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The influence of catalyst remnants on thermal degradation during melt processing of high melting ethylene–carbon monoxide copolymers

Bert Jan Lommerts*

Akzo Nobel Central Research, Velperweg 76, 6824 BM Arnhem, The Netherlands

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Abstract

The thermal stability of alternating ethylene–carbon monoxide copolymers (POK-C_2), synthesised using a palladium-bidentate catalyst, is predominantly determined by the amount of 'active' catalyst species present in as-synthesised polymer for a palladium content >6 ppm. For a lower active palladium content the intrinsic limitations to the thermal stability of the chemical structure become noticeable. It is demonstrated that the thermal stability of polymers prepared under optimised conditions, (e.g. low catalyst content) is sufficient to allow melt processing for at least a few minutes of residence time above the melting temperature. Homogeneous transparent melt crystallised films are obtained and small strands were drawn at 225°C to a ratio of 8. The mechanical properties of these oriented samples are comparable with commercially available PET and PA-6,6 melt spun fibres. The crystalline fraction in these samples is mainly present in the very dense POK-α form, indicating that the formation of a significant amount of bulky chain defects during thermal exposure, like Paal–Knorr and aldol type condensation products, is prevented.

Keywords: Catalyst remnants; Thermal degradation; Melt processing

1. Introduction

Olefin–carbon monoxide co- and terpolymers have attracted great scientific and commercial interest after the development of a new palladium-bidentate catalyst system [1]. This catalyst system enables the production of high melting, high molecular weight flexible chain polymers from cheap feed stock, viz. ethylene and/or propylene and carbon monoxide, at a high rate of polymerisation. High catalyst turnovers have been accomplished, whereas no chemical defects in the olefin–carbon monoxide chain sequence are observed. This polymer is envisioned to be a promising starting material for fibre and other advanced applications, because of the all-trans conformation of the carbon backbone in the crystalline state combined with the intermediate polarity of the slightly bulky carbonyl functionality [2].

An example of the developed catalyst system is the palladium 1,3-bis(diphenylphosphino) propane complex (Pd-DPPP) with weakly co-ordinating *p*-toluenesulfonate anions (*p*-TSA). This system is formed/dissolved in methanol and the polymerisation is carried out in this reaction medium under relatively mild conditions, viz. at an ethylene/CO pressure of 20–100 bar and at a temperature of 30–90°C. The product formed is a milky slurry consisting of white, fluffy high molecular weight polymer and methanol. After washing and drying, a polymer powder is obtained with a bulk density of 100–300 kg/m^3. In general, the as-synthesised polymer still contains remnants of active catalyst (see Fig. 1), and after dispersing in methanol and re-pressurising with ethylene/CO, the polymerisation is reinitiated (often at a different rate). From the mechanism of polymerisation it can be derived that the active catalyst is mainly present in the form of palladium-acyl end groups of non-terminated polymer backbones [1].

The Pd-DPPP/*p*-TSA catalyst is one of the very first systems developed and a modified, though comparable, system is presently used by Shell Chemicals for the commercial production of Carilon™; an ethylene–CO/propylene–CO terpolymer in which about 6 mole% of propylene defects are randomly incorporated into the polymer backbone to improve the melt processability (T_m = 220°C)[1] [3].

* Address. LATEXFALT b.v., P.O. Box 6, NL-2396 ZG Koudekerk aan den Rijn, The Netherlands.

[1] The construction of a second plant for commercial production of Carilon™ in the US has been announced by the Shell Chemicals group in various news media; see for example Ref. [3]. However, more recent information indicates that the strategy for Carilon™ is revisited by the Shell Chemicals group.

