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Scaling-up of poly(vinyl chloride) prepared by single electron transfer–degenerative chain transfer mediated living radical polymerization in water media—II: High molecular weight-ultra stable PVC

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ABSTRACT

This work reports the preparation and study of poly(vinyl chloride) (PVC) with medium and high molecular weight using a Living Radical Polymerization (LRP) method in aqueous systems. The synthesis of ultra thermal stable PVC that falls outside the typical values known for the PVC industry is presented and PVC thermal stability is evaluated using a standard industrial method. The results presented in this manuscript suggest that the single electron transfer–degenerative transfer mediated living radical polymerization (SET–DTLRP) mechanism is the main factor influencing the thermal stability, since the polymerization temperature has no detectable effect on this property. In contrast to the Free Radical Polymerization (FRP), where low temperatures lead to PVC with high thermal stability that corresponds to a high molecular weight polymer, the polymerization temperature in SET–DTLRP (range 21–42 °C) has no detectable effect on the thermal stability of PVC. The final molecular weight is defined by the $[\text{monomer}]_0/[\text{initiator}]_0$ ratio (degree of polymerization). The PVC synthesis reported in this manuscript was carried out in a 150 L pilot reactor, which represents a reliable approach in terms of hydrodynamic conditions, when compared with those at the industrial scale.

1. Introduction

The conventional polymerization of vinyl chloride monomer (VCM) based on FRP is the only process available for the industrial production of PVC, because it allows the preparation of high molecular weight PVC under mild conditions in an environmental friendly medium. However, there are some important disadvantages, namely the lack of control over the molecular weight and the side reactions responsible for the appearance of structural defects (Starnes, 2002, 2005; Starnes et al., 1983, 1992). All the technological breakthroughs in the PVC industry achieved in recent decades were related to the reaction optimization in larger reactors (Saeki and Emura, 2002), new free radical initiator systems (Burgess, 1982; Zimmermann, 1996), combination of initiators (Pinto and Giudici, 2001), different colloidal systems (Burgess, 1982), and development of more efficient processing technologies (Endo, 2002; Saeki and Emura, 2002). These approaches sought to optimize production for the purpose of cost reduction.

There have been important advances concerning the chemistry behind the polymerization process at the industrial level over the past 50 years. One of the main features of VCM polymerization is the fact that the molecular weight is determined by the ratio between the propagation rate and the chain transfer to monomer (CTM) (Burgess, 1982). Even at very low temperature, the chain transfer reactions cannot be prevented in the FRP, impairing the preparation of ultra-high molecular weight (UHMW) PVC. Alternatively, other strategies based on the addition of compounds that may "link" the growing chains are used (Coelho, 2006), resulting in a PVC with higher molecular weight. However, the molecular weight increment obtained with this strategy is very limited and sometimes does not justify its application. The preparation of a PVC with ultra high molecular weight is of outstanding importance since the compounding of this product displays an improved toughness (Attwood and Brookman, 1989) and thermal stability, which will certainly increase the range of PVC applications. From the theoretical standpoint, the only possibility of preparing UHMW is the use of a LRP method in which the side reactions are suppressed, including the chain transfer reactions, allowing the

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polymer to continue the growing process without chain breaks (Percec et al., 2004a).

The only available method for the polymerization of VCM leading to the preparation of linear PVC free of structural defects was discovered by Percec et al. (2004a, 2002, 2003, 2005d). This new process was called SET–DTLRP, and it is mediated by a combination of competitive single electron transfer and degenerative chain transfer. Aside from vinyl chloride, this methodology proved to be efficient in the polymerization of activated (Coelho et al., 2007, 2008a, 2008b, 2009a; Percec et al., 2005a, 2005b) and non-activated monomers (Percec and Popov, 2005b; Percec et al., 2004a, 2003, 2004b, 2005e) and in the synthesis of block copolymers based on PVC (Coelho et al., 2006a, 2006b, 2009b, 2006e, 2008c). The polymerization of VCM initiated from iodoform leads to the preparation of telechelic α,ω-di(iodo)polymers that can be successfully functionalized (Percec and Popov, 2005a) or used as macroinitiators for the synthesis of ABA block copolymers (Percec et al., 2005a, 2005b, 2005c). Previous studies from our group have demonstrated that PVC prepared by FRP has a maximum number molecular weight ($M_{n,TriSEC}$) of 92000 Da, even at 21 °C (Coelho et al., 2006c). The subscript TriSEC denotes the determination of the molecular weight using multi detector size exclusion chromatography Using the SET–DTLRP method, Percec proposed the preparation of UHMW PVC with $M_{n,TriSEC}$ around 160,000 at 21 °C, in water, after 12 days of polymerization (Percec et al., 2005d). This UHMW PVC presented an excellent thermal stability compared with a conventional HMW PVC. From a scientific standpoint, this result represented the first successful attempt to prepare UHMW PVC with exceptional thermal stability. In order to turn this methodology into an industrially feasible one, the reaction time must be significantly reduced.

