New Approach to Hyperbranched Polyesters: Self-Condensing Cyclic Ester Polymerization of Bis(hydroxymethyl)-Substituted ϵ-Caprolactone

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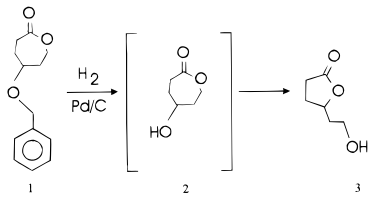
Received June 29, 1999
Revised Manuscript Received September 10, 1999

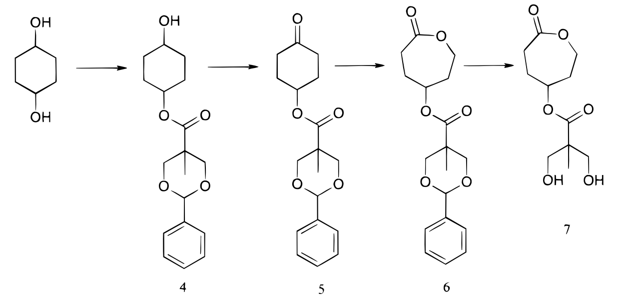
The introduction of controlled branching as a means of modifying the properties of synthetic macromolecules continues to be a central theme of research for advanced technological applications.[1] The mechanical, rheological, and solution properties of a material depend on the type and degree of branching. Nowhere is this more evident than in the case of polyethylene, where the branching type and extent exerts a pronounced effect on the morphology and properties of the material. Likewise, the interesting and unique features of star and graft polymers have been established as well as their technological relevance as emulsifiers and rheological control agents.[2] Over a decade ago, a new class of macromolecules emerged, denoted as dendrimers, which provided a standard for the investigation of the effects on the solution and physical properties of materials with precisely defined branched structures.[3] The multistep synthesis of dendrimers, however, limits their accessibility, and as a result less perfect elaborations have been synthesized including hyperbranched (AB_2 monomers), comburst, and related architectures.[4] One of the most noteworthy and versatile approaches to highly branched macromolecules was introduced by Fréchet et al.[5a] These authors demonstrated that vinyl monomers which contain a pendent initiating moiety (AB* monomers) will self-polymerize analogous to an AB_2 monomer. This new synthetic route to branched macromolecules, denoted as "self-condensing vinyl polymerization", has been further developed by Hawker et al., Matyjaszewski et al., Webber et al., and others[5b−g] by taking advantage of advances in controlled radical polymerization techniques.

It seems plausible to extend the self-condensing vinyl polymerization synthetic strategy to other monomer sets and polymerization procedures. For instance, the ring-opening polymerization (ROP) of cyclic lactones and lactides can be initiated from nucleophiles such as alcohols, amines, and so forth in the presence of a suitable organometallic promoter.[6] Toward this end, we surmised that an appropriately substituted cyclic ester may provide a new route to hyperbranched aliphatic polyesters. There are only a few reports of hyperbranched aliphatic polyesters, those derived from 2,2′-bis(hydroxymethyl)propionic acid (bis-MPA)[7a−c] and those from AB_2 macromonomers of poly(ϵ-caprolactone).[7d−h] In the latter case, the macromonomers were prepared by living ROP methods, while the hyperbranched formation was accomplished by a simple esterification procedure. In this article, we preliminarily detail our continuing work on hyperbranched polyesters employing a simple single-step method using only living ROP procedures. Here, we introduce the self-condensing cyclic ester polymerization of a bis(hydroxymethyl)-substituted ϵ-caprolactone monomer as a versatile approach to hyperbranched polyesters.

