



Synthesis of hyperbranched polymers via a facile self-condensing vinyl polymerization system – Glycidyl methacrylate/Cp₂TiCl₂/Zn

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ABSTRACT

A facile self-condensing vinyl polymerization (SCVP) system, the combination of glycidyl methacrylate, Cp₂TiCl₂ and Zn, has been firstly used to prepare novel hyperbranched polymers, consisting of vinyl polymers as the backbone, and cyclic ester polymers (poly(ε-caprolactone) or poly(L-lactide)) as the side chains. The polymerizations are initiated by the epoxide radical ring-opening catalyzed by Cp₂Ti(III)Cl which is generated in situ via the reaction of Cp₂TiCl₂ with Zn. The key to success is that the polymerizations can proceed concurrently via two dissimilar chemistries possessing the opposite active initiating species, including ring-opening polymerization (ROP) and controlled/living radical polymerization (CRP). We have demonstrated that this facile one-step polymerization technique can be applied successfully to prepare highly branched polymers with a multiplicity of end reactive functionalities including Ti alkoxide, hydroxyl and vinyl functional groups.

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1. Introduction

Poly(ε-caprolactone) (PCL) and poly(L-lactide) (PLLA) are usually synthesized by ring-opening polymerization (ROP) of ε-caprolactone (ε-CL) and L-lactide (L-LA), respectively [1]. The resultant polymers are typically linear aliphatic polyesters. Qualitatively, PCL and PLLA possess excellent biodegradability, biocompatibility, and bioadsorbility. Therefore, these polyesters are potential for many medical materials, including sutures, scaffolds, bone fixation, and drug release carriers [2]. In most of the reported studies, tailoring the properties of PCL and PLLA are firstly required, such as reducing the crystallinity or melt viscosity. It can be achieved by copolymerizing cyclic ester monomers with other comonomers [3]. Alternatively, another strategy is to introduce branched structure including grafted, star-shaped, dendritic, and etc, with the purpose to produce unique rheological and mechanical properties combining with the intrinsic biodegradation behavior [4]. In recent years, hyperbranched polymers have been attracting great interest as they have three-dimensional globular architecture which endows them with many unique advantages including low viscosity, high functionality and good solubility, and thus they are applied in

a wide range of fields, from viscosity modifiers to catalyst supports and drug carriers [5]. However, little attention has been paid to the preparation of hyperbranched polymers containing aliphatic polyesters from cyclic ester monomers to date [6].

In 1995, an important discovery coining as self-condensing vinyl polymerization (SCVP) for generating hyperbranched polymers was reported by Fréchet and his coworkers [7]. This method employs an initiator monomer, inimer, which possesses general AB* structure comprising a double bond (A) and a latent initiating site (B*) for vinyl polymerization, is always used to control the degree of branching in the synthesis of hyperbranched polymers. At present, this approach has been successfully propagated in cation [7], anionic [8], group-transfer [9], atom transfer radical polymerization (ATRP) [9b,10], reversible addition–fragmentation chain transfer (RAFT) [11] and nitroxide-mediated polymerization [12]. These research works have demonstrated the versatility of SCVP methodology, as evidenced by inhibiting the gelation and lowering polydispersity indices (PDIs) of products. However, there are still some disadvantages for SCVP method. For example, it usually requires tremendous efforts to design and synthesize the expensive, tailored vinyl monomer (inimer) with special functional groups. Moreover, to our best knowledge, there is no report on the preparation of biodegradable polyesters-embodied hyperbranched polymers from a vinyl SCVP system.

