

“Facile One-Spot Synthesis of Highly Branched Polycaprolactone”

Nam T. Nguyen,^{a,c} Kristofer J. Thurecht,^d Steve M. Howdle,^a and Derek J. Irvine^{a,b*}

^aSchool of Chemistry and ^bFaculty of Engineering, Department of Chemical and Environmental Engineering, University of Nottingham, Nottingham, NG7 2RD, UK

^cCurrent address - School of Biotechnology, International University, Vietnam National University, Ho Chi Minh City, Vietnam

^dAustralian Institute for Bioengineering and Nanotechnology and Centre for Advanced Imaging, The University of Queensland, St Lucia, QLD, 4072, Australia.

Corresponding author: Derek J. Irvine – Tel 00441159514088; Fax 00441159514115; E-mail derek.irvine@nottingham.ac.uk

Abstract

Reported is the first solvent-free (bulk) synthesis of degradable/bioresorbable, highly branched polymers *via* tin octanoate Sn(Oct)₂ catalysed controlled ring opening copolymerisation (ROP) of mono and di-functional lactone monomers that proceed to near quantitative conversion. The successful isolation of solvent soluble, highly branched structures was shown to be dependent on both the concentration of the di-functional monomer and the overall reaction time. Comparison with analogous systems utilising controlled radical polymerisation (CRP) to form the highly/hyper branched polymers suggested significant experimental differences between the two chain growth methods. The maximum proportion of di-functional monomer without gelation ensuing was found to be 0.6 equivalents w.r.t. mono-functional monomer (c.f. 1 with CRP) and the onset of significant levels of branching occurred at approximately 90% conversion (c.f. ~70% with CRP). These differences and significant disparity in reaction times were attributed to (a) the coordination and insertion (C+I) propagation mechanism adopted by the Sn catalyst and (b) the presence of additional trans-esterification reactions at high conversion. Evidence is presented to support the conclusion that there are two mechanisms contributing to the overall branching process in the ROP system at high conversion. First, the C+I mechanism promotes growth of linear polymer until approximately 90% conversion, after which both the C+I and trans-esterification processes contribute to the interchain branching process. The branched nature of the molecular structures was supported by confirmation plots generated from static light scattering. This data demonstrated that the polymers synthesised exhibit varying degrees of branching, consistent with the di-functional monomer (4,4'-bioxepanyl-7,7'-dione - BOD) concentration in the feed. The degree of branching was calculated using 3 different methods

and the results were shown to be independent of method. Finally, DSC analysis of the polymers demonstrated correlation between the degree of branching achieved and the observed T_m for the material where increased branching leads to a drop in the recorded T_m .

Introduction

The last two decades have witnessed a significant increase in the level of interest in both the synthesis and application performance of highly/hyper branched polymers. This has been as a direct result of the material properties they exhibit, which are often highly differentiated from those of linear equivalents of comparable molecular weight.¹⁻² Hyperbranched polymers exhibit application behaviour similar to dendrimers, whilst having the advantage of requiring far less time and less intensive synthetic strategies that are typically needed to produce dendritic structures. Hence, in spite of the fact that the synthetic strategies applied deliver poorer control over the molecular structure of these hyperbranched polymers when compared to “true” dendrimers, the economic and practical advantages from adopting these strategies are generally gained without significant negative impact upon the desired beneficial/differentiated material properties.^{1,3-12} In addition, these more affordable and accessible approaches have led to significant industrial interest targeted towards using these materials in larger scale applications such as imaging agents, reactive resins and industrial coatings.^{1,13-15}

Compared to linear polymers, highly/hyper branched polymers often exhibit improved solubility, lower (melt) viscosity, higher density of functional-groups and have a more compact/globular structure.¹⁻² Consequently, these materials have the potential to deliver improvement in both performance and processability of the final product. For example, the greater solubility and/or melt flow characteristics of these materials would allow larger molecular weight (Mwt) polymers to be successfully processed using standard industrial equipment than can currently be achieved with linear polymers. This subsequently allows materials with far higher mechanical strength than can generally be achieved using standard methods of synthesis. Alternatively, the higher density of chain end functionality contained in the hyperbranched structures lends them toward applications in which strong adhesion and/or complex formation is required. This is because the sheer number of attachment points that are available should ensure that both multiple anchoring/complexation points are created. This promising feature has been subsequently confirmed *via* the successful commercialisation of a number of hyperbranched polymers, including Hybrane^{TM,13-14} (poly (ester amides) from DSM), BoltornTM (polyester from Perstorp)¹⁶⁻¹⁷, LupasolTM (polyethyleneimines from BASF SE) and hyperbranched polyurethane-polyisocyanate (from BASF SE). More recently, there

has been an increase in literature reports of experimental studies which have exploited these properties of hyperbranched polymers in a vast array of medical applications,² including gene delivery,¹⁸⁻¹⁹ drug delivery,²⁰ bio-surfaces modification,²¹ and molecular imaging.²²⁻²³

In the field of biomedical polymers, polyesters are a class of material which find particular utility. This is because of their good thermal and mechanical properties, acceptable levels of chemical resistance, ease of synthesis, availability of monomer feed stocks and many are defined to be biodegradable.¹ Consequently, there has been significant interest in generating hyperbranched polyesters to deliver biopolymers with differentiated application performance. Both step growth and chain growth polymerisation strategies have been employed to synthesise hyperbranched and highly branched polyesters.¹⁻² The former approach has mainly been achieved by the polycondensation of multifunctional monomers such as AB₂, AB₂ + B_y²⁴ and A₂ + B_y type structures.²⁵ Meanwhile, the latter method has been based on a specific method called Ring-opening Multibranching Polymerisation (ROMBP) of latent AB₂ monomer, i.e. the ring-opening polymerisation of cyclic monomers in which the initiator is attached to the monomer ring.²⁶

In the particular case of polycaprolactone, which is the monomer used in this study, hyperbranched polymers have typically been synthesised *via* AB₂ polycondensation and ROMBP. The synthesis of hyperbranched PCL was first investigated by Hedrick *et al.* using an AB₂ macromonomer prepared using PCL and 2,2'-bis(hydroxymethyl) propionic acid (bis-MPA) as the branching point.²⁷⁻²⁸ This author also reported the synthesis of a second CL based AB₂ macromonomer *via* ring-opening polymerisation (ROP) of CL, using benzyl ester protected MPA and tin octanoate (Sn(Oct)₂).²⁸ Frechet *et al.* reported the preparation of 4-(2-hydroxyethyl)-caprolactone which was then used to produce hyperbranched polyester in a one-pot strategy.²⁶ Hedrick *et al.* also reported the synthesis of lactone-2, a bis(hydroxymethyl) substituted CL monomer.^{24,29}

To date there has only been one report which has described the synthesis of CL based branched polymers prepared *via* ring-opening copolymerisation of CL and a di-lactone.³⁰ In this report, Thurecht and co-workers³⁰ described the synthesis and characterisation of core-shell polymer, of which the core structure was either highly/hyper branched or highly crosslinked (microgel) PCL. The hyperbranched PCL core was prepared *via* ROP by copolymerisation CL with 4,4'-bioxepanyl-7,7'-dione (BOD) in the presence of Sn(Oct)₂ as a catalyst and a RAFT agent containing a hydroxyl functional group. Empirically, the above work reported the synthesis of branched PCL in the presence of BOD when conducted as a solution polymerisation. However, an in-depth understanding of the branching copolymerisation reaction is still lacking, especially for bulk ROP systems.

This study reports the branching ROP copolymerisation of CL and a dilactone in the presence of benzyl alcohol (BzOH)/Sn(Oct)₂ as the initiator/catalyst system when conducted in the bulk. To the best of our knowledge, this is the first investigation in which the ‘Strathclyde Method’ has been applied with a bulk (i.e. solventless), controlled ROP mechanism.^{3-4,9-12,31-40} The ‘Strathclyde Method’ was a pivotal early example of such a branching synthetic strategy and centred on the standard free radical (SFR) copolymerisation of monofunctional and difunctional vinyl monomers.⁹⁻¹² One of the main conclusions drawn from this work was that gelation, i.e. the formation of an extended crosslinked network, occurred when an average of two or more branch points per chain was achieved. Subsequently, controlled radical techniques (CRP) were successfully applied to conduct ‘Strathclyde Method’ type highly/hyper branching strategies.^{3-4,31-40}

To further probe this effect, this report focussed on investigating the impact that controlled characteristics has upon the outcome of the Strathclyde strategy for the synthesis of highly branched PCL when applied to bulk conditions.