Scheme 1



Scheme 2



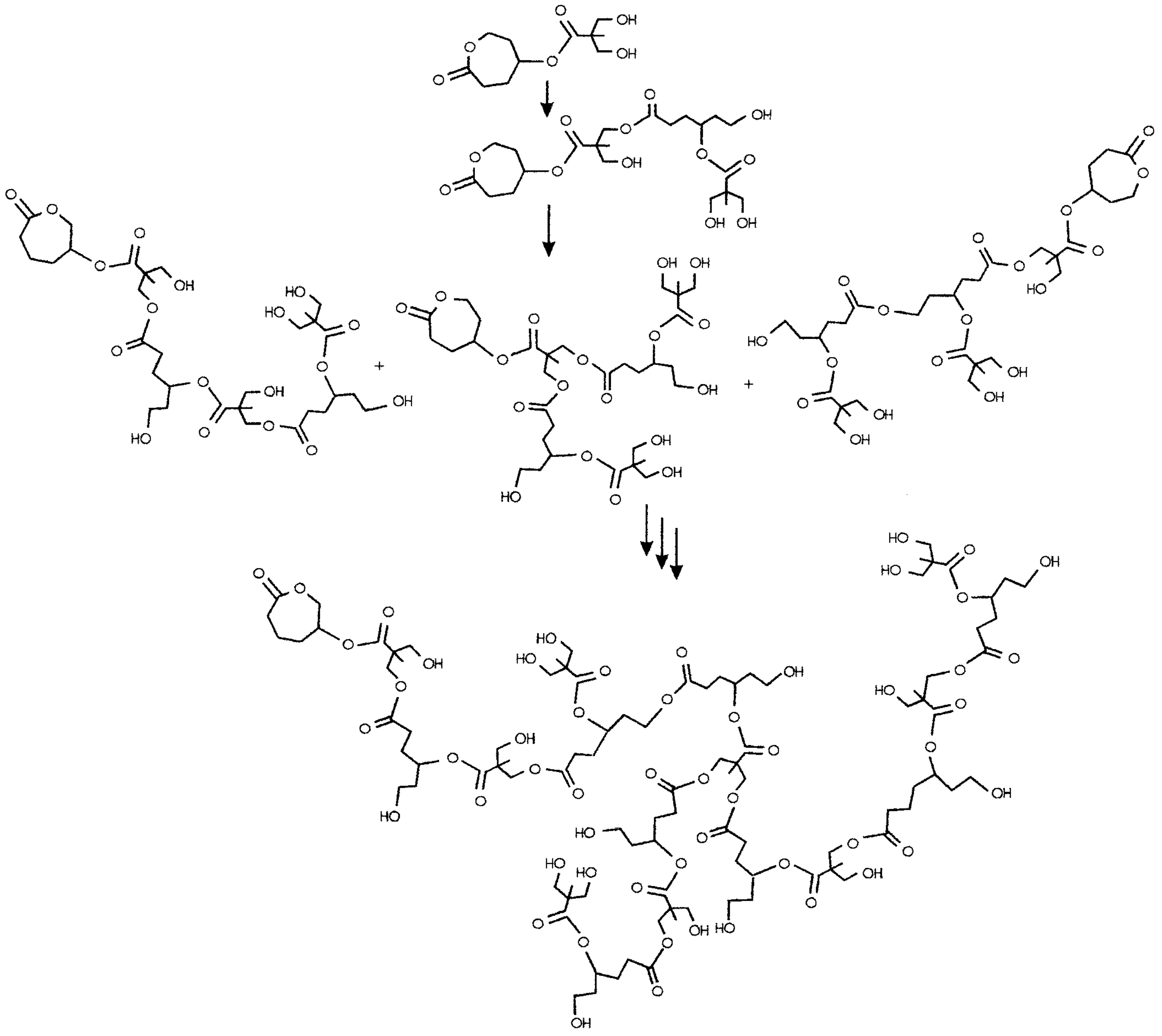
The choice of the bis(hydroxymethyl) substitution on the cyclic ester was based on two principles. First, we found that some functionalized lactones are prone to intermolecular rearrangement. For example, upon hydrogenolysis of 5-benzyloxy-ϵ-caprolactone (**1**) using Pd/H_2 the expected 5-hydroxycaprolactone **2** was not obtained, but rather the rearranged hydroxyethyl-functionalized cyclic δ-butyrolactone **3** was isolated (Scheme 1). This observation is consistent with the report by Pitt et al.,[8] and the mechanism of formation is believed to be an intramolecular transesterification. In this case, the five-member ring of the δ-butyrolactone does not homopolymerize under ROP conditions. Second, we have found the bis(hydroxymethyl) groups of 2,2′-bis(hydroxymethyl)propionic acid derivatives are particularly effective initiators for the ROP of lactides and lactones in the presence of $Sn(Oct)_2$.[7] Polymerizations of this type are living, producing narrowly dispersed products with controlled molecular weight and end group functionalities. The bis-MPA units also provide exquisite markers for the spectroscopic analysis of the polymers.