Recently, Asandei's group reported the ROP of ε-CL and L-LA via Cp₂Ti(III)Cl-catalyzed radical ring opening (RRO) of epoxides [13a]. The polymerizations proceed in a living fashion and produced well-

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defined polymers. Glycidyl methacrylate (GMA) containing a double bond and an epoxide group is an important commercial monomer. Therefore, it is potential for serving as a facile SCVP inimer for preparing hyperbranched polymers. Initially, Asandei and his coworkers reported the homopolymerization [13b,13c] of GMA and graft copolymerizations [13d,13e] initiated from PGMA and GMA copolymers with methyl methacrylate (MMA) and styrene (St) via $\text{Cp}_2\text{Ti(III)Cl}$ -catalyzed chemistry, with the purpose to prepare branched and graft polymers. However, due to a large excess of epoxide groups by comparison with available $\text{Cp}_2\text{Ti(III)Cl}$, the mediator $\text{Cp}_2\text{Ti(III)Cl}$ consumed fast and completely at the start of the polymerization. As a result, ATRP mediators (CuBr_2/bpy) were needed to introduce to prevent potential cross-linking [13c–e].

In this paper, hyperbranched polymers consisting of vinyl and cyclic ester polymers have been successfully prepared via this one-pot SCVP system—GMA/ $\text{Cp}_2\text{Ti(III)Cl}$ based on “living” ROP and controlled/living radical polymerization techniques, where no other mediators were introduced. The hyperbranched architectures have been confirmed by the combination of a triple detection size exclusion chromatography (Tri-SEC) and a conventional size exclusion chromatography (SEC) as well as ^1H NMR analyses.

2. Experiment

2.1. Materials

After passing through a column of alumina to remove inhibitor, GMA and ϵ -CL (Acros) were distilled prior to use. L-LA was purchased from Aldrich and purified by recrystallization from cold ethyl acetate. Bis(cyclopentadienyl)titanium dichloride (Cp_2TiCl_2 , Acros) and Zn powder (Beijing Chemical Factory) were used as received. Toluene was purified by Mbraun solvent purification system (M.Braun Co. Ltd., Germany). 1,4-Dioxane was distilled over Na/benzophenone.

2.2. Polymerization

A Schlenk polymerization tube filled with Cp_2TiCl_2 , Zn, CaH_2 (<10 mg, as trace moisture scavenger), and ϵ -CL was degassed by three freeze-pump-thaw cycles, charged with dried argon. The reduction of Cp_2TiCl_2 was finished in 10 min at room temperature and was accompanied by the characteristic lime-green color of $\text{Cp}_2\text{Ti(III)Cl}$. The tube was then cooled to -78°C in an acetone/dry ice bath. Degassed toluene and GMA were injected through the sidearm, and the mixture was redegassed by three freeze-pump-thaw cycles. The polymerization tubes were heated at 90°C in a thermostated oil bath. After a desired reaction time, the content was diluted with THF. When the mixture becomes a homogenous solution, the polymer was precipitated into a large excess of cold methanol. The resultant polymer was filtered and dried at 30°C in *vacuo*. The monomer conversions were determined gravimetrically.

2.3. Characterization

^1H NMR spectra were recorded on a Bruker 300-MHz spectrometer with CDCl_3 as the solvent and tetramethylsilane (TMS) as the internal standard. The weight-average molecular weights (M_w s) and PDIs of all samples were measured on a size exclusion chromatography (SEC) system, which consists of a Waters 510 HPLC pump, three Waters Ultrastayragal columns (500 , 10^3 , and 10^5), and a Waters 2414 RI detector, with THF as the eluent at a flow rate of 1.0 mL/min. The molecular weight analysis was performed at 40°C and calibrated by narrow polystyrene (PSt) standards. Additional measurements of M_w , PDI, and Mark–Houwink exponent α values were performed on a Triple Detection Size Exclusion

Chromatography (Tri-SEC) supplied by a Waters 1525 separation module (Waters Corp.) connected with M302 triple detector array (Viscotek Corp., Houston, TX), a combination of refractive index, light scattering (LS angle, 7° (LALS) and 90° (RALS), laser wavelength, $\lambda = 670$ nm), and viscosity detector. Two mixed bed SEC columns ($\text{GMH}_{\text{HR}}\text{-M}$, $\text{GMH}_{\text{HR}}\text{-H}$, Viscotek Corp.) were used. THF was used as the mobile phase at a flow rate of 1.0 mL/min and the column oven temperature was set to 30°C .