Experimental

Materials: ϵ -Caprolactone (99%) was purchased from Acros and used as received. Karl-Fisher titration was used to determine the water content of the monomer (67ppm). Tin 2-ethylhexanoate (96%) was purchased from Advocado. Anhydrous benzyl alcohol (99%) and the high molecular weight linear PCL (80,000 g/mol) used as a reference for analysis were purchased from Sigma-Aldrich. Bicyclohexanone was purchased from TCI Europe (Tokyo Chemical Company). All chemicals were used as received without any purification.

Characterisation -Determination of Monomer Conversion: ¹H NMR spectra were recorded in CDCl₃ using a Bruker DPX-300 spectrometer (300MHz) to determine monomer conversion for both homo and copolymerisations. Monomer conversion was determined by comparing the integral of methylene proton resonance adjacent to the oxygen of the carbonyl group for both monomer (-CH₂OCO-, δ =4.24 ppm) and polymer (-CH₂OCO-, δ = 4.07 ppm). For purified polymers, a Bruker DPX-400 spectrometer (400MHz) was used. Number-average molecular weight (M_n) was determined by end-group analysis using NMR spectra.

Determination of Degree of Branching by NMR: Solution ¹³C NMR measurements were carried out in CDCl₃. A BrukerDPX400400MHz instrument was employed and 128 scans were required to achieve a sufficient signal to noise ratio for linear PCL₅₀. However, 20,000

scans were needed with for the branched polymer to detect the methyne carbon signal characteristic of the branch points in the polymer.

Gel Permeation Chromatography (GPC): GPC measurements were obtained using a triple detection system in which a differential refractive index (DRI) detector, solution viscometer and Laser Light Scattering at 90° angle were used. A polymer solution of 7 mg/mL in HPLC grade THF was prepared, and filtered through a 0.2µm sieve into a GPC vial. The samples were then injected into a GPC calibrated using PS standards for a typical run-time of 36.4 min. This procedure produced data for GPC-DRI and bulk viscosity of the polymers. Multi-angle laser light scattering (MALLS) was also used for analysis of the branched polymers. In this case, seven different scattering angles are used and data were collected on Astra software. The dn/dc of highly branched polycaprolactone (PCL₅₀BOD_{0.6}) was measured in HPLC grade THF by measuring the refractive index values of five concentrations using a refractometer at 25 °C and was found to be 0.061.

Differential Scanning Calorimetry (DSC): Polymer glass transition (T_g) and melting (T_m) temperatures were determined using a Thermal Analysis (TA) Q2000 Differential Scanning Calorimeter (DSC) under a nitrogen stream (50 mL min⁻¹). Changes in heat flow were recorded between -80 °C and 80 °C over two cycles. Unless otherwise stated, the second scan was used in order to remove the thermal history of the polymer being analysed. To achieve this, a scan rate of 20 °C/min was employed, along with a 10 minute isotherm at either end of the temperature range to complete the cycle. In a typical procedure, a polymer sample of 3 mg was loaded into a standard pan and an empty pan was used as the reference. The instrument was calibrated using indium metal standards supplied by TA Instruments and has a quoted calorimetric precision and reproducibility of ±0.05 % and temperature control accuracy of ±0.1 °C. Analysis of the data was performed using Universal Analysis by TA and a series of repeat measurements on a single polymer product showed that the standard deviation from the mean T_g was ± 0.35 °C using this software.

Synthetic Procedures - The synthesis of 4,4'-bioxepanyl-7,7'-dione (BOD): 4,4'-bioxepanyl-7,7'-dione (BOD) was prepared using an adapted procedure from the literature.⁴¹ Urea hydrogen peroxide (CO(NH₂).H₂O₂) (20 g, 0.21 mol) was added to a 500 mL round- bottom flask containing formic acid (100 mL). The solution was stirred for 2h at room temperature. The flask was then immersed in an ice bath to control the exotherm resulting from the following stage of the procedure. Bicyclohexanone (10 g, 0.05 mol) was slowly added to the

solution over a period of 5-10 min. The reaction mixture was stirred for 4h whilst the ice bath was changed periodically. 200 mL of water was then added to the mixture followed by extraction with chloroform (200 mL x 4). The organic fraction was collected and washed with a saturated aqueous sodium bicarbonate solution then dried over night with Na₂SO₄. After removing the solvent under reduced pressure, a white powder was isolated and analysed by NMR and compared to the literature reported values.⁴¹

Homopolymerisation for a Fixed DP = 50 (BzO₁PCL₅₀): All polymerisations described in this section were conducted in bulk without further purification of the reagents. The typical protocol for the homopolymerisation of CL for a target DP 50 was as follows. CL (12g, 105 mmol) was weighed into a 50mL Schlenk tube and then SnOct₂ catalyst as a solution in toluene (0.25 mL of a 49.8×10⁻² g/mL solution) and anhydrous BzOH (218 μL, 2.10 mmol) were added *via* syringe. The flask was then fitted with a glass/PTFE paddle stirrer *via* a PTFE bearing and the contents were stirred until homogeneous. The flask was then immersed in a preheated oil bath at 150°C and vigorously stirred for the required reaction time. For kinetic studies, the mechanical stirrer was paused at set times throughout the reaction and aliquots of the reaction mixture were extracted from the polymerising melt by pipette, rapidly cooled and retained for GPC and NMR analysis. Upon cooling, the samples rapidly solidified.

Branching Copolymerisation for a Fixed DP=50 with various BOD concentrations (BzO₁PCL₅₀BOD_x; x=0.4-0.6): The typical protocol for a branching copolymerisation of CL for the targeted structure BzO₁-PCL₅₀-BOD_{0.6} was the following. CL (12g, 105 mmol) and BOD (0.285 g, 1.26 mmol) were weighed into a 50mL Schlenk tube. The solution was shaken until the BOD was fully dissolved in the CL. The remaining procedure is identical to that of the CL homopolymerisation detailed above and contained the identical amounts of BzOH and Sn(Oct)₂ solution.

Results and Discussions

Homopolymerisation: Initially, before investigating the copolymerisations to synthesise branched polymers, the analogous linear homopolymerisations were conducted to provide a suitable polymerisation control comparison. Both monomer conversion and degree of polymerisation achieved were determined and a linear relationship was obtained in the plot of evolution of Mwt versus the monomer conversion (see Figure 1).

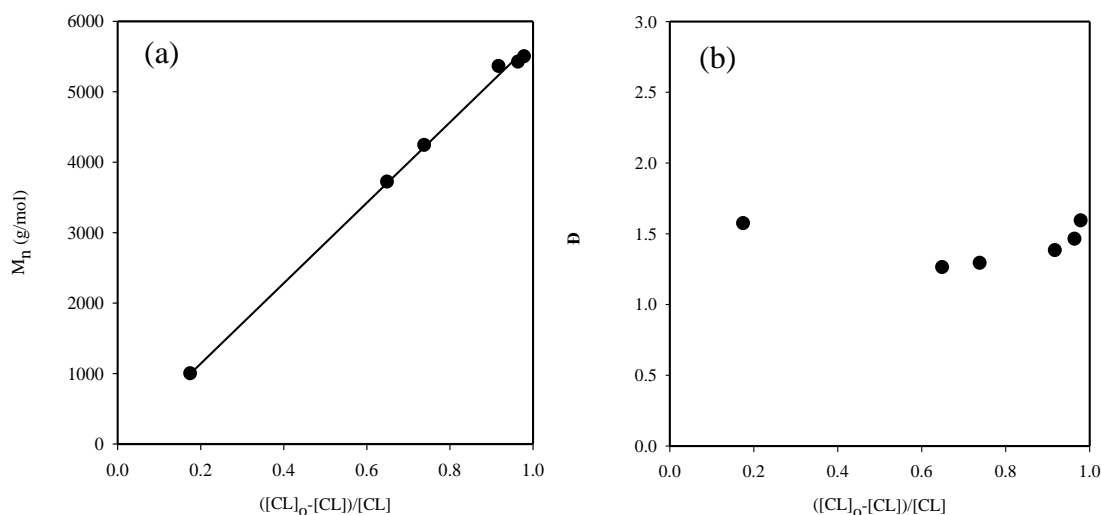


Figure 1.(a) Plot of the evolution of (a) polymer Mwt with conversion and (b) Polydispersity indexes (M_w/M_n) with conversion for the polymerisation of ϵ -CLat 150°C with a CL: BzOH: SnOct₂ relative molar ratio of 50: 1: 0.024.