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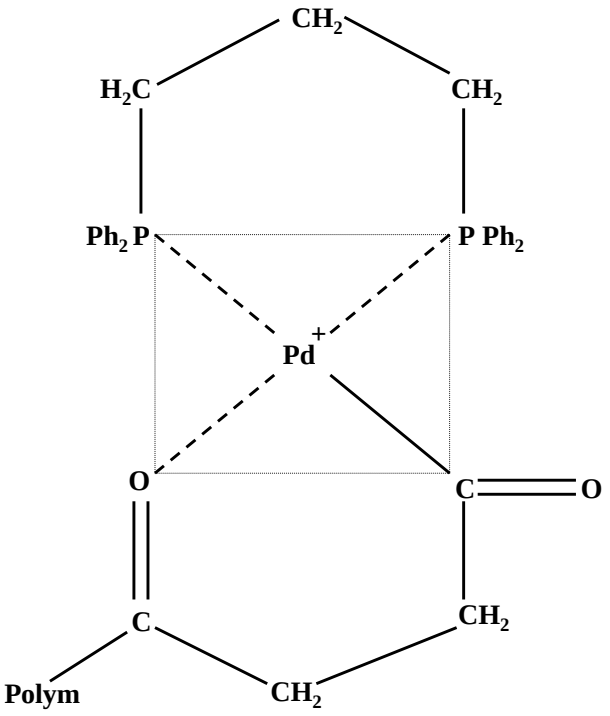

Fig. 1. Schematic presentation of an 'active' palladium-acyl end group in alternating ethylene–carbon monoxide copolymer; the weakly co-ordinating *p*-toluene sulfonate anion(s) are not depicted.

Although propylene defects are, at least to some extent, incorporated into the crystal lattice [2,4–6], the crystallinity, tensile modulus, and dimensional stability of oriented fibres are significantly deteriorated compared with high melting, defect-free ethylene–carbon monoxide copolymer (POK-C_2) [7,8].

To improve the processability of POK-C_2 an intriguing new technique has been developed by Piotrowski et al. [9], i.e. processing a POK-C_2/hemiketal polymer in the melt. The melting temperature of POK-C_2 can chemically, but reversibly, be lowered by means of the formation of a relatively small amount of ketal functionalities during polymerisation. During melt processing, the chemically bonded methanol is released and the melting temperature of the polymer increases with about 5–10°C. Chemical modification has been used for solution spinning purposes (for example cellulose acetate [10] or liquid crystalline cellulose formate [11,12]) followed by hydrolysis. But to our knowledge this approach has never been demonstrated in practice for melt spinning. Obviously, degassing the melt is still the major hurdle to turn this technique into a viable operation.

Processing POK-C_2 from solution has been investigated to avoid any thermal exposure of the polymer. Extensive solvent screening resulted in a practical way to produce fibre material from phenolic solutions, for example resorcinol/water mixtures [13], and excellent mechanical properties have been obtained. Nevertheless, melt processing and spinning is significantly more favourable in view of the far superior economics of these established processes.

In the present report, limitations to the melt processability of ethylene–carbon monoxide copolymers (POK-C_2; T_m = 257°C), produced using the Pd-DPPP/*p*-TSA catalyst system, will be discussed. This high melting polymer has been evaluated to gain insight into the ultimate processing window of as-synthesised polymer and to determine the maximum attainable properties of oriented melt crystallised material.

2. Experimental

2.1. Polymer synthesis

The synthesis of POK-C_2 is described in detail in Ref. [1]. The catalyst system is prepared by dissolving palladium acetate, *p*-toluene sulphonic acid (*p*-TSA) and 1,3-bis(diphenylphosphino) propane (DPPP) in either methanol or acetone in a molar ratio of 1:2:1, respectively. A slight excess of *p*-TSA and DPPP is used to compensate for any losses. After charging this catalyst and solvent to a high pressure autoclave, polymerisation is initiated by pressurising with an ethylene/carbon monoxide (1:1) gas mixture. Synthesis is acetone resulted in a polymer with a limiting viscosity number (LVN: *m*-cresol, 25°C) of 4.8 dl/g. Alcoholic solvents act as chain transfer agents during reaction and, therefore, polymerisation in methanol yielded a lower LVN (i.e. 1.8 dl/g).

2.2. Sample preparation

Extraction of residual palladium complexes can be conducted by means of extraction with 2,4-pentanedione in a temperature range of 80–120°C. Multiple step extraction results in further reduction of the palladium content. Films were produced by placing 5 g of polymer powder between two plates, which were subsequently pressed at sufficient load for 2–3 min at 270°C to obtain films with a thickness varying from 100 to 200 μm. The films were cut into strips of 2–3 mm and these strands were drawn at 225°C in a thermo-rheometer to the required ratio at a draw rate of 100–200%/min. Because some material close to the clamps remained undrawn, the effective draw ratio was determined by dividing the weight per unit of length of the drawn film by the weight per unit of length of unoriented material.