Previous studies related to the low molecular weight (LMW) LRP PVC scale-up suggested a significant increase of the reaction rate for higher reaction scales (Coelho, 2006; Coelho et al., 2011). Another important question to address is the discrepancy between the theoretical molecular weight (M_n^{th}), based on conversion, and $M_{n,SEC}$ obtained by size exclusion chromatography (SEC) using a refractive index detector (Percec et al., 2005d). According to the authors (Percec et al., 2005d), such differences might be related to the lack of Mark-Houwink-Sakurada (MHS) constants for the range of $M_{n,SEC}$ in the study. In the current work, the molecular weight ($M_{n,TriSEC}$) is determined using a TriSEC multi-detector (light scattering, viscosimeter and refractive index), allowing the determination of absolute molecular weight directly from the detector signals without the requirement of universal calibration. To our knowledge, it is the first time that the molecular weight of PVC with UHMW has been determined without the requirement for universal calibration. The method used to determine the molecular weight and molecular weight distribution was proposed in a previous publication of our group (Coelho et al., 2006c).

In this work the scaling-up for the synthesis of UHMW PVC in a 150 L reactor is reported, along with its thermal stability evaluation. The use of a 150 L reactor simulated the polymerization under hydrodynamic conditions similar to the industrial process.

2. Experimental

2.1. Materials

HPLC-grade uninhibited Tetrahydrofuran (THF), sand, alumina, iodoform (CHI_3) (99%), sodium dithionite ($Na_2S_2O_4$) (85%) and sodium bicarbonate (99%) were purchased from Sigma-Aldrich. The VCM was supplied by Shin-Etsu and used as received. The poly(styrene) standards were purchased from Polymer Laboratories. Methocel F50 was purchased from Dow Chemical Company. Poly(vinyl alcohol) (PVA) was purchased from Synthomer. The anti-fouling agent made of polyaryl phenols, Noxol WSW, was supplied by Akzo Nobel. The other materials used in the compounding were supplied by Previnil. The PVC samples used in the thermal stability tests were supplied by CIRES.

2.2. Preparation of α,ω-di(iodo)PVC macroinitiator in a 50 mL reactor (DP=4,800)

The procedure for preparation of PVC by SET–DTLRP catalyzed by $Na_2S_2O_4$ in water is described elsewhere (Coelho, 2006; Percec et al., 2004a).

2.3. Preparation of α,ω-di(iodo)PVC macroinitiator in a 150 L reactor

The procedure for operation of the 150 L pilot reactor concerning the compound handling, procedure design, reaction operation, sample withdrawal and its preparation for TriSEC analysis are fully described elsewhere (Coelho, 2006; Coelho et al., 2006c).

2.4. Characterization techniques

2.4.1. Size exclusion chromatography

The chromatography parameters of the samples were determined using a HPSEC; Viscotek (Dual detector 270, Viscotek, Houston, USA) with a differential viscometry (DV); right angle laser light-scattering (RALLS, Viscotek) and RI (Knauer K-2301). The column set consisted of a PL 10 μm guard column (50 mm × 7.5 mm) followed by two MIXED-B PL columns (300 mm × 7.5 mm, 10 μm). The HPLC pump (Knauer K-1001) was set with a flow rate of 1 mL/min. The eluent was previously filtered through a 0.2 μm filter. The system is also equipped with a Knauer on-line degasser. The tests were done at 30 °C using an Elder CH-150 heater. Before the injection (100 μl) the samples were filtered through a PTFE membrane with 0.2 μm pore size. The differential refractive index (dn/dc) for 670 nm was determined using the Viscotek Software 3.0. The analysis of light scattering data by Viscotek software was done assuming the second virial coefficient was zero, considering the low solution concentrations used in this work.

2.4.2. Sample preparation for size exclusion chromatography

Approximately 40 mg of PVC was allowed to completely dissolve in THF (10 mL) over 24 h. The PVC solution was passed through an alumina and sand column, precipitated in water and filtered under vacuum. The polymer was then dried in a vacuum oven at 40 °C until it reached constant weight. Approximately 20 mg of purified polymer was dissolved in 10 mL of THF under stirring for 24 h. The exact concentration was determined considering the weight measured and the 10 mL of solvent used (all the samples were prepared with concentrations around 2 mg/mL).

2.4.2.1. K_v-value determination (Coelho et al., 2006c). The PVC samples of 0.250 ± 0.002 g were weighed and added to 100 mL volumetric flasks. The flasks were filled at 2/3 total volume with cyclohexanone and carefully stirred in a temperature-controlled glycerol heating bath at 85 ± 5 °C until complete dissolution. The solutions were then allowed to cool to room temperature. The flasks were filled completely with cyclohexanone preheated at 85 ± 5 °C during 90 min, and placed in an isothermal bath at