# **Supporting Information**

# "Facile One-Spot Synthesis of Highly Branched Polycaprolactone"

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## Section S.1 -<sup>1</sup>H NMR of PCL<sub>50</sub>BOD<sub>0.6</sub>



Figure S.1. <sup>1</sup>H NMR for kinetic sample at 60 min copolymerisation for the synthesis of PCL<sub>50</sub>BOD<sub>0.6.</sub> DP was determined with a value of 49 (48.80) and the comonomer conversion was 99%.

## Section S.2- GPC-MALLS

 $M_w$  and  $R_g$  were extrapolated from Zimm equations<sup>1,3</sup> by limiting zero angle and zero concentration. Therefore, the linearity of the plot of K\*c/R( $\theta$ ) versus sin<sup>2</sup>( $\theta$ /2) is required for reliable analysis. These plots are shown for several eluted fractions in Figure S2. Eight different angles were used in the MALLS analysis, from 23.3 to 147.4°, which are equivalent to sin<sup>2</sup>( $\theta$ /2) from 0 - 1. The linearity of these plots suggests that reliable value of M<sub>w</sub> and R<sub>g</sub> has been obtained from this analytical technique to the PCL highly branched materials.



Figure S.2. The Zimm plots describes the relationship between  $K^*c/R(\theta)$  versus  $\sin^2(\theta)$ . The data were extracted using ASTRA software with at different elution volume

Section S.3–Confirmation plots



Figure S.3. The conformation plots of  $PCL_{50}BOD_x$  (x=0.4-0.6) (a) ( $R_g$  versus  $LogM_w$ : typical curvature of branched polymer

#### **Section S.4- Degree of Branching**

(a) NMR - To investigate the DB of the branched polymer synthesised in this study, <sup>13</sup>C NMR of PCL<sub>50</sub> and PCL<sub>50</sub>BOD<sub>0.6</sub> were measured and compared (see Figure S.3). In order to calculate DB, the signal of methyne carbon (-CH-) is expected to be located at the branch point which belongs to the BOD comonomer. The <sup>13</sup>C NMR spectrum showed that the spectra obtained for the proposed branched materials were the same as that of the linear polycaprolactone. There was no indication of the presence of branch points which should be located at ~ 45 ppm.



Figure S.4. The comparison of solution <sup>13</sup>C NMR spectra between linear and branched polymers. The data were recorded in CDCl<sub>3</sub> using a Bruker 400, with 128 scans for the linear polymer and 20000 scans for the branched polymer.

(b) Branching ratio - The contraction factor or branching ratio has the following physical meaning. In a given environment (solvent and temperature) a branched polymer exhibits a higher density, lower hydrodynamic volume and lower viscosity than that of a linear polymer of the same molecular weight.<sup>1-2</sup> In addition, the increase in the DB of a polymer leads to a smaller hydrodynamic volume and lower intrinsic viscosity i.e. a decrease in  $R_g^2$  and  $[\eta]$  respectively. Therefore, g and g' for linear polymers are 1.0, which decreases with the increase of degree of branching.<sup>2</sup> In this analytical programme, the values of  $g_M$  were derived from the MALLS analysis and the value of  $g_M$  was determined by GPC-viscometric analysis by measuring the solution viscosity based on the Mark-Houwink-Sakurada relationship.<sup>3</sup>The subscript M is attributed to these figures in order to emphasise that these ratios can only be derived from both linear and branched polymers of the same molecular weight.

The mean square radius of gyration  $\langle R_g^2 \rangle$  is related to the hydrodynamic volume of a polymer<sup>1,3</sup> and is measured using light scattering method. At the same molecular weight,  $g_M$  is defined as the ratio of  $R_g^2$  of a branched species compared to that of a linear polymer:

$$g_{M} = \frac{\langle R_{g}^{2} \rangle_{branched}}{\langle R_{g}^{2} \rangle_{linear}}$$

However, the issue with this technique resides in the fact that linear polymers with the equivalent molecular weights to those of the branched polymers are typically not readily available. Thus, the highest MW PCL polymer that was purchased and measured by GPC-MALLS was used as the equivalent for  $PCL_{50}BOD_{0.5}$  since they possess the most similar MW (see Table S.1). As a result, the  $g_M$  value was calculated for  $PCL_{50}BOD_{0.5}$  using  $R_g$  value of the linear polymer this particular polymer. Table S.1 summarises absolute  $M_w$  by GPC-MALLS, the root mean square RMS radius of the polymers and the branching ratio of the linear polymer and  $PCL_{50}BOD_{0.5}$ .