The synthesis of the bis(hydroxymethyl)-substituted ϵ-caprolactone was accomplished in four steps (Scheme 2).[9] 1,4-Cyclohexanediol was reacted with 0.8 equiv of 2,2′-bis(phenyldioxymethyl)propionyl chloride to yield the monofunctionalized product **4** in 40% yield. The isolated alcohol **4** was oxidized to the corresponding ketone **5** with pyridinum chlorochromate (PCC). Through a Bayer−Villiger oxidation, **5** was transformed into the corresponding cyclic ester **6** using 3-chloroperoxybenzoic acid. The benzylidene protecting group was removed by catalytic hydrogenolysis with H_2 over Pd/C to generate the desired bis(hydroxymethyl)-ϵ-caprolactone monomer **7**.[9]

The self-polymerization of **7** was performed in bulk at 110 °C in the presence of a catalytic amount of $Sn(Oct)_2$. Feijen et al.[10a] and Kricheldorf et al.[10b,c] have demonstrated molecular control in the polymerization

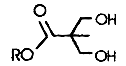
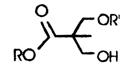
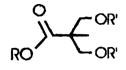
10.1021/ma991039v CCC: $18.00

Scheme 3



of ϵ-caprolactone and lactides with minimal transesterification side reactions at temperatures below 120 °C.[10b,c] However, we found that the ROP of both ϵ-caprolactone and lactides initiated from the bis(hydroxymethyl) groups of bis-MPA derivatives in the presence of Sn(Oct)$_2$ was a living process with the formation of narrowly dispersed products with controlled end groups and molecular weights.[7] In the self-condensing polymerization of the cyclic ester **7**, the molar concentration of initiating alcohols relative to Sn(Oct)$_2$ ([M]/[Cat]) was kept as high as practical (ratio 200−400) to minimize possible transesterification reactions. The catalyst-to-initiator concentration in the self-condensing vinyl polymerization of 4-chloromethylstyrene using ATRP was also reported to be critical in controlling the content of linear-to-branched species formed due to the unequal reactivity of the primary and secondary benzylic halide reactive sites.[5] This problem is eliminated in the ROP described, since both the initiating and the propagating moieties are identical.

This general polymerization procedure was applied to **7** in the presence and absence of ϵ-caprolactone (ϵ-CL) comonomer. Although the mechanism for the molecular weight increase is ring-opening polymerization, where the polymer molecular weight increases linearly with monomer conversion, the overall polymerization kinetics are consistent with a stepwise coupling similar to a condensation polymerization.[5a,11] Monitoring these polymerizations at various stages of reaction by SEC showed only dimers, trimers, tetramers, and so forth during the early stages, and the evolution of oligomers and polymer was not observed until high conversions were obtained (36−48 h) (Scheme 3). These data are consistent with earlier observations on analogous systems.[5] Scheme 3 shows a representative selection of the many possible pathways to high polymers. Polymerization of **7** either with or without ϵ-CL comonomers produced hyperbranched poly(ϵ-caprolactones) with molecular weights of 3000, 8000, and 7000 g/mol, relative to polystyrene standards, and polydispersities of 2.80, 2.81, and 2.30 (polymers **8**, **9**, and **10**), respectively. The molar ratios of **7**/ϵ-CL were 1/4 (**9**) and 1/5 (**10**) for the copolymerizations. These molecular weights are comparable to those reported for self-condensing vinyl polymerizations.[5b,c] The polydispersities are broad, characteristic of "self-condensing polymerizations", and are similar to those of other reports.[5] Nonetheless, they are far more narrow than those predicted by the theory of Müller et al. for an AB* system.[11] However, theory predicts narrower dispersities for copolymers,[11f] and little is known about the dispersity of an $A(B^*)_2$ system.