3. Results and discussion

3.1. Synthesis and characterization of Poly(ϵ -caprolactone)-contained hyperbranched polymers

The mechanism for the polymerization of ϵ -CL is illustrated in Scheme 1. $\text{Cp}_2\text{Ti(III)Cl}$ was prepared readily in situ via the reduction of Cp_2TiCl_2 with Zn at room temperature (eq. (1)), as evidenced by a characteristic color change from red to lime-green. The soluble paramagnetic $\text{Cp}_2\text{Ti(III)Cl}$ complex is an excellent one electron-transfer agent that can catalyze a variety of radical reactions besides the RRO of epoxides. Accordingly, the RRO reaction of GMA catalyzed by $\text{Cp}_2\text{Ti(III)Cl}$ produces two dissimilar active species including Ti alkoxide (Cp_2TiClOR) and epoxide-derived radical (eq. (2)). The former has been successfully used to initiate the ring-opening polymerization (ROP) of ϵ -CL, while the latter is an efficient initiator for the radical polymerization of vinyl monomer [13a,14–16]. Thus, we wonder whether both ROP (eq. (3)) and the radical polymerization (eq. (4)) would proceed simultaneously in the one-pot system. The addition of the radical in the PCL backbone to the methacrylate double bond derived from both GMA monomer and PCL propagation chain leads to a branched site, which may subsequently polymerize vinyl monomer or macromonomer to generate hyperbranched polymers (eq. (5)), comprising of PGMA and PCL as the backbone and the side chains, respectively. It must be also pointed out that the steric hindrance of growing PCL chains would decrease the rate of hyperbranching possibly leading to a star like structure or reduced branching. However, this process was limited as the propagation rate (k_p) of ROP is much lower than that of ATRP. Consequently, the polymerizations were investigated under the various conditions at 90°C as this reaction temperature has been demonstrated to be optimal for producing the greatest controlled/living characteristics during ROP of ϵ -CL initiated from epoxide. The representative results of polymerizations are summarized in Table 1.

Firstly, it is necessary to point out that all polymerizations were conducted under optimized $[\text{GMA}]/[\text{Cp}_2\text{TiCl}_2]/[\text{Zn}]$ molar ratios. As reported previously, the polymerizations of ϵ -CL initiated from RRO of epoxides is rather complicated. The reactants (Cp_2TiCl_2 , Zn, and epoxide combining with Cp_2TiCl_2 or Zn) and the resultant products ($\text{Cp}_2\text{Ti(III)Cl}$, and Ti alkoxide, i.e., Cp_2TiClOR) can initiate ROPs of ϵ -CL in various degrees [13a]. In particular, a much faster initiation was observed for $\text{Cp}_2\text{Ti(III)Cl}$, i.e., 55% monomer conversion within 26 h at 90°C . Therefore, to eliminate these side initiations and to encourage the normal initiation via the Ti alkoxide species (Cp_2TiClOR , $R = \text{alkyl}$ and propagation chain), the $[\text{GMA}]/[\text{Cp}_2\text{TiCl}_2]/[\text{Zn}]$ molar ratios should be exactly set to ensure the complete consumption of the species including $\text{Cp}_2\text{Ti(III)Cl}$, Cp_2TiCl_2 , Zn, and epoxide. In view of the above analyses, all polymerizations were performed at a constant $[\text{GMA}]/[\text{Cp}_2\text{TiCl}_2]/[\text{Zn}]$ molar ratio of 1:1:0.5. Thus, the system is simplified greatly, and there are mainly two species in the medium after the RRO reaction of GMA, i.e., the monomer (ϵ -CL) and the initiating species Ti alkoxide (Cp_2TiClOR).