2.3. Analysis

The overall palladium content in the as-synthesised or extracted polymers was determined using standard ICP-MS techniques with an accuracy of ±0.5 ppm. A measure for the thermal stability is obtained by determining the residual melting temperature of the polymer after a thermal exposure in a nitrogen atmosphere, using thermal analysis

techniques. The following temperature program was applied: heating run to 280°C, immediately followed by a cooling run to 20°C, heating run to 280°C, 10 min at 280°C, cooling run to 20°C, and a heating run to determine the residual melting temperature of the polymer. All heating and cooling was performed at a rate of 20°C/min. Time or ageing effects can be excluded as samples aged for 4–8 weeks showed comparable residual melting temperatures (<0.5% variation).

The mechanical properties of the oriented films were determined using an Instron Tensile Tester operating at a crosshead speed of 10%/min at 21°C and 65% relative humidity. The intensity of the 200 and 210 reflections of both the POK-α and POK-β crystal structure was determined by means of radial X-ray diffraction scans. The fraction present in the POK-α form was determined by dividing the intensity of the α-reflections by the intensity of the α and β structures combined.

3. Results and discussion

The chemical nature of the POK-C_2 polymer is such that the polymer is intrinsically sensitive towards thermal and oxidative degradation. The main thermally induced degradation mechanisms are resulting in both intra- and intermolecular condensation reactions, like Paal–Knorr type and aldol type of condensation reactions.

To study the extrinsic effects of residual active catalyst on the thermal stability of POK-C_2, a high molecular weight polymer was synthesised in acetone instead of methanol. This specific solvent has been chosen in order to prevent methanolysis of relatively stable palladium-acyl end groups and subsequent reduction of the palladium compound after polymerisation has been terminated by releasing the CO/ethylene pressure in the autoclave. The as-synthesised polymer was subsequently washed with acetone and dried under mild conditions to avoid decomposition of active catalyst species.

Because of the bulkiness of the thermally induced chain defects (e.g. furan and aldol functionalities), it is assumed that complete exclusion of these defects from the crystalline phase will occur [2,4]. This assumption is not valid for imperfectly alternating copolymers, containing ethylene–ethylene defects, or ethylene–CO/propylene–CO terpolymers. The latter smaller defects can, at least to a certain extent, be accommodated in the orthorhombic POK-β crystal lattice [2].

An indication for the amount of chain defects introduced during thermal treatment can be obtained by measuring the residual melting temperature of the polymer, using standard thermal analysis techniques. The Flory–Huggins relation [14,15] can be applied to relate the amount of thermally induced chain defects to the residual melting temperature.

$$\frac{1}{T} - \frac{1}{T_0} = -\frac{R}{\Delta H_f}\ln(1 - x_{defect}) \quad (1)$$

Assuming first order kinetics in the amount of carbonyl functionality's (C_{CO}) and assuming that the active palladium-acyl end groups act as catalyst for degradation, the rate of defect formation (R/(mole/s)) can be described by

$$R_{defect} = k^* C_{Pd} C_{CO} \quad (2)$$

Combining the Flory–Huggins relation and this first order kinetic expression for initial conditions and constant temperature and time experiments the following simple linear relation is obtained

$$\frac{1}{T} - \frac{1}{T_0} \approx C_{Pd} \quad (3)$$

where T and T_0 are the residual and initial melting temperatures, respectively, and C_{Pd} is the residual active palladium content.

In Fig. 3 the residual melting temperature of the POK-C_2 polymer after a rather extended thermal treatment (10 min, 280°C) is depicted versus the residual active palladium content. For the majority of the experiments, the palladium content in the as-synthesised polymer was varied by means of extraction with 2,4-pentanedione under various conditions (i.e. by variation of extraction time, temperature and washing steps).

The obtained linear dependency allows extrapolation to zero palladium content, and the intercept at $T = T_0$ for $C_{Pd} = 0$, indicates that the thermal degradation mechanism is predominantly of an extrinsic nature.

These findings imply that for active palladium contents >6 ppm, the primary degradation mechanism is determined by hydrolysis (or methanolysis) of palladium-acyl end groups followed by reduction of the palladium compound. This reaction sequence will finally yield metallic palladium and a strong Lewis acid (*p*-TSA). Obviously, the released acid subsequently catalyses both intra- and intermolecular condensation reactions (see Fig. 2).