	Structure	ppm($-CH_3$)
T		0.99-1.04
L		1.14-1.15
D		1.19-1.21

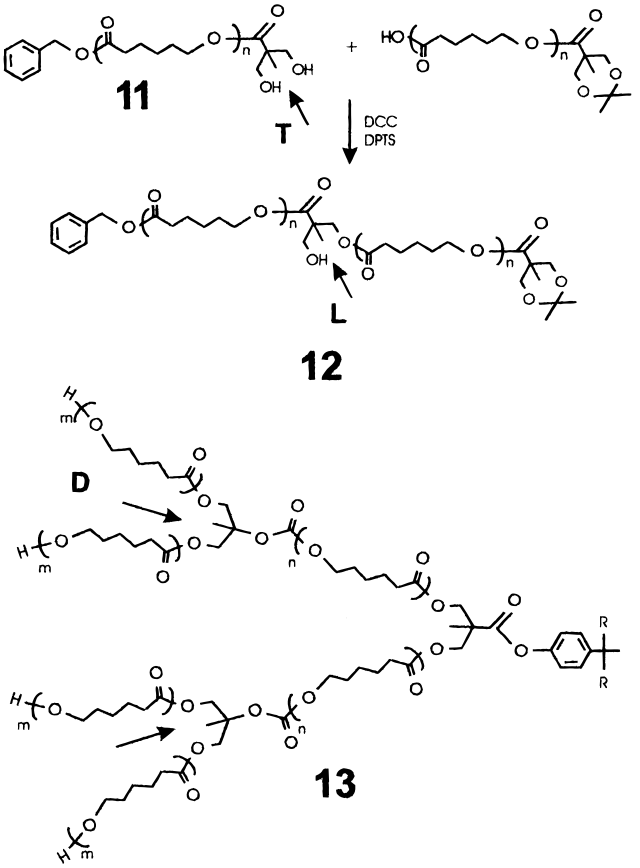


Figure 1. Model compounds and the ^{1}H-NMR chemical shifts ($CDCl_3$) of the possible repeating units in hyperbranched poly(ϵ-caprolactone).

One of the most interesting and important properties of any hyperbranched polymer is the degree of branching. The most common method for measuring the degree of branching was developed by Fréchet et al.[12] By their method, hyperbranched polymers derived from AB_2 monomers usually have a degree of branching around 0.5. In this study, the ^{1}H-NMR resonances of the CH_3 protons in bis-MPA were used to study the degree of branching. The positions of these resonances are sensitive to the substitution on the neighboring hydroxyl groups, and these peaks were assigned by the use of model compounds **11** (terminal unit), **12** (linear unit), and **13** (dendritic unit) (Figure 1). The synthesis of these model compounds has been described previously.[7b,g] The chemical shifts of the methyl groups in the linear, dendritic, and terminal units were found to be 1.14, 1.19, and 1.04, respectively, consistent with values reported by Hult et al.[7b] Figure 2 shows the ^{1}H-NMR spectra of the two polymers **8** and **9**. For polymer **8**, the expanded spectra in D_2O clearly show three distinct CH_3 resonances corresponding to dendritic, linear, and terminal units in a ratio of 1.00, 3.90, and 2.95, respectively. Using the definition of Fréchet et al.,[12] this corresponds to a degree of branching of 0.50. Interestingly all three of these peaks are split in a similar manner. The cause of these splittings is presently under investigation. Figure 2b shows the same region for copolymer **9**. This spectrum ($CDCl_3$) also shows three distinct peaks. Although each peak is not completely split, the tendency is clearly observed. This observation suggests that the splitting is caused by the $A(B^*)_2$ structure, which allows the dendritic, linear, and terminal units to experience two different chemical environments, respectively. The degree of branching for polymer **9** was calculated to be 0.6. However, it has been shown that this equation is incorrect for the determination of the degree of branching in the presence of residual monomer,[11g] since the linear units generated by the comonomer are neglected. Thus, for polymer **9**, the degree of branching with respect to the initiator-to-monomer ratio (having a fourfold excess of comonomer) is 0.60/4 or 0.15. Figure 2 reveals that the ratios of the three units are completely different in polymer **9** than in bis-MPA. This is the result of diluting the $A(B^*)_2$ monomer with ϵ-caprolactone. Not surprisingly, the ^{1}H-NMR spectra suggest that the branching in polymer **9** is similar to that found in hyperbranched poly(caprolactone) generated from intrinsically branched AB_2 macromonomers.[7] In addition, we have previously shown that bis-MPA is a very effective initiator for $Sn(Oct)_2$-catalyzed ring-opening polymerization, which mainly produces disubstituted units.[4g,7] The amount of disubstituted units has been found to be a function of the degree of polymerization, which can be predicted by the ratio of bis-MPA to cyclic monomer. In polymer **9**, where the initial ratio of bis-MPA to cyclic monomer is 1:4, >40% of the bis-MPA units are disubstituted. To corroborate the results of the ^{1}H-NMR analyses, ^{13}C-NMR spectra were obtained on monomer **7** and polymer **9**, since the resonance of the quartenary carbon of bis-MPA is known to depend on whether the structure is mono-, di-, or unsubstituted.[7g] Figure 3 shows the quartenary carbon region of the ^{13}C-NMR spectrum for **7**. This spectrum reveals a single peak at 49.5 ppm, which corresponds exactly to that previously reported for unsubstituted bis-MPA itself. Polymer **9** shows two peaks in this region, one major peak at 46.5 ppm corresponding to disubstituted bis-MPA and a smaller peak at 48.5 ppm, which corresponds to monosubstitution, as previously reported for monosubstituted bis-MPA.[7g] The ^{13}C-NMR spectra corroborate the ^{1}H-NMR analysis data, which suggest that polymer **9** contains mainly mono- and disubstituted bis-MPA. This relative increase in the degree of branching for the copolymers has been predicted by Müller et al. for AB* systems with monomers.[11f]