The data in Table 1 show that the polymerizations can be controlled over a broad range of monomer conversion (51.8–99.5%) depending on the molar ratios of $[\epsilon\text{-CL}]/[\text{GMA}]$. Noticeably, the

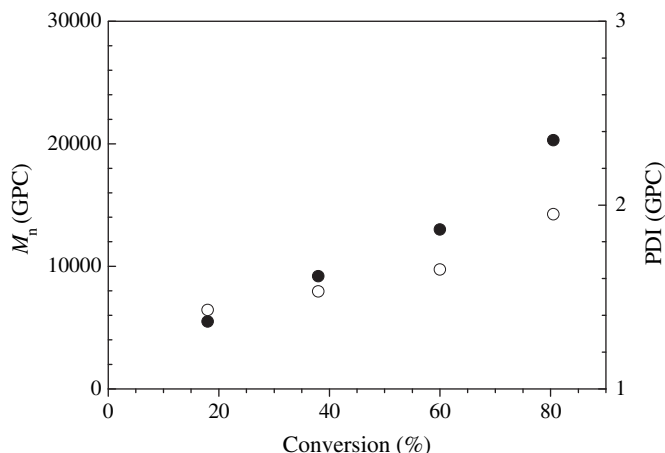


Fig. 2. Plots of M_n (●) and PDI (○) of hyperbranched polymer measured by SEC versus monomer conversion. $[\epsilon\text{-CL}]/[\text{GMA}]/[\text{Cp}_2\text{TiCl}_2]/[\text{Zn}] = 100:1:1:0.5$, $T = 90^\circ\text{C}$, $\epsilon\text{-CL}/\text{toluene} = 1/1$ (v/v).

a sharp increase at the later polymerization stage. It possibly reflects the increase of the degree of branching (DB). The same results can also be found in the development of the molecular weight distributions (Fig. 2), i.e., they showed a tendency of broadening as a result of the gradual increase of DB. Importantly, the molecular weight distributions of the resultant polymers are broader than the corresponding values in the previous reports [6]. It can be attributed to some termination reactions originated from the radical polymerization mechanism.

SEC curves of the resultant polymers obtained at different molar ratios of $\epsilon\text{-CL}$ monomer to initiator are shown in Fig. 4. Obviously, the molecular weights increased with the $[\epsilon\text{-CL}]/[\text{GMA}]$ molar ratios. This observation also suggests that the polymerizations of $\epsilon\text{-CL}$ initiated from $\text{Cp}_2\text{Ti(III)Cl}$ -catalyzed RRO of GMA possess the characteristics of living/controlled polymerization, which is in consistent with the evolution of the molecular weights with the polymerization proceeding.

The most powerful evidence for the formation of hyperbranched polymers can be obtained from ^1H NMR analyses. To probe into the polymerization reaction, the experiment with a low $[\epsilon\text{-CL}]/[\text{GMA}]$ molar ratio of 10:1 was conducted, with the purpose to obtain

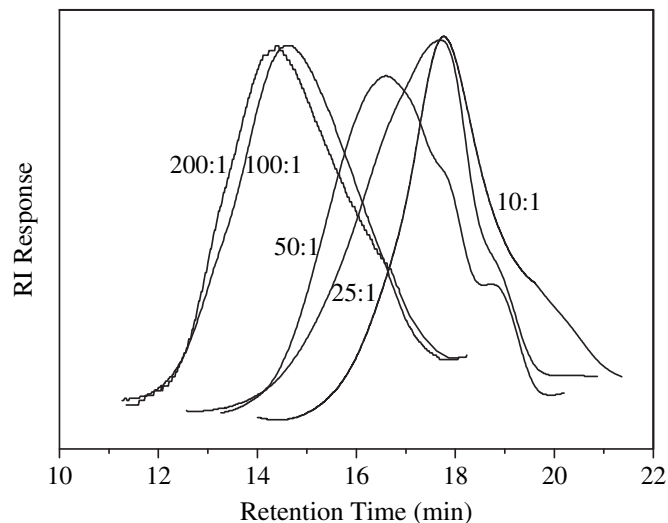


Fig. 4. SEC traces of hyperbranched polymer via $\text{Cp}_2\text{Ti(III)Cl}$ -catalyzed radical ring opening (RRO) of GMA at different molar ratios of $[\epsilon\text{-CL}]/[\text{GMA}]$. $[\text{GMA}]/[\text{Cp}_2\text{TiCl}_2]/[\text{Zn}] = 1:1:0.5$, $T = 90^\circ\text{C}$, $\epsilon\text{-CL}/\text{toluene} = 1/1$ (v/v).