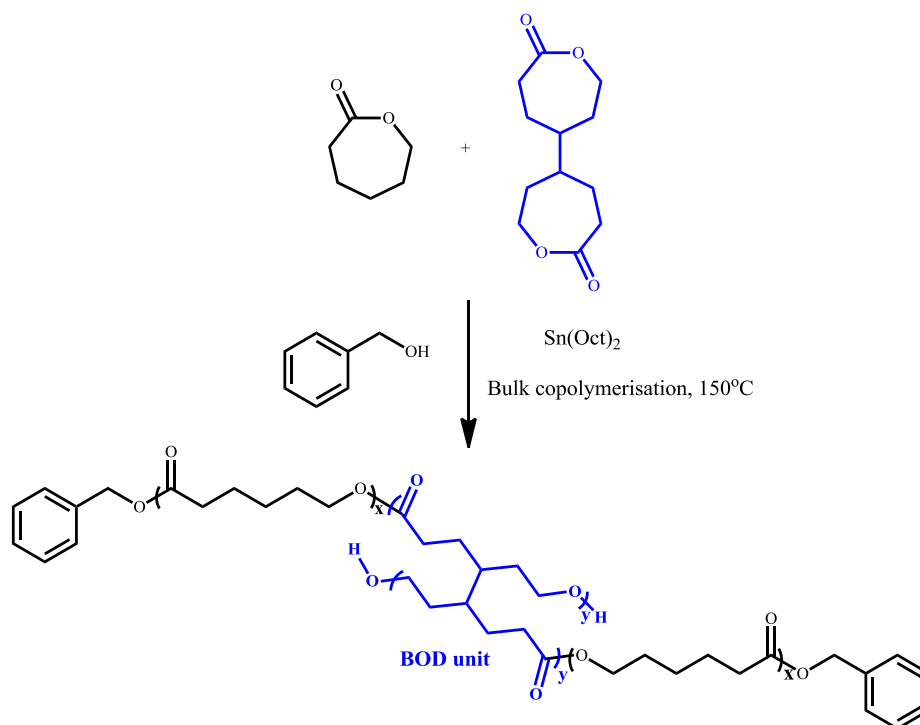
This confirmed that the solvent free ROP conducted using this method exhibited controlled characteristics, where 98 % conversion was obtained within 1 hour under these conditions. Typically, the dispersity (\bar{M}) values of the final polymers obtained was found to be within the 1.4-1.7 range at high conversion (see Figure 1(b)), but below 80% conversion the \bar{M} s were shown to be in the 1.2 to 1.3 range. This broadening has been attributed to the onset of transesterification reactions at high conversion.⁴² These side reactions may affect the targeted branching process in the copolymerisation with BOD and consequently these effects are discussed in more details later sections of this report.

Branching Copolymerisation

PCL₅₀BOD_{0.6}: According to classical Flory-Stockmayer theory, the onset of gelation is predicted when 0.50 units of fully reacted branching comonomer per primary chain is achieved, when assuming equal reactivity of the monomers and no intramolecular cyclisation.⁵⁻⁷ More recently however, results reported by Sherrington and Armes suggested that gelation could be avoided with up to, but below, 1 divinyl unit per primary chain, when copolymerising vinyl monomer and divinyl comonomers under certain reaction conditions. Subsequently, this approach has been studied for radical polymerisation using many techniques including ATRP and RAFT.³⁻⁴ In the context of this paper, for this technique to be applicable to ROP, it must therefore be assumed that the existence of both intra- and intermolecular trans-esterification side-reactions in ROP will not vastly disrupt the branching process involving the di-functional co-monomer. Therefore, the target of 0.6 BOD units per

primary chain was chosen for the initial study. This was a ratio well below the threshold limit of 1, in order to ensure that gelation was avoided. In practice, the control over the number of units of BOD per chain was achieved by adjusting the molar ratio of $[BOD]_0/[BzOH]_0$, since the choice of this initiator/catalyst system ensured that a controlled polymerisation results.

Consequently, the kinetics of ϵ -CL and BOD copolymerisation using BzOH and $Sn(Oct)_2$ was studied at 150 °C in bulk, with a target linear polymer equivalent DP of 50 ($BzO_1-PCL_{50}-BOD_{0.6}$). To do this the concentration of $Sn(Oct)_2$ was calculated such that it delivered a relative molar ratio $[CL]:[BzOH]:[BOD]:[Sn(Oct)_2] = 50:1:0.6:1.4 \times 10^{-3}$ (see Scheme 1).



Scheme 1. Synthesis of highly branched polymers *via* copolymerisation of CL and 4,4'-bioxepanyl-7,7'-dione (BOD) by ROP using BzOH/ $Sn(Oct)_2$ as the initiator/ catalyst system in bulk at 150 °C.

By comparison to the kinetics of a homopolymerisation of a DP 50 polymer, it was predicted that full-conversion (i.e. 99%) should be achieved within 60 min of commencing the polymerisation, assuming the di-functional monomer was incorporated at an equal rate to the mono-functional monomer. Therefore, the kinetics of a $PCL_{50}BOD_{0.6}$ copolymerisation was followed for 60 min with 10 min interval allowed between samples and this demonstrated that the branching copolymerisation also achieved 99% conversion in 60 min.

The product polymer was observed to be completely soluble in organic solvent, thus it was concluded that the material did not possess an extended 3 dimensional network structure. The 1H NMR spectrum of the product polymer was observed to be essentially identical to that of linear PCL (see ESI, Figure S.1) and the value of DP, which was also determined by 1H NMR, and was defined to be 49. Additionally, the branching process of the copolymerisation

between CL and BOD was investigated by observing the relationship between the evolution of both the M_w s and \bar{D} s of the branched polymers versus monomer conversion at the time of sampling *via* GPC analysis, which also predicted the M_w of the material at 99% conversion approximately 90,000 g.mol⁻¹, (see Figures 2 and 3).

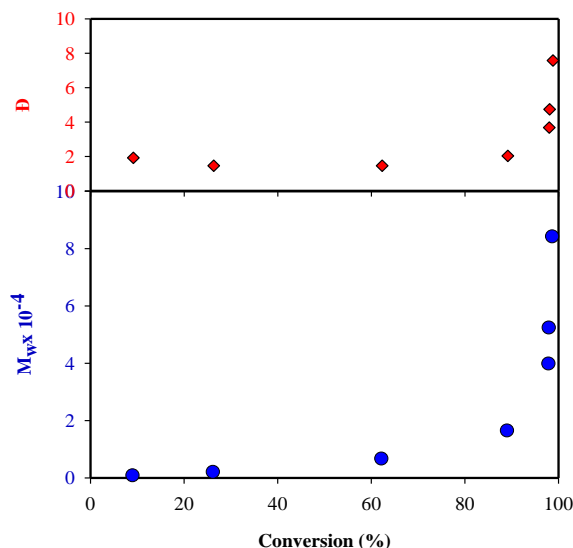


Figure 2. Plot of the evolution of M_w and \bar{D} values versus total conversion of monomer for the synthesis of branched PCL₅₀BOD_{0.6} copolymer. A THF GPC calibrated with PS was used.