In summary, a new route to hyperbranched aliphatic polyesters has been demonstrated. A bis(hydroxymethyl)-substituted ϵ-caprolactone was synthesized and

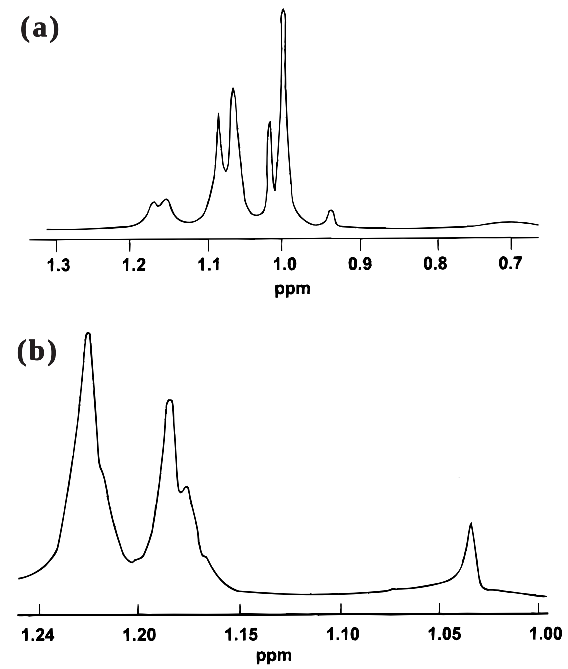


Figure 2. (a) Enlarged CH$_3$ region of the ^{1}H-NMR spectra (D$_2$O) of polymer **8**. (b) Enlarged CH$_3$ region of the ^{1}H-NMR spectra (CDCl$_3$) of polymer **9**.

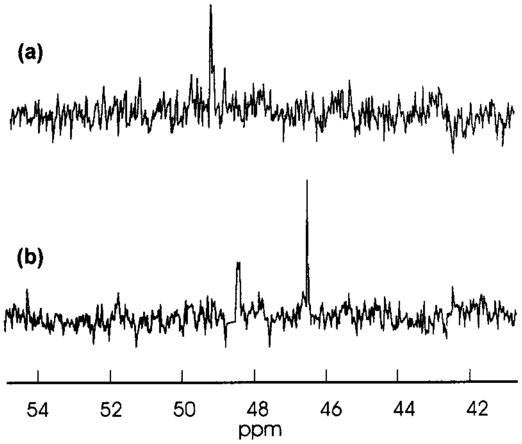


Figure 3. ^{13}C-NMR spectra of the quaternary carbon region of the different bis-MPA units in (top) **7** and (bottom) polymer **9**.

employed as a self-polymerizing monomer. The self-polymerization of this new monomer either with or without ϵ-caprolactone as a comonomer was accomplished at 110 °C in the presence of Sn(Oct)$_2$. Although the ROP procedure was living, the molecular weight increase followed polycondensation kinetics, typical of a self-condensing polymerization. Moderate molecular weights were obtained with the expected broad polydispersities. ^{1}H-NMR and ^{13}C-NMR studies show the presence of both dendritic and linear units. This new procedure represents the first report of hyperbranched polyesters using living self-condensing ROP techniques. Hyperbranched polyesters prepared from this monomer manifested an abundance of hydroxyl functionality. This significantly improved the hydrophilicity, a goal long sought for aliphatic polyesters. Future publications will discuss the use of bis(hydroxymethyl)-substituted ϵ-caprolactone and related monomers as components in linear and dendrimer-like star amphiphilic macromolecules.

Supporting Information Available: Experimental details and compound characterization (4 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

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MA991039V