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Intelligent monitoring of solid state polymerization via molecular rotors: The case of poly(butylene succinate)



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ABSTRACT

Solid state post-polymerization (post-SSP) was performed on poly(butylene succinate) (PBS) commercial- and synthesized-grades and monitored for the first time by means of a fluorescent probe: (9-2-carboxy-2-cyanovinyl)julolidine or CCVJ. CCVJ is a molecular rotor and was simply incorporated in the PBS bulk (100 ppm) for fluorescent labelling. Post-SSP runs were then performed following a one- or two-step process. During the one-step process, CCVJ labelled PBS presented a moderate molecular weight (MW) increase (up to 1.15 times) along with a post-crystallization effect. Next, the SSP effectiveness was improved (in terms of MW- up to 4.2 times- and thermal characteristic upgrade) with the addition of a precrystallization step (two-step process). Labelled PBS showed a decrease of the CCVJ fluorescence intensity and a respective significant wavelength shift (blue shift) with SSP time. According to CCVJ calibration, this behavior was ascribed to the resultant MW increment and to the decrease of the acidic index (AI) during SSP. CCVJ was proven a reliable sensor able to act as a molecular rotor as well as a solvatochromic probe sensing both the molecular weight and polarity changes in the course of PBS SSP process.

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1. Introduction

Nowadays, the increasing concerns about the depletion of the petrochemical resources as well as the inconsiderate utilization of conventional nondegradable plastics and their improper disposal have intensified the efforts of industry and academia towards developing sustainable biodegradable polymers suitable for general-purpose materials [1–6]. Among them, poly(butylene succinate) (PBS) is an aliphatic polyester with promising upcoming applicability, and properties competitive to those of polyethylene (PE) and polypropylene (PP) [7]. On account of its lower glass transition temperature ($T_g = -32\text{ °C}$) [8,9], PBS possesses a more flexible structure compared to poly(lactic acid) (PLA, $T_g \sim 60\text{ °C}$) [8] and thus is more easily and at

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lower cost melt processable [8,10,11]. Apart from that, its relatively high melting point ($T_m = 112\text{--}114\text{ }^\circ\text{C}$) [12,13] compared to other polyesters derived from aliphatic diols and diacids, its controllable biodegradation rate [12,14], its balanced mechanical properties [12] and its versatile structure [8,14,15] jointly make possible the use of PBS to a wide application field. Finally, the high potential for bio-based PBS industrial production based partially or exclusively on biomass resources, has stimulated the interest for its research and development [8,14,15]. In particular, the ameliorated fermentation processes gave rise to the industrial production of its diacid monomer i.e. bio-based succinic acid (SA) [15–21], while its diol monomer i.e. 1,4 butanediol (BDO), can also be prepared from bio-based SA [8,14].

For the reasons stated above, many reports have dealt with the synthesis of PBS. In literature, it is conventionally prepared via a two-stage melt polycondensation technique (Fig. 1) [13,15,22–26]. However, melt polymerization processes suffer from significant drawbacks, such as high reaction temperatures, yellowing generated by titanium-based catalysts, low selectivity and possibility of side reactions. Furthermore, the heat and mass transfer limitations induced by the increased melt viscosity may be detrimental for the quality of the resultant polyester.

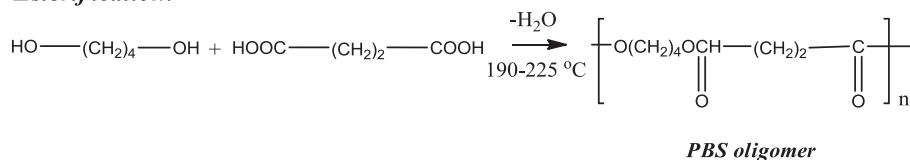
These problems can be circumvented by the introduction of solid state polymerization (post-SSP) in the production scheme, as already suggested in a recent work of Papaspyrides et al. [27]. Accordingly, SSP can be implemented as an extension of the melt phase polycondensation, which is interrupted at the point where the above problems start to appear; it involves heating the prepolymer at a temperature higher than the glass transition point and lower than the melting, so as polymerization reactions are possible to occur in the mobile amorphous phase [28–41].

Usual SSP monitoring techniques involve solution viscometry, ^1H NMR spectroscopy [42], ^{23}Na and ^{13}C solid-state NMR spectroscopy [43], FT-IR [44], gel permeation chromatography (GPC) [42], in situ time-resolved X-ray Diffraction (XRD) [45] and thermogravimetric analysis (TGA) [34]. An alternative and original monitoring technique is suggested in the current paper for the remote sensing of SSP. This technique is applied on PBS and based on a selected fluorescent probe. Indeed, fluorescent spectrometry is a powerful and sensitive tool widely utilized to study thermal [46] and phase transitions, polymerization kinetics, aging and degradation [47]. For such sensing, probes are either embedded in the polymer bulk or grafted onto the polymer backbone.

Fluorescent probes like molecular rotors as julolidine malononitrile probes are promising ones when simply incorporated in polymers. From their intrinsic rotational relaxation (see the inset in Fig. 2 as an example of an internal twisting), information can be collected about the local microscopic rigidity (mobility) of their surrounding media. Indeed, the fluorescent intensity (quantum yield) of the rotor probes is correlated to the viscosity (or mobility) of their local environment. In more mobile media, the increased rotational freedom of the electron donor and acceptor parts of the probe leads to the quenching of fluorescence [48]. In literature, such probes have been successfully used to monitor polymerization reactions [49] as the chain mobility is often related to the polymer molecular weight [50]. For example, the fluorescence intensity of DCVJ (9-(2,2-dicyanovinyl)julolidine) or derivatives like FCVJ (a hydrophobic ester of (2-carboxy-2-cyanovinyl)-julolidine or farnesyl-(2-carboxy-2-cyanovinyl)-julolidine) increases significantly with the MW during polystyrene polymerization [50,51]. This is related to the reduction of the free volume, which led to inhibit the internal molecular rotation of the julolidine malononitrile probe, and consequently the fluorescence enhancement as already described.

In addition, the maximum fluorescence of julolidine malononitrile rotors present an interesting shift when the dielectric constant of the media is changed. This latter characteristic (also called solvatochromic effect) can be utilized to determine the polarity of the probe surrounding media [52]. According to Rumble et al. [53] CCVJ is considered as “not a simple molecular rotor”, but also as a solvatochromic probe. Several studies have shown that CCVJ has a low mobility in high viscous environment resulting in an intensity increase [54]. Moreover, CCVJ exhibits a higher sensitivity to the solvent polarity, which is manifested by a blue shift in an organic solvent like methanol and ethanol [55]. On the contrary, CCVJ acidification in ethylene glycol led to a red shift and narrowed emission spectra [53].

Esterification:



Transesterification:

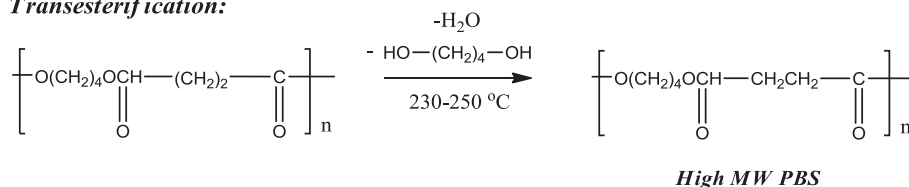


Fig. 1. Common synthetic route of PBS via a two-step melt polycondensation process.

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