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Synthesis and characterization of star polymers in supercritical CO_2: influence of the catalytic system on polymer architecture

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ABSTRACT

The use of bio-based building blocks and greener synthesis pathways to synthesise star-shaped polymers composed of a *D*-sorbitol core and polycaprolactone (PCL) arms by ring opening polymerisation (ROP) was investigated. To this aim, ROP was performed in supercritical carbon dioxide ($scCO_2$) in the presence of two catalytic systems: the traditional tin (II) 2-ethylhexanoate ($Sn(Oct)_2$) and the enzyme Novozym 435. The influence of the catalyst on the molecular weight, dispersity and architecture of the PCL stars were studied by nuclear magnetic resonance (NMR) spectroscopy, size exclusion chromatography – multi-angle light scattering (SEC-MALS) and matrix assisted laser desorption and ionisation-time of flight mass spectrometry (MALDI-TOF MS). We proved that $scCO_2$ is compatible with the use of enzyme and different star architectures were obtained depending on the catalyst employed.

INTRODUCTION

The accumulation of non-biodegradable plastics on earth has resulted in an increasing need for biodegradable polymers, ideally produced by green technologies. In addition, the simultaneously occurring depletion of fossil resources has lead to significant developments in the research and application of naturally occurring building blocks.[1] At the same time, star-shaped polymers have attracted attention as they exhibit remarkable mechanical and thermal properties and improve degradability compared to their linear equivalents.[2] In this work, a greener route for star polymer synthesis was implemented by using renewable initiator, $scCO_2$, and, preferentially, a biocatalyst. In particular, we have chosen a core-first approach by employing *D*-sorbitol, a biomass derived polyol, as an initiator for the ROP of ε-caprolactone (ε-CL). Two different catalysts were investigated: the metal-based catalyst $Sn(Oct)_2$, and the enzyme Novozym 435. The influence of both catalysts on the architecture of star *D*-sorbitol-PCL in $scCO_2$ was studied, thereby avoiding organic solvents as the reaction medium.

RESULTS AND DISCUSSION

Star *D*-sorbitol-PCL polymers, were synthesised in $scCO_2$ at 95 and 60 °C in the presence of conventional $Sn(Oct)_2$ catalyst and lipase enzyme Novozym 435, respectively (Figure 1).

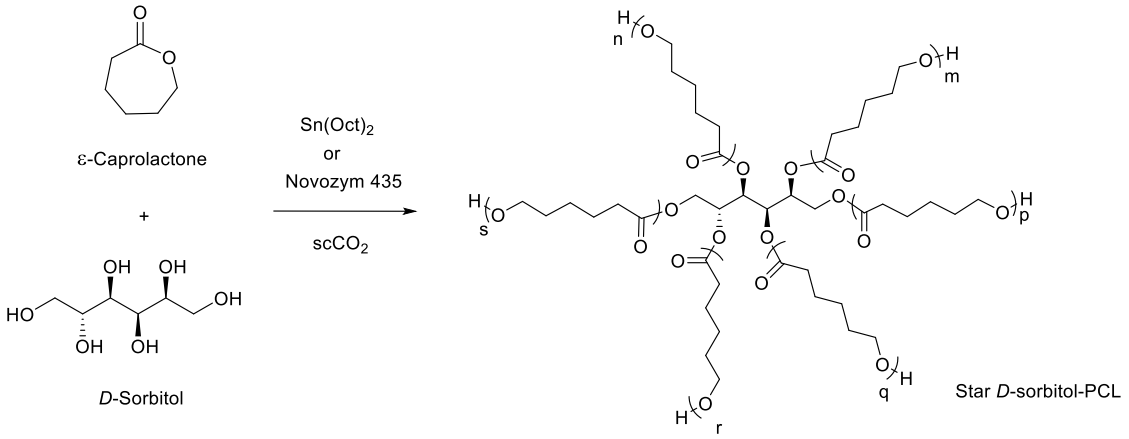

Figure 1. ROP of ε-caprolactone from *D*-sorbitol to afford a star *D*-sorbitol-PCL polymer using the conventional metal catalyst $Sn(Oct)_2$ or the enzyme Novozym 435 in $scCO_2$.

Polymerisation results are collected in Table 1.

Table 1. Synthesis of star *D*-sorbitol-PCL by ROP in $scCO_2$ in the presence of $Sn(Oct)_2$ and Novozym 435

Entry	Catalyst	T (ºC)	t (h)	^{1}H NMR	SEC-MALS	
				M_n $^{H\text{-}NMR}$ (arm) [a] (g mol^{-1})	M_n ^{SEC} [b] (g mol^{-1})	$Đ$ [b]
1	$Sn(Oct)_2$	95	48	1250	6100	1.11
2	Novozym 435	60	24	3200	8800	1.24

[a] Determined by ^{1}H NMR peak intensity ratio . [b] Determined by SEC-MALS with THF as an eluent (RI detector), $Đ$ = dispersity.