polymer with a low molecular weight and thus to confirm its end groups. The polymer was obtained at a nearly quantitative monomer conversion (99.5%). As illustrated in Fig. 5, the unreacted methacrylate group can be assigned to peaks a and b, whereas the reacted methacrylate group corresponds to peaks a' and b'. Compared the peak j from $\epsilon\text{-CL}$ unit with peak b', the molar ratio of $\epsilon\text{-CL}$ to GMA is close to 10:1. Likewise, the integral sum of peaks c, e and j at ca. 3.6 ppm is twice as the integral of peak b'. These results indicate the complete conversion of methacrylate double bonds and the final polymer obtained from RRO of GMA possesses the high chain-end functionality with a multiplicity of end reactive functionalities including Ti alkoxide, hydroxyl and vinyl functional groups, which can be further applied to other chemical modifications and post-polymerization mechanisms. Therefore, ^1H NMR data does support that GMA is indeed involved in the polymerization reaction and the architecture of the resultant polymer belongs to hyperbranched type. Furthermore, it is obvious that the additional double bonds at 4.5–6.6 ppm are also clearly observed in

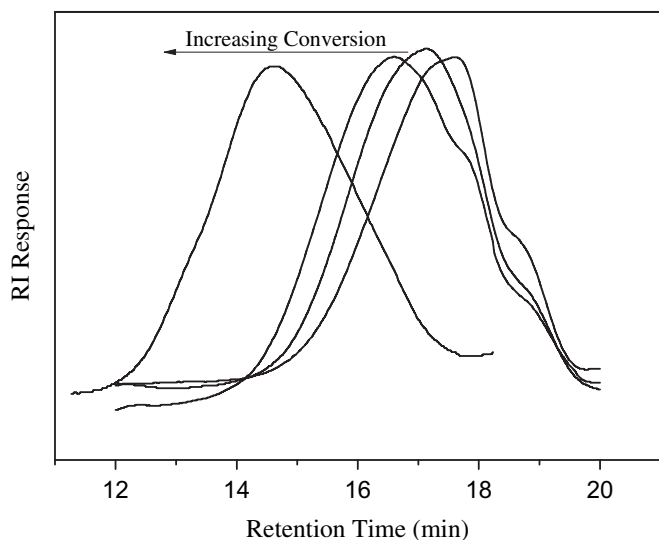


Fig. 3. SEC traces of hyperbranched polymer with monomer conversion: 18%, 38%, 60%, and 80.5%. $[\epsilon\text{-CL}]/[\text{GMA}]/[\text{Cp}_2\text{TiCl}_2]/[\text{Zn}] = 100:1:1:0.5$, $T = 90^\circ\text{C}$, $\epsilon\text{-CL}/\text{toluene} = 1/1$ (v/v).