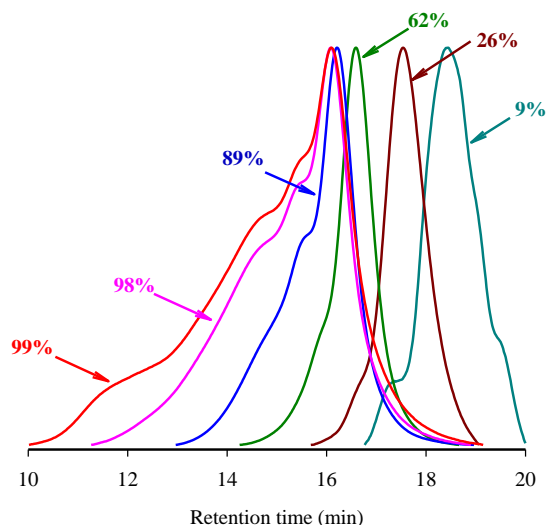


Figure 3. GPC traces recorded using a DRI detector with PS as polymer standard for the bulk-ROP of PCL₅₀BOD_{0.6} copolymer at 150°C for a fixed DP 50 PCL and BOD copolymer which is limited to 0.6 units per chain. The appended percentage figures define the conversion achieved at the time of sampling.

Conventional GPC utilising a DRI detector could only provide an indicative molar mass relative to standards (in this case, polystyrene). However, it could provide an accurate measurement of variation in \bar{D} between different kinetic samples, and thus was used to define the point in the reaction where significant *onset* of branching occurred. This point was indicated by a sharp increase in the \bar{D} values exhibited by the kinetic sample. The GPC data

in Figure 3 showed that, whilst there is some branching induced by the presence of the BOD at monomers conversions as low as 9%, as indicated by the small shoulder at shorter retention time. The onset of significant levels of branching was observed at approximately 90% of total monomer conversion, when both an abrupt increase in the \bar{M}_w values and the development of significant multimodal nature in the GPC traces were observed. This was a significant difference from the reports in which both ATRP and RAFT were used for branching copolymerisation of vinyl monomer, where the onset of branching was reported to be at around 70% monomer conversion.³⁻⁴ Therefore, in this chain growth ROP which proceeds *via* a coordination-insertion (C+I) mechanism, the onset of high levels of branching would seem to be postponed to much higher conversion level due to the steric hindrance related to the second ring structure on the BOD once it is incorporated into the chain. It was proposed that the additional steric bulk around the “pendant” BOD ring would favour the coordination of free CL to the Sn catalyst centre until the monomer concentration has been significantly depleted. In an attempt to support this hypothesis, ¹³C NMR analysis of these materials was conducted across the whole conversion range. Unfortunately, the resulting spectra proved to be highly convoluted and difficult to interpret with a necessary degree of certainty. This was attributed to (a) a combination of the low concentration of branch points, (b) the presence of the second potentially dominating branching mechanism (transesterification) and (c) the constrained molecular environment in the branched core of these materials making NMR difficult to both perform and interpret.

The multimodal GPC traces from the polymerisation kinetic samples, shown in Figure 3, suggested that the final product was composed of polymers with very varied molecular structures and levels of branching. Additionally, the retention of peaks with relatively narrow \bar{M}_w s within the overall profiles of the chromatographs of high conversion samples demonstrated that these materials contain both linear and branched polymer species.⁴ Interestingly, despite the variation in polymerisation mechanism (i.e. ROP versus RAFT or ATRP) and the later onset of branching as a result, the use of a difunctional monomer to introduce branching has resulted in a polymer product which exhibits GPC profiles that are very comparable to those reported by Armes *et al.* for these controlled radical techniques.³⁻⁴ Furthermore, the fact that a significant proportion of linear chains remain at the end of the branching copolymerisation was also reported by Armes and co-workers, which they concluded to be a result of the purely statistical branching process by which these materials are synthesised.⁴ In fact, when using the DRI detector, the most prominent signal within the GPC trace of the > 90% conversion product polymer corresponds to linear polymer chain.

This can clearly be seen in Figure 4, which overlays the characteristic GPC traces for a linear PCL₅₀ homopolymer prepared without BOD and the branched copolymer at 99% conversion.

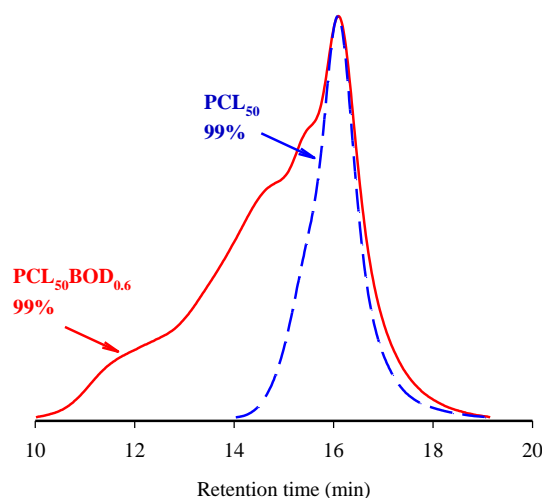


Figure 4. Comparison of GPC traces for linear PCL₅₀ and PCL₅₀BOD_{0.6} 99% conversion.

This data indicated that either there was (a) significant linear material still present in the branched polymer and/or (b) the branched polymer consists of statistically linked linear chains. Further studies are on-going in an attempt to elucidate which of these is the true structural characteristic of the final polymer mix. This data also confirmed that molecular weight growth observed at these higher conversions was related to the presence of the BOD co-monomer and was not a direct result of the normal trans-esterification processes known to occur with this ROP in linear polymer systems. However, in this high conversion region the actual hyperbranching process may be as a result of either/both the C+I or the trans-esterification mechanisms.

Consequently, in order to determine whether a greater degree of branching could be achieved using this strategy, branching copolymerisations were conducted with higher BOD ratios per chain (i.e. PCL₅₀BOD_{0.7-1}). Unfortunately, all of these reactions resulted in macrogelation at high conversion, i.e. gelation occurs after 50 min of copolymerisation resulting in polymer networks which were insoluble in DCM. Soluble material could be isolated from reactions conducted with these higher BOD levels, if the reaction was stopped at times below 50 minutes. However, inspection of the GPC traces (Figure 3) showed that this was prior to significant branching and so the product consisted of only relatively low Mwt linear polymer. Therefore, it was concluded that to ensure branching of ROP with BOD produced a solvent soluble, highly branched material at high monomer conversion, the BOD

concentration was required to be a maximum of 0.6 per primary chain and the conversion was required to be $\geq 90\%$.

Effects of Trans-esterification on Gelation: According to the theory proposed by Flory and Stockmeyer and the experimental data obtained by Sherrington and Armes, in order to prevent gelation when using a di-functional comonomer at high conversion, the number of branching units per polymer chain must be equal to or less than 1. However, using the procedure discussed in this study, the number of branching units is limited to 0.6 BOD per primary chain for the synthesis of soluble highly branched PCL. This deviation from theory could be caused by two possible factors: (a) the propagation mechanism is occurring in an uncontrolled way such that much greater amounts of BOD are incorporated in some of the polymer chains or (b) a secondary mechanism is occurring that deviates from standard chain-growth mechanism. As discussed earlier, the deviation from Flory-Stockmeyer theory in “linear” ROP of CL has been attributed to the presence of the well-known inter- and intra-chain trans-esterification reactions that occur as the reaction moves toward completion. As indicated in Figure 1(b), the trans-esterification leads to higher \bar{D} values at high conversion. Intra-molecular cyclisation has also been reported by Armes and co-workers in reactions that form highly branched polymers involving divinyl monomers controlled by RAFT.³⁻⁴ Therefore, it was proposed that $\text{PCL}_{50}\text{BOD}_x \geq 0.7$ is the threshold of high conversion gelation was a consequence of the presence/influence of these “additional” interchain trans-esterification reactions. This also suggests that the intermolecular trans-esterification dominates over the intramolecular cyclisation in this reaction system which should delay the onset of gelation. Furthermore, this effect cannot be circumvented by restricting the overall conversion of the reaction as in the case of free radical branching polymerisation of vinyl monomers because the significant branching onset is found to be in this high conversion region.^{3-4,43}

To test the hypothesis that trans-esterification affects the branching process, the branching copolymerisation was repeated for the synthesis of $\text{BzO}_1\text{PCL}_{50}\text{BOD}_{0.6}$ with a reaction period that extended well beyond the time needed to achieve complete conversion. The reaction conditions were identical to that used for the synthesis of $\text{BzO}_1\text{PCL}_{50}\text{BOD}_{0.6}$ which had been shown to produce the soluble branched polymers. However, in these experiments, instead of terminating the reaction at 60 min, it was allowed to continue for 19h. During this time, kinetic samples were taken after 20, 40, 60, 120 min and 19h. Consequently, if trans-esterification was the dominant mechanism at high conversions rather than the coordination and insertion of monomer, then applying a reaction time which exceeded complete

conversion of monomer should initially develop higher Mwt polymers containing microgels which are difficult to dissolve and ultimately lead to gelation resulting in insoluble polymers. The GPC traces in Figure 5 show the evolution of molecular weight with conversion for this 19 hour reaction.