Whatever the catalyst used, ε-CL was successfully polymerised in $scCO_2$ from *D*-sorbitol. Indeed, $scCO_2$ solubilises the monomer and the resulting mixture plasticises *D*-sorbitol.
The star polymers were characterized by ^{1}H NMR, SEC-MALS and MALDI-TOF MS analyses in order to emphasise the influence of the catalyst on the polymer architecture. Figure 2 shows the ^{1}H NMR spectrum of *D*-sorbitol-PCL synthesized in the presence of Novozym 435. Due to the poor solubility of *D*-sorbitol in $CDCl_3$, the corresponding signals were not visible in the ^{1}H NMR spectrum of *D*-sorbitol-PCL. However, the signals corresponding to the PCL arms, including the end-groups in α-position of the hydroxyl functions, are well visible and it was possible to estimate the average molecular weight of a star polymer arm ($M_n^{H\text{-}NMR}$ (arm)).

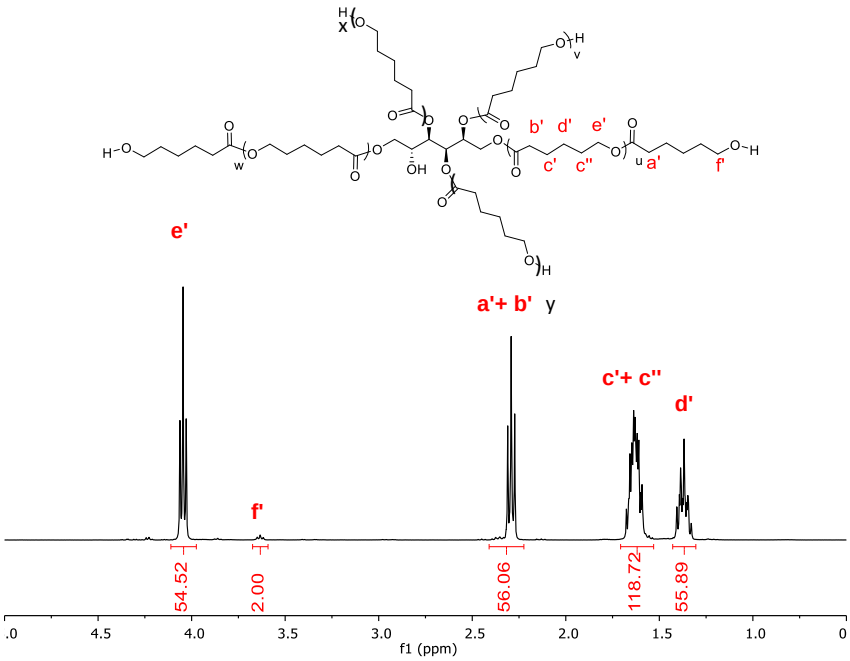

Figure 2. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of Novozym 435 catalysed star *D*-sorbitol-PCL polymer.

$M_n^{H\text{-}NMR}$ (arm) of $Sn(Oct)_2$ catalysed star *D*-sorbitol-PCL (1250 g mol^{-1} - Table 1 Entry 1) was lower than that obtained with Novozym 435 (3200 g mol^{-1} - Table 1 Entry 2). The same trend was observed regarding the molecular weight of the complete star polymers, as determined by SEC-MALS analyses. However, dispersity is slightly higher in the case of Novozym 435 catalysed ROP ($Đ$ = 1.24 *vs* 1.11).

MALDI-TOF MS analyses enabled to confirm the insertion of *D*-sorbitol inside the polymer backbone and to highlight the presence of possible side reactions. Thus, MALDI-TOF MS spectrum of star PCL catalysed by $Sn(Oct)_2$ shows only one distribution corresponding to PCL chains initiated by *D*-sorbitol, confirming the formation of star *D*-sorbitol-PCL without any other side products. In the case of star PCL catalysed by Novozym 435, signals corresponding to *D*-sorbitol-initiated PCL were also visible. However, two other populations attributed to water initiated PCL and to PCL macrocycles were also present. The latter may be due to intramolecular transesterification reactions (back-biting reaction) or may be formed *in situ* during the MALDI-TOF analysis.

Lastly, we estimated that $Sn(Oct)_2$ catalysed star *D*-sorbitol-PCL exhibits about 5 arms whereas an average number of 2.7 arms was calculated in the presence of enzyme. This phenomenon may be due to the regioselectivity[3,4] and enantioselectivity[5,6] of Novozym 435 lipase.

CONCLUSION

A green route towards sustainable synthesis of star shaped *D*-sorbitol PCL has been demonstrated using ring-opening polymerisation of ε-CL from bio-based *D*-sorbitol molecule. The synthesis of star *D*-sorbitol-PCL was successfully performed in $scCO_2$ in the presence of $Sn(Oct)_2$ or enzyme Novozym 435 catalysts, leading to regular or mikto-arm star polymers, respectively. The influence of the catalyst is mainly visible on the molecular weights and the average number of arms of the star polymers. We have demonstrated that a combination of enzyme catalyst and $scCO_2$ can be used to prepare star polymers in the complete absence of any volatile organic solvent or metal catalyst.

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