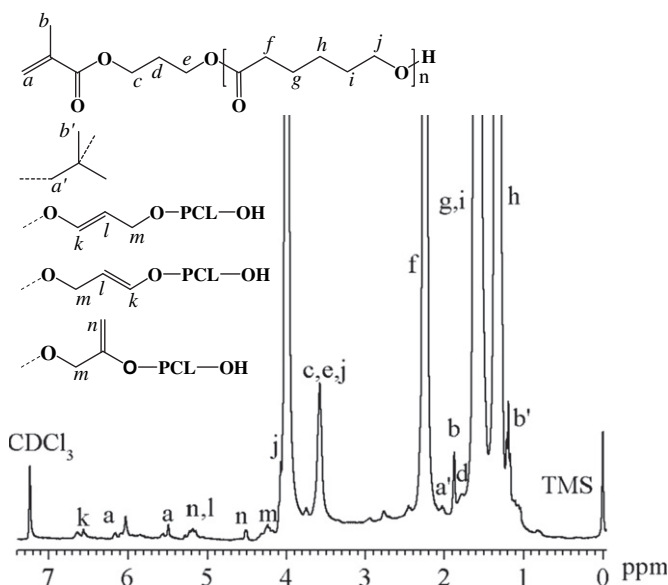
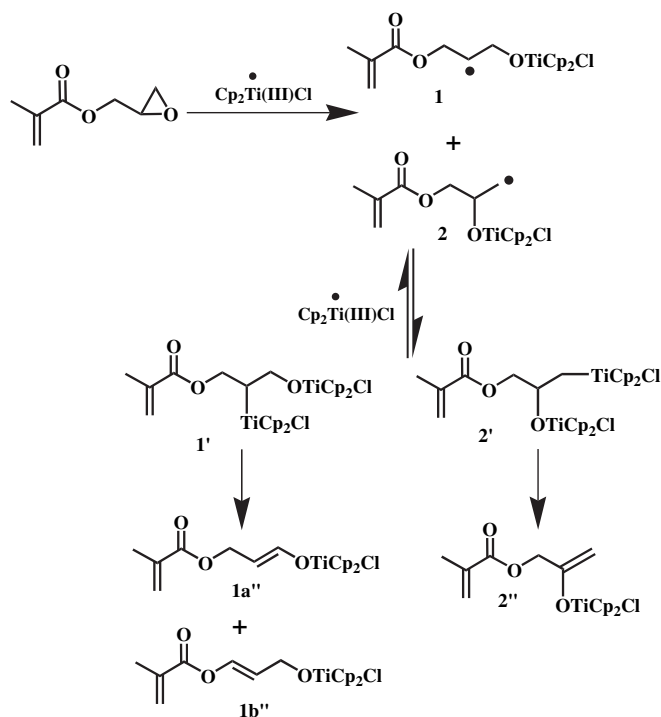


Fig. 5. ^1H NMR spectrum of hyperbranched polymer via $\text{Cp}_2\text{Ti(III)Cl}$ -catalyzed radical ring opening (RRO) of GMA obtained in entry 2 of Table 1.

Fig. 5. The result can be explained as shown in Scheme 2. During the RRO reaction of GMA with $\text{Cp}_2\text{Ti(III)Cl}$, two kinds of epoxide-derived radicals 1 and 2 were generated. In addition to initiate the radical polymerization, the radicals can also undergo the radical trapping and isomeric alkoxide-alkyls 1' and 2' are formed. Further β -H eliminations give the unsaturated isomeric Ti alkoxides 1a'', 1b'', and 2'', which subsequently initiate the polymerization of ϵ -CL to produce additional vinyl functionalities in the PCL as shown in the inset molecular structure in Fig. 5. Moreover, the integral ratio of peaks k–n is close to 5:1, suggesting that the route for producing 1a'' and 1b'' is predominant. It directly supports the favored generation of the stable secondary radical 1 during ϵ -CL polymerization initiated from the RRO of GMA.

Generally, hyperbranched polymers display longer retention times due to less hydrodynamic volumes than those linear counterparts [17a,18]. As a result, the MW values of hyperbranched polymers determined by a conventional SEC analysis with refractive index (RI) detector are relatively low. Thus, the M_w measurement of hyperbranched polymers is usually a difficult issue. To obtain the true M_w values, we employ Tri-SEC analyses with triple detectors including RI, light scattering (LS), and viscosity (IV-DP) to characterize hyperbranched polymers, and the results are presented in Table 1. The increase in MWs and PDIs can be also observed in all reaction entries of Table 1. Importantly, LS shows a higher molecular weight than RI detector, possibly indicating the formation of hyperbranched architecture. The huge difference between the PDI values obtained from SEC and Tri-SEC analyses was also observed for other hyperbranched polymer in SEC analyses [18]. Therefore, PCL-based polymers synthesized via the initiation of the GMA RRO reaction own hyperbranched structures.

In contrast with linear polymer, hyperbranched polymer has unique solution properties, i.e., its intrinsic viscosity is lower than its linear counterpart, suggesting a denser and compacter structure for the former [5]. The intrinsic viscosities of hyperbranched PCL are obviously lower than those of linear PCL as a result of less interaction between solvent and hyperbranched polymers (Fig. 6),



Scheme 2. Strategy for the formation of vinyl groups in the polymerization initiated from $\text{Cp}_2\text{Ti(III)Cl}$ -catalyzed radical ring opening (RRO) of GMA.

which is typically encountered with densely branched polymers. More accurately, the compact hyperbranched structure is confirmed by lower Mark–Houwink exponent α values than linear analogues [18d,19]. As determined by the slope of $\log [\text{IV}]$ versus $\log M$, the Mark–Houwink exponent α value for hyperbranched polymer (0.35) initiated from the $\text{Cp}_2\text{Ti(III)Cl}$ -catalyzed RRO reaction of GMA is less than that of linear PCL (0.63).

