 Chromium(III) and oxovanadium(IV) complexes used as the catalysts

in the case of [Cr(dipic)₂][Cr(bipy)(dipic)H₂O]·2H₂O. 85% of the oligomer obtained using [Cr(2-pic)₂(H₂O)₂]NO₃. The oligomer synthesized when applied [Cr(dipic)(H₂O)₃]Cl as the catalyst is characterized by 35% mass loss up to 90 °C and 25% mass loss in the temperature range 100–620 °C. Analyzing the thermal decomposition of oxalate complexes, it can be concluded that the 80% oligomer obtained using *cis*-K[Cr(C₂O₄)₂(H₂O)₂] as the catalyst undergoes the thermal decomposition up to 120 °C. On the other hand, the product of the oligomerization with *trans*-K[Cr(C₂O₄)₂(H₂O)₂]·3H₂O decomposes 85% up to 100 °C. For the complexes of oxovanadium(IV), thermal decomposition occurs in clearly marked stages. The first stage of

the thermal decomposition of the oligomer obtained with [VO(oda)(H₂O)₂] includes 10.2% mass loss up to 200 °C. The second stage continues up to 360 °C and includes 45% mass loss. In the case of [VO(oda)(bipy)]·2H₂O, two steps of the mass loss about 20% are observed up to 340 °C and 480–500 °C. The oligomers synthesized using [VO(oda)(phen)]·1.5H₂O, [VO(ida)(H₂O)]H₂O, and [VO(ida)(bipy)]·2H₂O decompose in three steps: 5% (up to 90 °C), 40% (300–340 °C), 10% (480–520 °C); 6% (100 °C), 45% (220–420 °C), 10% (460–560 °C); and 10% (up to 280 °C), 20% (up to 360 °C), 12% (380–520 °C), respectively. In the case of oligomer obtained using [VO(ida)(phen)]·2H₂O, thermal decomposition occurs in two stages: first at 100 °C

(5% mass loss) and the second in the temperature range 275–500 °C (30% mass loss). The oligomers of 2-chloro-2-propen-1-ol decompose with release CO₂, H₂O, HCl, and CO. The oligomers of poly(2-chloroallyl alcohol) thermally decompose in such a way that first water is released, then CO and HCl, and finally in the largest amounts of CO₂. The fact that some oligomers undergo thermal decomposition in two or three stages may be due to different cross-linking of the chains. The oligomers obtained using the following catalysts decompose the longest as a function of temperature: [VO(oda)(phen)]·1.5H₂O, [VO(ida)(H₂O)] H₂O and [Cr(dipic)(H₂O)₃]Cl. These oligomers thermally decompose to temperatures over 500 °C. The oligomer obtained with using [VO(oda)(bipy)]·2H₂O is the most thermally stable. It only decomposes above 340 °C. The thermal behavior of oligomers is very similar for almost every complex compounds used as catalysts. This may indicate that the oligomers obtained have a similar structure and crosslinking in all cases tested.

The glass transition temperature values for the oligomers obtained using the polycarboxylate complexes of chromium(III) and oxovanadium(IV) were determined by DSC method. An example graph obtained by the DSC method for the oligomer obtained using complex [Cr(2-pic)₂(H₂O)₂]NO₃ as the catalyst is shown in Fig. 2, and the glass transition temperature values for all oligomers are shown in Table 1. Figure 2 shows that the glass transition consists of the following stages: at –89.5 °C is onset, mid-stage occurs at –87.3 °C, deflection is observed at –87.1 °C, and the end of the process occurs at –83.9 °C.

Table 1 Glass transition temperature values for oligomers obtained using these complexes as catalysts

Compound	$T_g/^\circ\text{C}$
[Cr(2-pic) ₂ (H ₂ O) ₂]NO ₃	–87.3
[Cr(dipic) ₂][Cr(bipy)(dipic)H ₂ O]·2H ₂ O	–86.2
<i>cis</i> -K[Cr(C ₂ O ₄) ₂ (H ₂ O) ₂]	–87.5
<i>trans</i> -K[Cr(C ₂ O ₄) ₂ (H ₂ O) ₂]·3H ₂ O	–89.0
VO(oda)(H ₂ O) ₂	–90.5
[VO(oda)(bipy)]·2H ₂ O	–85.9
[VO(oda)(phen)]·1.5H ₂ O	–85.4; –10.3
[VO(ida)(bipy)]·2H ₂ O	–84.5; –15.9
[VO(ida)(phen)]·2H ₂ O	–85.4; –14.6
[VO(ida)(H ₂ O)]·H ₂ O	–87.0
[Cr(dipic)(H ₂ O) ₃]Cl	–86.8; –16.7

The glass transition temperature for polyvinyl chloride (PVC) ranges from 77 to 80 °C depending on the molecular mass [18]. However, for amorphous styrene oligomers, glass transition temperatures are in the range of –53 °C to –3 °C [10]. It is also worth noting that amorphous styrene oligomers undergo thermal decomposition in two stages only [10].

The tested oligomers in this report are of a kind of PVC derivative; however, the glass transition temperature values are diametrically different. It is probably because PVC is a polymer sample, but the samples studied and described in this report are short oligomer chains [19, 20].

Fig. 2 TG, DTG, and DSC curves of the sample of the oligomer obtained using [Cr(2-pic)₂(H₂O)₂]NO₃

Conclusions

Twelve oligomer samples have been tested for thermal stability and to determine their glass transition temperatures. One compound among the tested catalysts, i.e., $[\text{VO}(\text{oda})(\text{bipy})]\cdot 2\text{H}_2\text{O}$, produces the oligomer with the highest thermal stability up to 340 °C. The glass transition temperature values were determined for the oligomers synthesized with using the dipicolinate, oxalate and 2-picolinate complexes of chromium(III) and for oxydiacetate and iminodiacetate complexes of oxovanadium(IV) as the catalysts. The determined glass transition temperature values have very low values in the range from – 90.5 to 10.3 °C. This range is due to different tactics and crosslinking of oligomer chains.

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