



# Particle features and morphology of poly(vinyl chloride) prepared by living radical polymerisation in aqueous media. Insight about particle formation mechanism

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## ABSTRACT

The aim of this work is to evaluate PVC resins prepared by Single Electron Transfer Degenerative Chain Transfer Living Radical Polymerisation (SET-DTLRP) in a 150 L reactor under industrial conditions. The product features were analysed considering the standard resin features of PVC prepared by the conventional free radical polymerisation (FRP) method. It was proved that the FRP and SET-DTLRP have different particle growing mechanism and led to grains with completely different features (particle size, particle size distribution and morphology). It is critical for the PVC producers the preparation of PVC with a predetermined grain shape, particle size distribution and porosity which have an indubitable influence on polymer processing. It is presented a detailed study on the particle formation of the PVC synthesised by SET-DTLRP providing first insights into PVC features associated with a new polymerisation technique taking into account the normal requirements of the PVC industry. A possible mechanism of the SET-DTLRP particle formation is proposed.

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## 1. Introduction

The development and industrial implementation of new LRP technologies that may create products based on PVC with associated high value is extremely important for this industry that traditionally works with low-profit products. Moreover, new processes may lead to PVC macrostructures with new features (topology, architectures and morphology) which today are impossible to achieve by using the FRP, and certainly will widen the range of the PVC applications. The FRP of VCM results in the unavoidable formation of polymer chains bearing unwanted fragments known as structural defects [1,2]. Besides, the molecular weights which

can be achieved by FRP are very limited, making impossible, for example, the preparation of very low molecular weight PVC with reasonable thermal stability. The latter would be extremely interesting, for instance, in applications that require low viscosity or low glass transition temperature ( $T_g$ ) polymers. The decrease of molecular weight is proportional to the reduction of viscosity of hot melt, enabling the polymer processing [3]. Polymerisation methods based on LRP that combine the advantages of a living process with a radical mechanism have caused considerable interest. Thus, the preparation of PVC in large scale production without the traditional problems maybe possible to achieve [4]. Percec and co-authors began developing a new polymerisation process which produces PVC free from structural defects, along with the so-called active chain ends that enable a further copolymerisation or functionalisation [5–14]. Over the years, the methodology proposed by Percec and co-authors became more attractive from the industrial standpoint, resulting in a process called single electron transfer degenerative chain transfer mediated living radical polymerisation [12]. The complete description of the development of the SET-DTLRP process from the basic principles of the LRP is described elsewhere [4]. This method presents several advantages [15] over the common LRP processes, which have been thoroughly studied [16–19]. Among those, the SET-DTLRP works in an aqueous medium using the only widely available compounds which represent an important advantage from an economic and environmental

*Abbreviations:* CTM, Chain transfer to monomer; CTP, Chain transfer to the polymer; DMTA, Dynamical mechanical thermal analysis; DT, Degenerative chain transfer; FRP, Free radical polymerisation; LRP, Living radical polymerisation; PSD, Particle size distribution; PTC, Phase transfer catalyst; PVA, Poly(vinyl alcohol); PVC, Poly(vinyl chloride); SA, Stabilising agent; SEM, Scanning electron microscopy; SET, Single electron transfer; SET-DTLRP, Single electron transfer degenerative chain transfer living radical polymerisation; TriSEC, Multidetector size exclusion chromatography; VCM, Vinyl chloride monomer.

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perspective. This technology is being scaled-up for industrial application dealing with the optimisation and development of suitable conditions to fulfil the industrial requirements of the SET-DTLRP for homopolymers [15,20–22] and copolymers [23,24].

It is widely accepted that the main objective of PVC producers is to prepare PVC with a defined molecular weight (or  $K_v$ ) and morphological features through a safe and efficient process, enabling products to be easily handled and processed. The foremost breakthroughs in the FRP process over the last decades were related to the reaction optimisation and the development of new processes to increase the efficiency associated with the PVC processing [25]. Based on this, the development of this new LRP method using the same facilities for preparing and processing the polymer represents an important step forward to enhance the possibility of its implementation in industrial production. The scaling-up of this technology in larger pilot reactors was successfully performed and described in two previous publications [26,27]. The kinetics have shown that the SET-DTLRP works even better with higher monomer conversions for larger scales. In this study, these products were evaluated according to the standard procedures used in the PVC industry. Additionally, the main problems identified during the scaling-up and processing tests are discussed and solutions are presented for some of them.

## 2. Experimental information

### 2.1. Preparation of $\alpha,\omega$ -di(iodo)PVC and the conventional FRP PVC in a 150 L reactor

The procedures used to prepare the PVC by SET-DTLRP and FRP in the 150 L pilot reactor are fully described elsewhere [4] [26,27].