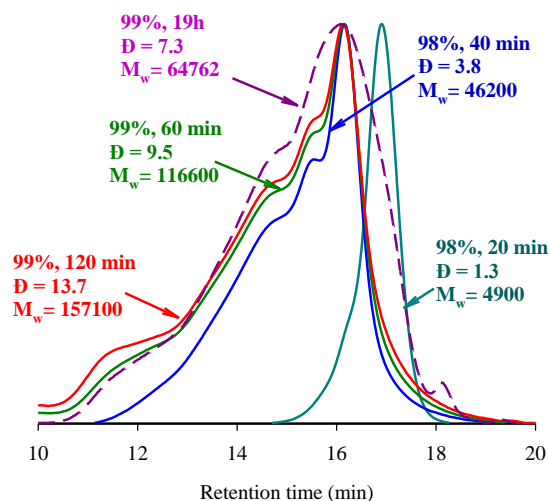


Figure 5. GPC traces for bulk-ROP synthesis of PCL₅₀BOD_{0.6} copolymer at 150°C for a fixed DP 50 of CL with BOD limited to 0.6 unit per chain, where the reaction was continued beyond completed conversion.

As in the previous cases, the polymerisation was observed to have reached near quantitative conversion (i.e. > 99%) after 60min, when the M_w and \bar{D} measured by GPC-DRI were 116,000 g/mol and 9.47 respectively. Meanwhile, for the sample taken at 120min (99%), the M_w and \bar{D} were found to 157,000 g/mol and 13.69 respectively. Since ^1H NMR analysis showed that there was no longer any monomer present in the reaction mixture during the extended reaction period, this indicated that trans-esterification was indeed an alternative reaction occurring at these high conversions. Interestingly, although higher M_w and \bar{D} were obtained in this experiment for the sample taken at 120 min, it was found to easily pass through 0.2 μm filter prior to GPC analysis, indicating the presence of a soluble polymer and the absence of significant macro-gelation. This may indeed suggest that trans-esterification may be a mechanism that contributes to the formation of the branching links at high conversion. Therefore, it was proposed that the steric bulk around the “pendant” BOD ring of a chain incorporated monomer results in the expected tin based C+I mechanism dominating < 90 % conversion, to promote propagation to form linear chains *via* the insertion of free monomer. Then at high conversion, the difficulty on achieving coordination of the “pendant” BOD to the Sn complex due to its proximity to the chain may also allow trans-esterification to result in the inter-reaction of two chains to create additional branching links. This data certainly practically demonstrated that the presence of low levels of BOD in the CL chains

resulted in the isolation a very different product polymer and that BOD was clearly promoting the occurrence of branching, whichever mechanism was driving the branching process.

However, when the polymerisation continued for 19h prior to GPC analysis, significant blockage of the GPC filter occurred when preparing the THF based polymer solution. Thus it was concluded that only certain lower Mwt polymers from this distribution passed through the filter before the blockage, where these exhibited a GPC profile (see Figure 5- dash line) similar to that of the 120 minute sample. The formation of polymer species that were unable to be filtered indicated that trans-esterification induced formation of a gel or very high Mwt polymers if the reaction was allowed to react for extended periods, even for the polymerisation conditions were below/at the key BOD threshold of $PCL_{50}BOD_{0.6}$. This observation supports our hypothesis in which trans-esterification is the main reason for the microscopic and macroscopic gelation that occurs at higher reaction times at BOD concentration above 0.6. Thus it has been concluded, when using these ROP mechanistic/reaction conditions to produce highly branched polymers, that both (a) the maximum/optimal BOD concentration is 0.6 equivalents and (b) a controlled reaction time length needs to be assured, in order to obtain a correct balance between branching and trans-esterification during the "monomer consumption" phase of the reaction and ensure generation of solvent soluble materials.

Soluble highly branched $PCL_{50}BOD_x$ ($x \leq 0.6$): We also investigated the polymer products that resulted when smaller amounts of BOD were used in an attempt to prepare less-branched polymer and Table 5.1 summarises the synthesised polymer data, including radius of gyration (R_g) and the slope of R_g versus M_w , which indicate the presence of branched structures (See ESI, S3).

Table 1. Summary of reaction conditions and polymer analytical data for branched polymers synthesised with different amounts of BOD. MWts and Đs were determined by GPC-DRI

Target composition	Time (min)	Conv (%)	M_w^a (g/mol)	\bar{D}^a	M_w^b (g/mol)	\bar{D}^b	R_g (nm)	R_g/M_w slope
$PCL_{50}BOD_{0.4}$	60	99.0	32570	2.8	27900	2.5	9.3	0.37
$PCL_{50}BOD_{0.5}$	60	99.0	61600	5.7	70800	4.6	15.8	0.31
$PCL_{50}BOD_{0.6}$	60	99.0	93900	7.6	141900	6.0	24.0	0.28

(a) GPC-DRI (b) GPC-MALLS

The monomer conversions achieved were generally high (99%) for all these polymerisations. As observed previously, the M_n values of these polymers are approximately 11,000 g/mol, while M_w and \bar{D} were noted to increase with increasing BOD concentration. The comparison of GPC chromatograms obtained from both DRI and MALLS detectors shows the evolution of the trace profiles with the increasing amount of BOD are shown in Figure 6.

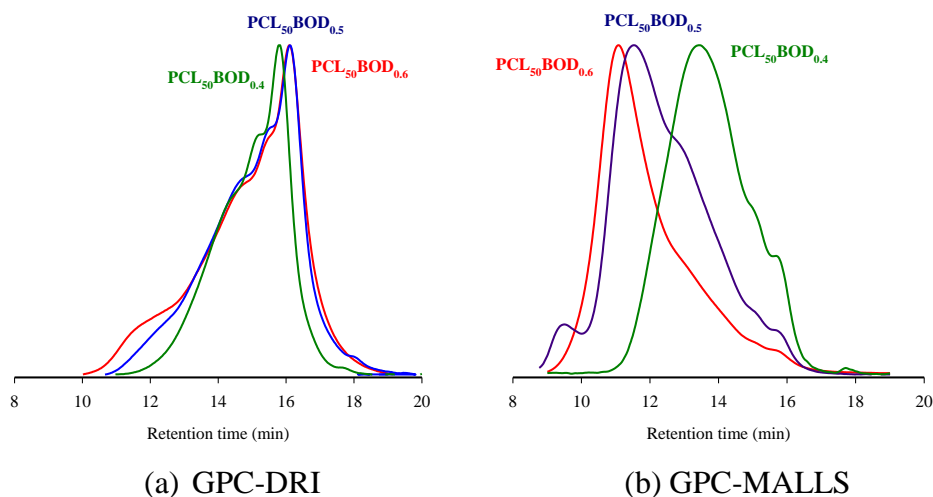


Figure 6. GPC traces for bulk-ROP synthesis of $PCL_{50}BOD_x$ ($x=0.4-0.6$) copolymer at 150°C for a fixed DP 50 PCL using (a) DRI detector with PS standards and (b) MALLS detector.