Free acids can already be present in as-synthesised polymer, due to the catalyst preparation procedures. To exclude the influence of these free acids on the rate of thermal degradation, the same polymer was re-crystallised from solution in propylene carbonate. This solvent is a good acid scavenger, however, the re-crystallised polymer showed no improved thermal stability at a corresponding residual active catalyst content, compared with the as-synthesised polymer (see Fig. 3). Hence, this observation corroborates that the thermal stability of POK-C_2 is predominantly determined by the active palladium content for a palladium content >6 ppm and other effects, like the presence of free acidic remnants, are of minor importance.

This knowledge can be used to further optimise the polymerisation conditions, while applying the same catalyst system. We succeeded in a significant improvement of the thermal stability of as-synthesised polymers [16]. This has been accomplished, amongst others, by increasing the reactor output, optimisation of polymerisation conditions and by improving the washing/extraction procedures. The residual

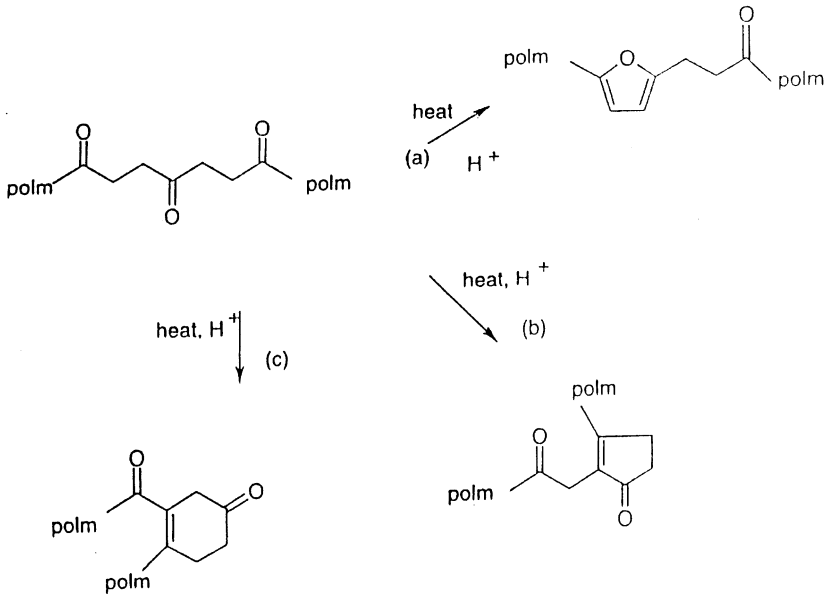

Fig. 2. Acid catalysed heat degradation reactions of 1,4-polyketones: (a) Paal–Knorr furan synthesis; (b) and (c) intramolecular versions of aldol condensations in this polyketone (note that intermolecular versions lead to cross-linking).

melting temperature of these polymers after a thermal treatment at 280°C corresponds to a value for $(1/T - 1/T_0)$ of 0.04–0.07 $[10^3\,K^{-1}]$ for an overall palladium content ranging from 6 to 15 ppm. In this range the thermal stability for polymers synthesised in methanol becomes less dependent on the residual palladium content, which can most likely be attributed to the presence of reduced palladium in the polymer samples.

The accomplished improvement of the thermal stability is sufficient to allow the processing of the polymer in the melt for at least a few minutes, even without the use of certain acid scavenging stabilisers or anti-oxidants. Melt crystallised films (LVN = 1.8 dl/g) were prepared by compression moulding at a temperature of 270°C. A white homogeneous, transparent, flexible film is obtained and only some gas inclusions were visible at the edges of the films, which can be attributed to oxidative degradation. By contrast, compression moulded films prepared from less stable as-polymerised unwashed polymer, hence, samples with a high active catalyst content, are rubber-like and have a dark green or brown colour and small black spots can be observed visually. Moreover, these samples show a significant increase in melt viscosity during compression moulding due to severe cross-linking.