3.2. Effect of the $[\epsilon\text{-CL}]/[\text{GMA}]$ molar ratios on hyperbranched architecture

The previous results indicate that the resultant polymers initiated from $\text{Cp}_2\text{Ti(III)Cl}$ -catalyzed RRO of GMA display hyperbranched architecture (entries 2–6 in Table 1), as evidenced by higher molecular weight (MW) difference between traditional SEC and Tri-SEC results than the control experiment (entry 1 in Table 1). Furthermore, hyperbranched products exhibit higher PDIs (5.10–24.0 for Tri-SEC results), and usually display lower Mark–Houwink exponents (Table 1) than those of the linear analogues. The phenomena are typically reflected in hyperbranched macromolecules. However, Mark–Houwink exponents varied significantly. Therefore, it is important to investigate the effect of the $[\epsilon\text{-CL}]/[\text{GMA}]$ molar ratios on hyperbranched architecture.

As shown in Table 1, the MarkHouwink exponents increased from 0.19 to 0.39 with an increase in $[\epsilon\text{-CL}]/[\text{GMA}]$ from 10:1 to 200:1. This rule suggests the decrease of DBs. Particularly, the Mark–Houwink exponent α is 0.19 for a $[\epsilon\text{-CL}]/[\text{GMA}]$ molar ratio of 10:1 (entry 2), which is much lower than that (0.39) for a higher $[\epsilon\text{-CL}]/[\text{GMA}]$ molar ratio (200:1 for entry 6). Under the same reaction conditions, the decrease of $[\epsilon\text{-CL}]/[\text{GMA}]$ means an increase in the concentration of both methacrylate vinyl groups $[\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(=\text{O})\text{O}-]$ and the radicals, and thus enhances the probability of branching or cross-linking. Consequently, the densest and the most highly branched polymer is obtained in entry 2 via the initiation from a low $[\epsilon\text{-CL}]/[\text{GMA}]$ molar ratio of 10:1. In a word, to synthesize a hyperbranched PCL with a high DB, a simple method is to maintain the $[\epsilon\text{-CL}]/[\text{GMA}]$ molar ratio as low as possible.

3.3. Synthesis of Poly(L-lactide)-contained hyperbranched polymers

Based on the previous results, the facile SCVP system—GMA/ $\text{Cp}_2\text{TiCl}_2/\text{Zn}$ has been demonstrated to provide the excellent efficiency of preparing PCL-based hyperbranched polymers. Therefore, it is

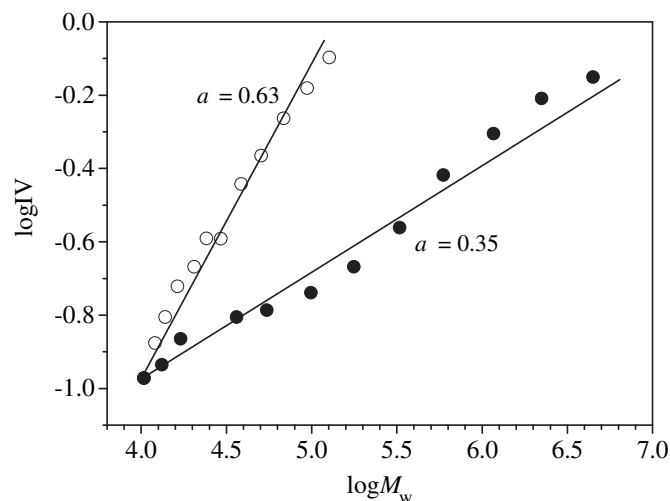


Fig. 6. Plot of intrinsic viscosity versus molecular weight for hyperbranched polymer (●) (entry 5, Table 1) and linear PCL (○) (entry 1, Table 1).