Multi-angle Laser Light Scattering:

The resultant M_w and R_g for the branched PCL polymers with various BOD levels were analysed by GPC-MALLS and the absolute M_w measured by GPC-MALLS were observed to have the same trend as those measured by GPC-DRI (see Table 1). Typically, the M_w measured by MALLS is generally observed to be higher than those obtained by DRI and increase as the BOD level is increased from 0.4 to 0.6, whilst the MALLS \bar{D} values are noted to be slightly smaller when compared to DRI. This can be attributed to the sensitivity of MALLS towards higher molecular weight region of the chromatogram, since the light scattering intensity is proportional to both concentration and Mwt of each chain.⁴⁴ The R_g was also found to increase when BOD concentration increased, suggesting that the increase in BOD concentration resulted in a greater amount of chain coupling leading higher M_w , rather than a more compact structure. This data indicated that the structure of branched polymer was dependent on the number of BOD per primary chain. Since $BzO_1PCL_{50}BOD_{0.6}$ could be readily prepared after 60 min without any gelation, it was chosen as an example for the comparison of the GPC-DRI and GPC-MALLS data, as shown in Figure 7 (see ESI, Section S.2 for determination of both M_w and R_g).

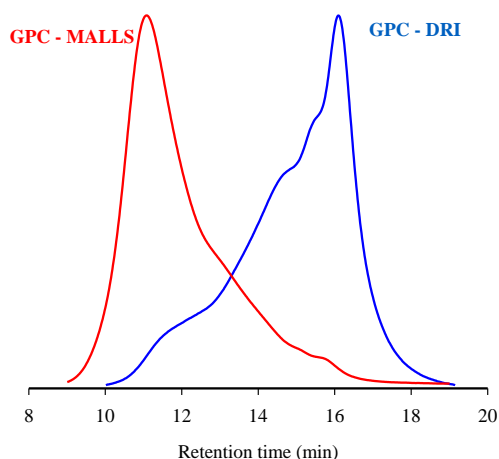


Figure 7. The GPC trace comparison measured by GPC-MALLS (Red) and GPC-DRI (Blue). $\text{PCL}_{50}\text{BOD}_{0.6}$ in THF was chosen as an example.

Conformation Plots: The conformation plot, in which R_g is plotted against $\text{Log } M_w$ (see ESI Figure S.3) and/or M_w (see Figure 8), provided more evidence to support the conclusion that these polymers possess a significant quantity of branched structures.

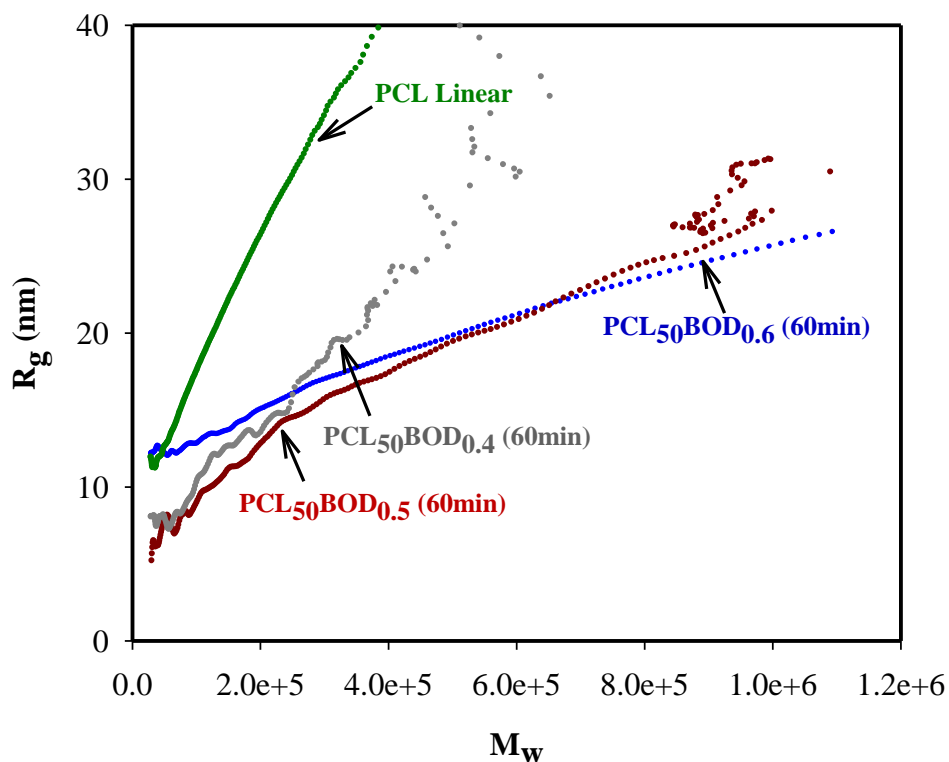


Figure 8. The conformation plots of $\text{PCL}_{50}\text{BOD}_x$ ($x=0.4-0.6$) R_g versus M_w within the range of interest: 30kDa – 1MDa

The slope of the conformation plot can provide information related to the molecular shape of the polymer and permits linear and branched polymers to be distinguished.⁴⁵ For linear random coils, the gradient values are generally within the 0.5 – 0.6 region, whereas for branched polymers the values are typically lower.⁴⁶ For these product polymers, the conformation plots (see Figure 8 and ESI Figure S.3) were shown to be non-linear in nature, which is typical for branched polymers, indicating that there are differences in branching within the series. Furthermore, close examination of the data obtained from these R_g against M_w plots (see Figure 8 and Table 2) strongly indicated that there was a progression in both level of branching compared to linear and relative to branching number achieved as the BOD concentration was increased.

Table 2. Summary of the absolute M_w , conformation slope, and branching ratios

Target copolymer composition	M_w -MALLS (g/mol)	R_g - M_w slope	g_M	g'_M	$M_{w-DRI}/M_{w-MALLS}$
PCL linear	99900	0.70	1.0	1.0	1.05
PCL ₅₀ BOD _{0.4}	27900	0.50	—	0.37	0.61
PCL ₅₀ BOD _{0.5}	70800	0.20	0.56	0.27	0.51
PCL ₅₀ BOD _{0.6}	141900	0.10	—	0.19	0.35

Degree of Branching (DB) by GPC-MALLS and GPC-Viscometer: The DB values of these highly branched PCL₅₀BOD_x materials were investigated using several methods including NMR, GPC-MALLS and GPC-Viscometry. Unfortunately, because it has generally proved impossible to determine DB by either solution or solid state ¹³C NMR, average contraction factors parameters such as g_M and g'_M , have typically been used in previous literature reports to describe the DB of the branched polymers.^{1,46-47} The mathematical equations that describe these parameters can be found in the ESI (Section S.4). They are calculated based on the mean radius of gyration and intrinsic viscosity of the polymer respectively, where the mean square radius of gyration $\langle R_g^2 \rangle$ is related to the hydrodynamic volume of a polymer,^{44,47} and is measured using light scattering methods. 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. 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. Similarly, the ratio of the intrinsic viscosity $[\eta]$ of a branched polymer to that of a linear one is expressed as g'_M . The GPC-viscometer technique relies on the universal calibration which plots $\log[\eta]$ versus $\log[M_w]$ of linear PS standards (see ESI section S.3 for more information). In addition to these ratios, it has been proposed 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.⁴⁶ The explanation for this relationship 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. The relative level of branching in these PCL-co-BOD_x structures calculated using different methods are listed in Table 2 (See ESI, Section S.3 for more information).

The data in Table 2, strongly suggested that the polymer products did indeed possess a branched architecture. Conformation slopes obtained when plotting the Mwt range of 30kDa to 1MDa indicated that for linear PCL the slope value is more than 0.5 (0.7) as expected, while lower values observed with lower number of BOD were strong evident of branching (see Figure 8).⁴⁵ In particular, PCL₅₀BOD_{0.6}(0.1) with the lowest value of the slope exhibits its highly branched characteristic compared to PCL₅₀BOD_{0.4} and PCL₅₀BOD_{0.5} (0.5 and 0.2 respectively).