Target copolymer	M <sub>w</sub> -MALLS	R <sub>g</sub>	$g_M$
composition	(g/mol)	(nm)	
PCL linear	99900	21.2	1.0
PCL <sub>50</sub> BOD <sub>0.4</sub>	27900	9.3	_
PCL <sub>50</sub> BOD <sub>0.5</sub>	70800	15.6	0.56
PCL <sub>50</sub> BOD <sub>0.6</sub>	141900	25.6	_
PCL <sub>50</sub> BOD <sub>0.6</sub> <sup>a</sup>	245700	37.8	_

#### Table S.1. The summary of absolute M<sub>w</sub> measured by GPC-MALLS, RMS radius and g<sub>M</sub>.

(a) An experiment was repeated for the synthesis of  $PCL_{50}BOD_{0.6}$  for a much longer reaction time

Similarly, the ratio of the intrinsic viscosity  $[\eta]$  of a branched polymer to that of a linear one is expressed as  $g_{M}$ , as follows:

$$g_{M}' = \frac{[\eta]_{branched}}{[\eta]_{linear}}$$

The GPC-viscometer technique relies on the universal calibration which plots  $\log[\eta]$  versus  $\log[M_w]$  of linear polystyrene standards. The  $M_w$  of different polymers were then derived from the viscosity based on this plot. In practice, the  $[\eta]_{branched}$  values were measured directly using the solution viscometer coupled with GPC, whilst the  $[\eta]_{linear}$  values for linear polymers with the equivalent molecular weights were calculated using Mark-Houwink-Sakurada equation  $([\eta]_{linear} = KM^{\alpha})$ .

For instance, the calculation of  $g_M$  is shown below for the case of PCL<sub>50</sub>BOD<sub>0.6</sub>. According to Table 5.4, this branched polymer has a value  $M_w = 141,900$  g/mol with  $[\eta]_{branched} = 0.27$  dL/g. Therefore, by assuming a linear polymer which has  $M_w = 141,900$  g/mol, the  $[\eta]_{linear}$  can be calculated using K=1.09×10<sup>-3</sup> dLg<sup>-1</sup> and  $\alpha$ =0.6021<sup>4</sup> as follows:

$$[\eta]_{linear} = 1.09 \times 10^{-3} \text{ x} (141900)^{0.6} = 1.38 \text{ dL/g}$$

Therefore,  $g'_{M=} [\eta]_{branched} / [\eta]_{linear} = 0.27 / 1.38 = 0.19$ . The values of all parameters including  $\alpha$ ,  $[\eta]_{Linear}$ ,  $[\eta]_{Branched}$  and g'<sub>M</sub> are listed in Table S.2.

Table S.2. The summary of the absolute  $M_w$  by GPC-MALLS, the exponential factor  $\alpha$ , intrinsic viscosity of equivalent linear polymers calculated based on the Mark-Houwink-Sakurada, intrinsic viscosity of the polymers measured directly by GPC-viscometer in THF and the branching ratio  $g'_M$ .

Target	M <sub>w</sub> -MALLS	$[\eta]_{Linear}$	$[\eta]_{Branched}$	$g_M$
composition	(g/mol)	$(dL/g)^b$	(dL/g) <sup>c</sup>	
PCL linear	99900	1.12	1.12	1.0
PCL <sub>50</sub> BOD <sub>0.4</sub>	27900	0.52	0.19	0.37
PCL <sub>50</sub> BOD <sub>0.5</sub>	70800	0.91	0.25	0.27
PCL <sub>50</sub> BOD <sub>0.6</sub>	141900	1.38	0.27	0.19
PCL <sub>50</sub> BOD <sub>0.6</sub> <sup>a</sup>	245700	1.92	0.26	0.14

(a) An experiment was repeated for the synthesis of  $PCL_{50}BOD_{0.6}$  for a much longer reaction time (b) Calculated from the Mark-Houwink-Sakudara relationship based on the absolute  $M_w$ , K=1.09×10<sup>-3</sup> dLg<sup>-1</sup> and  $\alpha$ =0.6021.

(c) Measured directly from GPC-Viscometer in THF.

In addition to these ratios, Podzimek and Vlcek<sup>2</sup> suggested that the branching ratio can be calculated as the ratio of weight-average molecular weight ( $M_w$ ) derived by conventional GPC analysis (i.e. DRI detector) to that determined by GPC/MALLS:

Branching ratio = 
$$\frac{M_{w}(GPC - DRI)}{M_{w}(GPC - MALLS)}$$

The physical meaning of this relationship, suggested by the author, was that  $M_w$  (GPC-DRI) is proportional to hydrodynamic volume and  $M_w$  (GPC-MALLS) is the absolute value. Thus at constant  $M_w$ , this ratio will be seen to decrease with increasing DB and give a qualitative measure of the relative degree on branching through a range of materials with similar compositions.

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- (2) Podzimek, S.; Vlcek, T. Journal of Applied Polymer Science 2001, 82, 454.
- (3) Sperling, L. H. *Introduction to physical polymer science*; John Wiley & Sons, Inc.: Hoboken, New Jersey, 2006; Vol. 4th Edition.
- (4) Heuschen, J.; Jerome, R.; Teyssie, P. Macromolecules 1981, 14, 242.