### 2.2. Characterisation techniques

The PVC grains were gold-coated in vacuum and the morphology was examined by scanning electron microscopy (SEM) using a Leica/Cambridge S360. The particle size distribution (PSD) was determined using a Malvern laser diffraction equipment (Hydro 2000S) from Malvern Instruments Ltd. Hydro 2000S is equipped with a continuously variable ultrasonic probe. All PVC samples were washed and dried until constant weight before the PSD determination.

## 3. Results and discussion

As stated above, the PVC producer's main target deals with the production of resins with controlled morphology, particle size and particle size distribution, ensuring an optimum material for processing. This represents another particular feature of this market in comparison with other polymer markets, where successful production is concerned with the control of molecular weight distribution, rate or level of crystallisation, relative density, melt flow index, and so on [28]. To allow their control it is necessary to understand each step of the VCM suspension polymerisation process, from the polymerisation through the bulk handling, as well as the different parameters which can influence them. In two previous publications [26,27] several batches were carried out under different conditions in order to evaluate its influence on the reaction kinetic and thermal stability of the PVC [26,27]. Apart from the higher thermal stability of the SET-DTLRP PVC, the results [26,27] suggested a completely different mechanism involved in the particle formation between the FRP and the new process. The particle features of the PVC prepared by SET-DTLRP were evaluated through the determination of the PSD and morphology.

### 3.1. Drying process

As expected from any suspension process, the SET-DTLRP of VCM produces a mixture of granules dispersed in water which can be easily separated from the water before the drying process using a cloth filter. The polymer was dried in a fluidised bed batch drier at 70 °C for 2 h. Even considering that the morphology and PSD of this new polymer is different from the standard product (see below), it was possible to dry this product to commercial specification ( $M_v < 0.5\%$ ) using the same equipment typically used for the conventional FRP PVC. This result is extremely important since it was obtained using the existent facilities for the conventional suspension PVC.

### 3.2. Particle size distribution

Particle size distribution is one of the most important requirements that should be respected by PVC producers. Therefore, the PVC prepared by SET-DTLRP was compared with the conventional product. Properties such as grain shape, particle size distribution and porosity have an indubitable influence on polymer processing [3]. The first scaling-up carried out in a 150 L reactor has produced very large grains of around 3 mm which were extremely easy to break down into a fine powder. The increase in the amount of the stabilising agent (SA) mitigated this problem to a great extent. However, it was clear since the beginning that the grain properties presented by this material were different from the conventional PVC. For that reason, the procedure used to determine the PSD was adapted by changing the ultrasonic pre-treatment time defined on the Malvern equipment. Fig. 1 shows the differences observed between the PSD of PVC prepared by FRP and by SET-DTLRP after the given times of ultrasonic treatment.

Fig. 1 shows important differences between the PSDs obtained by the two polymerisation methods. The PSD of the PVC prepared by SET-DTLRP is much broader (and bimodal) than the PVC prepared by FRP. Moreover, the results do not show any effect of the ultrasonic treatment time in the PSD obtained for the FRP resin. Thereby, it is shown that the FRP grain particle is perfectly aggregated, and therefore it witnessed the main processes involved in the grain formation during the polymerisation. In an opposite trend, the PSD of PVC grain prepared by SET-DTLRP polymerisation shows an important change with the ultrasonic treatment. Apparently, the main agglomerations (around 400  $\mu\text{m}$ ) disappear after a certain time of ultrasonic treatment, which reveals the presence of structures with a very low degree of agglomeration. Nevertheless, the ultrasonic treatment did not narrow the particle size distribution for the particles  $\leq 100 \mu\text{m}$ , which suggests a certain degree of aggregation/fusion, albeit not as uniform as the FRP process, due to broader PSD obtained for the SET-DTLRP process. Another important difference is observed in the  $d_{50}$  value between the two polymers: the PVC prepared by SET-DTLRP leads to the formation of small grains. Further studies related to the optimisation of the suspending agents and its relation to the stirring speed were conducted to prepare polymer without large aggregates [4]. Different SET-DTLRP of VCM led invariably to broad PSD. This result is likely to be a direct consequence of a different mechanism of nucleation since some of the reactions such as chain transfer to monomer (CTM) and back-biting were not present or almost imperceptible [12,29], which in turn induces a different mechanism of the particle formation. Several polymerisation aspects have an important influence on the PVC grain size and morphology. On this matter for the FRP process [28], cited the influence of different polymer/isolation stages of degassing, dewatering and drying, and their influence on the subsequent steps from the bulk handling, through mixing, processing and shaping. Based on this, the samples characterised in this study were obtained

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