Further inspection of the branching ratio data (g_M , g'_M and $M_{w-DRI}/M_{w-MALLS}$) suggested that the polymer architecture varied with BOD concentration both corroborated this observation and provided convincing proof of branched structures. They all predicted branching ratios well below 1.0 for all the branched polymers synthesised. As expected, low concentration of BOD lead to lower branching ratios (hence lower DB), which is highly convenient as polymers with different DB can be tailored to deliver particular desired effects in differing applications. Furthermore, the fact that the DB values obtained for linear polymer remained constant highlighted the validity of these three methods of accessing branching ratios.

The g'_M calculation relies on obtaining the $[\eta]$ values of both branched and linear polymer. The branched value can be obtained directly from GPC-viscometer, whilst the linear polymer of interest is assumed to have the same M_w as that of the branched one so that Mark-Houwink-Sakurada equation could be applied (see ESI, Section S3 for a more detailed explanation). The data from Table 2 confirmed that for linear polymer, $g'_M = 1$, and that this decreased with increasing DB and hence branching ratio. The g'_M value PCL₅₀BOD_{0.6} was noted to be particularly small when compared to both that of linear polymer and also the polymers containing lower BOD levels, again demonstrating its highly branched structure. Only one approximate g_M value was calculated due to the fact this calculation should be based on the R_g of linear and branched polymers with the same Mwt. In practice, due to limited availability of linear PCL with the Mwt of interest, the g_M value in Table 2 is only

approximate, yet still shows a much lower branching ratio compared to linear polymer. Similarly, because estimation of branching ratio relies upon hydrodynamic volume, it also showed a descending trend with higher BOD level. This set of data indirectly suggested that at certain Mwt, the hydrodynamic volume decreases with higher DB. Again, the branching ratio of the branched polymer was noted to be smaller than that of linear polymer and the PCL₅₀BOD_{0.6} was observed to exhibit a significantly smaller value when compared to less branched PCL₅₀BOD_{0.4} and PCL₅₀BOD_{0.5}. Overall, the consistency of the descending trends detailed in Table 2, relative to ascending BOD concentration, strongly indicated that branching was significantly influencing the physical properties of the resultant polymers such as their Mwts and architectures. Furthermore, these conclusions are in agreement with analogous work with free radical based branching polymerisations.⁴⁶

Differential Scanning Calorimetry: The thermal behaviour of linear PCL has been extensively studied and it has been shown to be a semi-crystalline polymer exhibiting both a melting (T_m) and a glass transition temperature (T_g). Typical literature quoted values for these properties lie in the following ranges; T_m of 56 to 65 °C and T_g of -65 to -60 °C.⁴⁸⁻⁴⁹ However, the introduction of branching into polymers has been reported to affect these thermal properties.^{12,50-51} In part, this has been attributed to the introduction of branches limiting the ability of the polymer chain to undergo crystallisation. If this is the case then, in this study, the introduction of a branching comonomer into linear PCL should lead to change in the T_m , where the observed value would be expected to decrease as DB increases (i.e. as the amount of BOD used increases). Consequently, the effect that the branching in the PCL₅₀BOD_x (x=0.4, 0.5 and 0.6) materials had upon the observed T_m and hence crystallisation was investigated by DSC.

In a series of experiments, the DSC temperature profile was collected from -80°C to 80°C with the heating rate of 20°C per minute under N₂. Table 3 contains the observed T_g and T_m values of both the branched polymers and commercially purchased, high molecular weight linear polymer.

Table 3. Transition temperatures T_g and T_m , measured by DSC from -80°C to 80°C with a heating rate of 20°C per minute.

Target copolymer composition	T_g (°C)	T_m (°C)
High MW PCL linear	-61.47	59.7
PCL ₅₀ BOD _{0.4}	-56.76	58.4
PCL ₅₀ BOD _{0.5}	-60.75	56.6
PCL ₅₀ BOD _{0.6}	-61.50	56.1

The experimentally measured T_g values were observed to vary between approximately -56 to -62°C, such that they all lie in the region of literature quoted T_g values for linear PCL, as reviewed by Labet et al (-65 to -60°C).⁴⁹ Thus, the T_g of these highly structures were shown to be similar to those of the linear equivalents. However, there was also a defined trend in the branched polymer data. The material containing the lowest level of BOD or branching (PCL₅₀BOD_{0.4}) exhibited the highest T_g value, then as the BOD level was increased so the T_g was observed to decrease until it returned to a value close to that of the linear PCL for PCL₅₀BOD_{0.6}. It was postulated that this was unlikely to be due to an increase in the chain ends present due to the direction of the data trend, i.e. taking the value back to that of the linear polymer. Rather, it was attributed to the fact that the introduction of branching may alter the overall level of inter-chain interaction achieved within the material.

The T_m values of the branched polymers also demonstrated a clear linear trend with DB. As the amount of BOD and so DB increased, the T_m values were observed to decrease. However, in this case, the melting transition was noted to move away from that of the linear material to a lower temperature in a sequential fashion related to the BOD concentration, this data is shown in Table 3. Therefore, this observed trend in T_m indirectly corroborated that both branched structures had been produced and the DB was related to the BOD level present in the feed. It also supported the proposal detailed in the literature that crystallisation behaviour is affected by the branched nature of the molecular structures. However, because a T_m is still recorded, this data also defined that these highly branched PCLs are still semi-crystalline in nature and so there must still be crystallites present in the structure. At this point it is not clear if this is as a result of the presence of the linear PCL material in the final product polymer or indicates that the branching levels achieved in these materials is not sufficient to prevent to onset of longer range order in the material. Rather, it defines that there are still sufficient linear characteristics in the overall product material that crystalline domains can form.

CONCLUSION

The synthesis of highly branched PCL was successfully conducted for the first time *via* a solvent free (bulk), ROP of CL and BOD in the presence of BzOH/Sn(Oct)₂. The branching copolymerisation was conducted *via* application of a synthetic method similar to the Strathclyde type approach and it was concluded that the polymerisation proceeded *via* a random statistical branching copolymerisation. These reactions were demonstrated to result in the isolation of mixed branched polymer materials that contained a certain quantity of

linear polymer by-products. High conversions were achieved for all polymerisations, and whilst the appearance of branching was observed when conversion was as low as 9 %, the onset of significant levels of branching were not observed until approximately 90% conversion had been achieved. This differs from the “classical” Strathclyde method with vinyl monomer in which significant branching is observed at/or around 70% conversion.

In contrast to highly branched polymers that are synthesised *via* a free radical mechanism, it was concluded that the number of BOD units per primary chain had to be kept at a level which was lower than 0.6 equivalents (*c.f.* 1 equivalent of BzOH) in order to produce a soluble highly branched polymer (i.e. $\text{BzO}_1\text{PCL}_{50}\text{BOD}_x$, $x \leq 0.6$). Furthermore, it was clearly demonstrated that the trans-esterification reactions which occur in ROP reaction that use this C+I type mechanism are an important factor that contribute significantly to system gelation to form an extended, non-solvent soluble 3 dimensional network. It is these side reactions that restrict the level of BOD that can be introduced to 0.6 equivalents above which level gelation occurs. In the absence of such side reactions, theoretical models predict that gelation should occur when the di-functional monomer level exceeds 1 equivalent. Additionally, a fixed reaction time was required in order to prevent these transesterification processes resulting in gelation after complete monomer conversion was achieved. These observations may point to the fact that steric hindrance may result in two differing mechanisms contributing to the formation of the highly branched species at high conversion. Where linear chain growth is achieved by the expected Sn centred C+I propagation until ~90% conversion, after which branching occurs *via* either the “pendant” BOD ring by a combination of Sn catalysed C+I or interchain trans-esterification reactions.