Table 2

Polymerization results of L-lactide initiated from $\text{Cp}_2\text{Ti(III)Cl}$ -catalyzed radical ring opening (RRO) of GMA.^a

No.	[L-LA]/[GMA]/ [Cp_2TiCl_2]/[Zn]	Time (h)	Conv. (%)	M_w (kDa)	PDI	α^b
1	Control ^c	8	65.8	6.50	1.28	0.73
2	25:1:1:0.5	6	57.7	19.1	5.57	0.27
3	50:1:1:0.5	8	70.0	21.6	4.16	0.35
4	100:1:1:0.5	24	78.1	65.0	3.10	0.42
5	200:1:1:0.5	24	50.0	50.2	2.80	0.45

^a Polymerization conditions: $T = 90^\circ\text{C}$, solvent: dioxane/toluene = 1:1 (v/v).

^b Mark–Houwink exponent α .

^c [L-LA]/[SO]/[Cp_2TiCl_2]/[Zn] = 50:1:1:0.5.

interesting to investigate whether this SCVP system can be extended to another important cyclic ester monomer, lactide. The L-LA polymerizations were performed at the same molar ratios of [GMA]/[Cp_2TiCl_2]/[Zn] as the ϵ -CL polymerizations, i.e., 1:1:0.5. As summarized in Table 2, under the same reaction conditions, these polymerizations yielded medium-to-high monomer conversions. However, compared with ϵ -CL, L-LA shows a decreasing trend for the rates of the polymerizations. It can be ascribed that L-LA possesses two strong polar ester groups, and thus it exhibits too strong and irreversible coordination ability with $\text{Cp}_2\text{Ti(III)Cl}$, which directly leads to the decrease in the concentration of the Ti alkoxide (Cp_2TiClOR) and the epoxide-derived radical, corresponding to the initiators for cyclic ester and vinyl monomers, respectively [14c]. Consequently, the rates of L-LA polymerizations initiated from the RRO reaction of GMA decreased as a result of the loss of active initiating species.

Noticeably, compared with the control polymerization initiated from SO (entry 1) which produces a linear PLLA with a lower molecular weight and a PDI as low as 1.28, the measured number-average molecular weight values of the polymers initiated from GMA (entries 2–5) enhanced greatly, and PDIs of PLLA-contained hyperbranched polymers (2.80–5.57) are also much higher than that of the corresponding linear analogues. Furthermore, the Mark–Houwink exponents of PLLAs via the initiation of GMA remained within a range of 0.27–0.45, which is obviously lower than that (0.73) of linear PLLA. It accurately reflects their hyperbranched structures. Likewise, in consistent with the ϵ -CL polymerizations, the DBs decrease with the increase of the [L-LA]/[GMA] molar ratios, as confirmed by the corresponding decrease of the Mark–Houwink exponents.

4. Conclusions

The biodegradable hyperbranched polymers containing PCL and PLLA have been successfully prepared via a facile SCVP system — GMA/ Cp_2TiCl_2 /Zn. The key requirement is that the polymerizations proceeded concurrently via two dissimilar chemistries (ROP and CRP) possessing two opposite active specie types. Tri-SEC and conventional SEC as well as ^1H NMR analyses confirm the formation of hyperbranched structures, as evidenced by high molecular weights and low Mark–Houwink exponent α values. Furthermore, the polymerizations possessed the characteristics of the controlled/living polymerization, i.e., the molecular weights of polymers increased with monomer conversions and the molar ratios of monomer to initiator. In contrast, the degrees of branching enhanced with a decrease in the molar ratios of cyclic ester monomer to initiator. Finally, the resultant hyperbranched polymers possess the epoxide-derived Ti alkoxide, vinyl, and hydroxyl end functional groups, which can be further applied to other chemical modifications and post-polymerization mechanisms. We believe that this simple strategy can be extended to incorporate monomers with varied physical and chemical properties for producing a wide range of hyperbranched polymers.

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