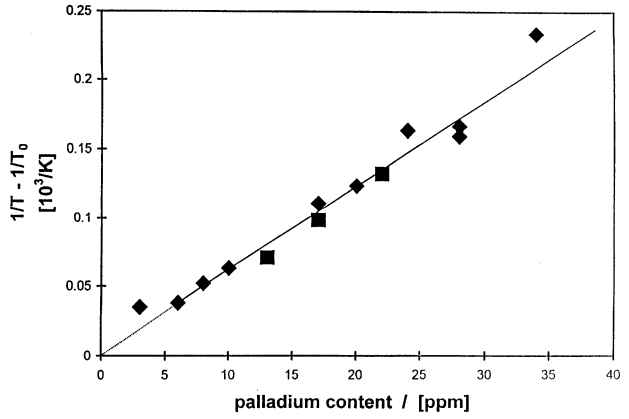

Fig. 3. The influence of the residual 'active' catalyst content on the residual melting temperature of POK-C_2 polymer after 10 min of thermal treatment at 280°C (T_0 = 530 K is used for all polymer samples). ◆ — as-synthesised polymer synthesised in acetone and subsequent extraction with 2,4-pentanedione under various washing conditions. ■ — re-crystallised polymer from propylene carbonate and subsequent palladium extraction with 2,4-pentanedione.

The colourless films prepared from thermally stable polymer were cut into thin strands, which were drawn at a temperature of 225°C; the maximum attainable draw ratio was limited to a value of 9. The observed mechanical properties of oriented samples drawn to a ratio of 8 are listed in Table 1.

In view of the applied sample preparation and drawing procedure the potential of melt crystallised POK-C_2 for fibre applications is evident; the attained tensile strength is simi-

Table 1
Comparison of the mechanical properties of melt crystallised oriented POK-C_2 films, drawn to a ratio of 8, with commercially available poly(ethylene terephthalate) and polyamide-6,6 fibres

Fibre	Tenacity (GPa)	Tensile modulus (GPa)	Elongation at break (%)
Oriented POK-C_2 film	0.9–1.0	10–11	10–11
PET Diolen™ 1125	1.0	15	10
PA-6,6 Enka Nylon™	1.0	7	19

lar to those of commercially available high speed melt spun industrial poly(ethylene terephthalate) or polyamide-6,6 fibres.

A second indication for the good thermal stability of the as-synthesised polymer samples under consideration is derived from the observed crystal structure in the oriented samples. In solution spun defect-free oriented POK-C_2 samples solely the dense POK-α (orthorhombic) structure is observed at room temperature [2]. The incorporation of more than 2–3 mole% of propylene defects into the polymer chain already prevents the exclusive formation of the POK-α structure and a certain amount of the less dense POK-β (orthorhombic) structure is observed at room temperature. In the latter structure the carbonyl dipoles are differently arranged than in the POK-α structure and due to its lower density, this structure is better suited to accommodate chain defects [4]. Samples with a propylene defect content above 5–6 mole% crystallise exclusively in the POK-β form.

More bulky defects, like the thermally induced furan or aldol type of functionalities, will have a stronger deteriorating effect on the formation of the dense POK-α structure, than for example propylene defects. In addition to the larger size of these thermally induced defects, also the conformation characteristics of an extended chain are significantly distorted (see Fig. 2).

For the oriented samples, produced from the melt crystallised films, the crystalline fraction is for 60–90% present in the POK-α form and, hence, the formation of the less dense POK-β form is strongly avoided. This result implies that the formation of bulky chain defects, due to thermal degradation, is limited.

4. Conclusions

The thermal stability of alternating ethylene–carbon monoxide copolymers (POK-C_2) is mainly determined by the residual active catalyst content, present in the form of non-terminated palladium-acyl bonds. At elevated temperatures the palladium complex decomposes forming metallic palladium and a strong Lewis acid (*p*-TSA), which subsequently catalyses various intra- and intermolecular condensation reactions in the 1,4-polyketone. The effect of thermal treatment on the residual melting temperature of the polymer can be described by means of first order kinetics in combination with the Flory–Huggins melting point relation.

At palladium contents <6 ppm, intrinsic limitations to the thermal stability of the 1,4-polyketone structure become noticeable. However, the thermal stability for polymers prepared under optimised conditions is sufficient to allow melt processing of the polymer for at least a few minutes of residence time above the melting temperature. Even without the use of appropriate stabilisers, homogeneous, transparent films can be moulded in which no discoloration was observed. Hot drawing results in oriented structures with mechanical properties similar to those of commercially available meltspun fibres. The crystalline fraction in these fibres is mainly present in the dense POK-α form.

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