The branched structures of these polymers have been confirmed by characterisation *via* GPC-DRI, viscometer and MALLS. The multimodal elution traces obtained by DRI detector suggest the formation of highly branched polymers. Additionally, the absolute Mwts (M_w) were determined using GPC-MALLS and the resultant conformation plots also supported the structural assignments. These structural conclusions were further corroborated by the values of the branching ratios (contraction factors). It is concluded that the number of BOD per primary chain affected the degree of branching and hence had an impact on these physical values. The g_M and g'_M also support the conclusion that these reactions produce branched structures with increased branching as the BOD level is increased. Finally, the presence of branching was further corroborated by the trends exhibited in the T_m and T_g values. Both thermal properties demonstrated linear trends that reflected the level of branching present in the material, i.e. sequentially varied with BOD concentration. Therefore, it was concluded that the number of BOD per primary chain affected the DB and hence had a direct impact on

these physical values exhibited by these materials. However, it was also observed that for these highly branched structures the thermal properties were close to those of the linear materials. This may be as a result of the fact that there is still quantities of linear material present in the final product, but may suggest that much higher branching levels may be required if significantly differentiated thermal/physical properties are to be achieved.

References

- (1) Voit, B. I.; Lederer, A. *Chemical Reviews***2009**, *109*, 5924.
- (2) *Hyperbranched Polymers: Synthesis, Properties and Applications*; Yan, D.; Gao, C.; Frey, H., Eds.; John Wiley & Sons, Inc.: Hoboken, New Jersey, 2011.
- (3) Rosselgong, J.; Armes, S. P.; Barton, W.; Price, D. *Macromolecules***2009**, *42*, 5919.
- (4) Rosselgong, J. Armes, S. P.; Barton, W. R. S.; Price, D. *Macromolecules***2010**, *43*, 2145.
- (5) Flory, P. J. *Journal of the American Chemical Society***1941**, *63*, 3083.
- (6) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
- (7) Stockmayer, W. H. *J. Chem. Phys.* **1944**, *12*, 125.
- (8) Vögtle, F.; Richardt, G.; Werner, N. *Dendrimer Chemistry*; WILEY-VCH Verlag GmbH & Co. KGaA: Weinheim, 2009.
- (9) O'Brien, N.; McKee, A.; Sherrington, D. C.; Slark, A. T.; Titterton, A. *Polymer***2000**, *41*, 6027.
- (10) Baudry, R.; Sherrington, D. C. *Macromolecules***2006**, *39*, 5230.
- (11) Baudry, R.; Sherrington, D. C. *Macromolecules***2006**, *39*, 1455.
- (12) Chisholm, M.; Hudson, N.; Kirtley, N.; Vilela, F.; Sherrington, D. C. *Macromolecules***2009**, *42*, 7745.
- (13) Jikei, M.; Kakimoto, M.-a. *Journal of Polymer Science Part A: Polymer Chemistry***2004**, *42*, 1293.
- (14) Froehling, P. *Journal of Polymer Science Part A: Polymer Chemistry***2004**, *42*, 3110.
- (15) Hult, A.; Johansson, M.; Malmström, E. In *Branched Polymers II*; Roovers, J., Ed.; Springer Berlin / Heidelberg: 1999; Vol. 143, p 1.
- (16) Perstorp; Perstorp: Ohio, USA; Vol. 2011.
- (17) Hult, A. J., M.; Malmstroem, E. *Advances in Polymer Science***1999**, *143*, 1.
- (18) Neu, M.; Fischer, D.; Kissel, T. *The Journal of Gene Medicine***2005**, *7*, 992.
- (19) Tan, J. H.; McMillan, N. A. J.; Payne, E.; Alexander, C.; Heath, F.; Whittaker, A. K.; Thurecht, K. J. *Journal of Polymer Science Part A: Polymer Chemistry***2012**, *50*, 2585.
- (20) Li, X.; Lu, X.; Lin, Y.; Zhan, J.; Li, Y.; Liu, Z.; Chen, X.; Liu, S. *Macromolecules***2006**, *39*, 7889.
- (21) Ostuni, E.; Chapman, R. G.; Holmlin, R. E.; Takayama, S.; Whitesides, G. M. *Langmuir***2001**, *17*, 5605.
- (22) Thurecht, K. J.; Blakey, I.; Peng, H.; Squires, O.; Hsu, S.; Alexander, C.; Whittaker, A. K. *Journal of the American Chemical Society***2010**, *132*, 5336.
- (23) Munnemann, K.; Kolzer, M.; Blakey, I.; Whittaker, A. K.; Thurecht, K. J. *Chemical Communications***2012**, *48*, 1583.
- (24) Jikei, M.; Kakimoto, M.-a. *Progress in Polymer Science***2001**, *26*, 1233.
- (25) Lin, Q.; Long, T. E. *Macromolecules***2003**, *36*, 9809.
- (26) Liu, M.; Vladimirov, N.; Fréchet, J. M. J. *Macromolecules***1999**, *32*, 6881.
- (27) Trollsås, M.; Atthoff, B.; Claesson, H.; Hedrick, J. L. *Macromolecules***1998**, *31*, 3439.
- (28) Trollsås, M.; Hedrick, J. L. *Macromolecules***1998**, *31*, 4390.

- (29) Trollsås, M.; Löwenhielm, P.; Lee, V. Y.; Möller, M.; Miller, R. D.; Hedrick, J. L. *Macromolecules***1999**, *32*, 9062.
- (30) Zheng, Y.; Turner, W.; Zong, M.; Irvine, D. J.; Howdle, S. M.; Thurecht, K. J. *Macromolecules***2011**, *44*, 1347.
- (31) Isaure, F.; Cormack, P. A. G.; Graham, S.; Sherrington, D. C.; Armes, S. P.; Butun, V. *Chemical Communications***2004**, 1138.
- (32) Wang, A. R.; Zhu, S. *Macromolecules***2002**, *35*, 9926.
- (33) Li, Y.; Armes, S. P. *Macromolecules***2005**, *38*, 8155.
- (34) Bannister, I.; Billingham, N. C.; Armes, S. P.; Rannard, S. P.; Findlay, P. *Macromolecules***2006**, *39*, 7483.
- (35) Bouhier, M.-H.; Cormack, P. A. G.; Graham, S.; Sherrington, D. C. *Journal of Polymer Science Part A: Polymer Chemistry***2007**, *45*, 2375.
- (36) Yu, Q.; Qin, Z.; Li, J.; Zhu, S. *Polymer Engineering & Science***2008**, *48*, 1254.
- (37) Liu, B.; Kazlaucius, A.; Guthrie, J. T.; Perrier, S. *Macromolecules***2005**, *38*, 2131.
- (38) Norisuye, T.; Morinaga, T.; Tran-Cong-Miyata, Q.; Goto, A.; Fukuda, T.; Shibayama, M. *Polymer***2005**, *46*, 1982.
- (39) Lin, Y.; Liu, X.; Li, X.; Zhan, J.; Li, Y. *Journal of Polymer Science Part A: Polymer Chemistry***2007**, *45*, 26.
- (40) Vo, C.-D.; Rosselgong, J.; Armes, S. P.; Billingham, N. C. *Macromolecules***2007**, *40*, 7119.
- (41) Wiltshire, J. T.; Qiao, G. G. *Macromolecules***2006**, *39*, 4282.
- (42) Williams, C. K. *Chemical Society Reviews***2007**, *36*, 1573.
- (43) Barker, I. A.; El Harfi, J.; Adlington, K.; Howdle, S. M.; Irvine, D. J. *Macromolecules***2012**, *45*, 9258.
- (44) Sperling, L. H. *Introduction to physical polymer science*; John Wiley & Sons, Inc.: Hoboken, New Jersey, 2006; Vol. 4th Edition.
- (45) Podzimek, S.; Vlcek, T.; Johann, C. *Journal of Applied Polymer Science***2001**, *81*, 1588.
- (46) Podzimek, S.; Vlcek, T. *Journal of Applied Polymer Science***2001**, *82*, 454.
- (47) McKee, M. G.; Unal, S.; Wilkes, G. L.; Long, T. E. *Progress in Polymer Science***2005**, *30*, 507.
- (48) Van de Velde, K.; Kiekens, P. *Polymer Testing***2002**, *21*, 433.
- (49) Labet, M.; Thielemans, W. *Chemical Society Reviews***2009**, *38*, 3484.
- (50) Jabarin, S. A. *Journal of Applied Polymer Science***1987**, *34*, 97.
- (51) Alamo, R. G.; Viers, B. D.; Mandelkern, L. *Macromolecules***1993**, *26*, 5740.