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COMMUNICATIONS

Control of Polymer Topology through Transition-Metal Catalysis: Synthesis of Hyperbranched Polymers by Cobalt-Mediated Free Radical Polymerization

Zhibin Guan*

Department of Chemistry, 516 Rowland Hall, University of California, Irvine, California 92697-2025

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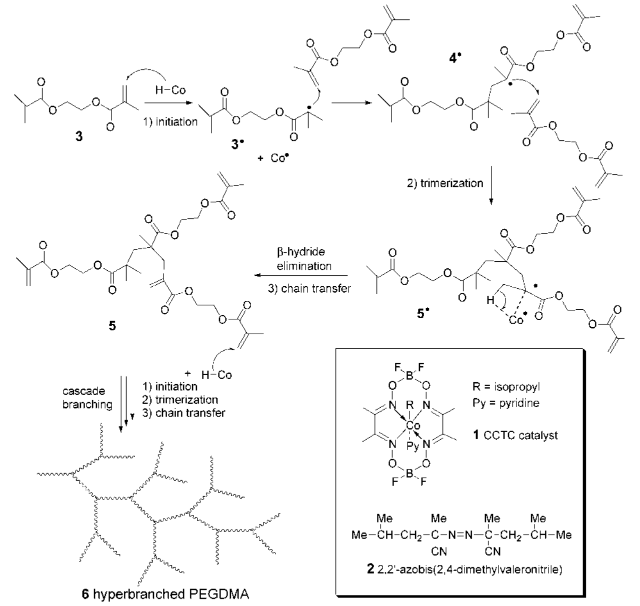
Polymer topology is an important molecular parameter for determining polymer properties.[1] Driven by the need of creating polymers with new and improved properties, tremendous efforts have been devoted to the synthesis of polymers with new architectures and topologies.[2] I have been exploring a new concept of controlling polymer topology by direct polymerization of simple commercial monomers using transition-metal catalysts.[3] Instead of designing new monomers, it was attempted to achieve new polymer topologies by controlling the covalent assembly of simple monomers through catalysis. I have previously demonstrated this concept [3a,b] for the coordination polymerization of ethylene using the Brookhart's palladium−bisimine olefin polymerization catalysts.[4] By controlling the competition between monomer insertion and chain walking, high-molecular weight polyethylenes were synthesized with a broad spectrum of topologies ranging from linear to hyperbranched to "dendritic".[3a,b] Others have reported recently the synthesis of short-chain branched [5a] and hyperbranched polyolefins using different transition-metal complexes.[5b] In this communication, I report a new approach for controlling polymer topology through a transition-metal-mediated radical polymerization.

In this approach, hyperbranched polymers were synthesized by direct free radical polymerization of commercially available divinyl monomers by controlling the competition between propagation and chain transfer using a chain transfer catalyst. Free radical polymerization is one of the most widely used polymer production methods with major advantages in the generality of monomer choice and the robustness of reaction conditions. However, free radical polymerization usually produces only a limited array of polymer architectures due to the nature of linear radical propagation. It is of both fundamental and practical interests to develop general methods for the preparation of polymers with new topologies by direct free radical polymerization. Two types of self-condensing "living" radical polymerizations have been reported for the syntheses of hyperbranched polymers; however, in both cases specially designed monomers are required, and the branching was introduced by the inherent structures of the monomers.[6] In this study, a cobalt chain transfer catalyst (CCTC) **1** was used to control the propagation of free radical polymerization of a divinyl monomer. A series of cobalt complexes were shown to afford efficient catalytic chain transfer reaction to free radical polymerization of vinyl monomers.[7] According to the generally accepted mechanism, the cobalt complexes bind reversibly to growing radical centers, and this leads to β-hydride abstraction to terminate the propagating chains while generating cobalt−hydride species to reinitiate new propagating chains.[7] I reasoned that if a dimethacrylate monomer is used and if the CCTC is chosen at the concentration for trimerization of methacrylate, the repetitive trimerization of a dimethacrylate monomer will lead to a hyperbranched polymer. The concept is illustrated in Scheme 1 for the radical polymerization of ethylene glycol dimethacrylate (EGDMA), **3**, initiated with an azo initiator **2** and controlled by **1**. The cobalt−hydride (Co−H) formed in the catalytic cycle initiates a new radical chain, $\mathbf{3}^{\bullet}$. Because the CCTC concentration was chosen specifically for trimerization, statistically the new chain only propagates twice to form a trimer radical, $\mathbf{5}^{\bullet}$, which is subsequently terminated by β-hydride abstraction by the CCTC. The terminal methacrylate groups of the trimer **5** will be reinitiated by the Co−H, followed by trimerization and β-hydride abstraction to form another branching point. Since every trimerization generates a branching point, the cascade trimerization of EGDMA leads to a hyperbranched polymer. Due to the statistical nature of chain transfer process, a distribution of oligomeric structural units with an average value of a trimer are expected in the polymers.

Scheme 1



The CCTC used in this study has a chain transfer constant, C_s, in the order of 10^3 for free radical polymerization of methyl methacrylate (MMA).[8] Estimated by the Mayo equation,[9] the catalyst concentration is about 0.1% of MMA concentration to form trimer in MMA polymerization. Therefore, a series of EGDMA polymerizations were conducted in bulk or in solution with [**3**]/[**1**] around 10^3. The polymerizations were monitored by size exclusion chromatography (SEC). Initially, short oligomers of **3**, such as dimers, trimers, tetramers, gradually built up. The oligomers decreased in concentration with time, and polymeric material increased correspondingly. In both bulk and solution polymerizations, soluble polymers were obtained with the monomer conversion

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* To whom correspondence should be addressed. E-mail: zguan@uci.edu.

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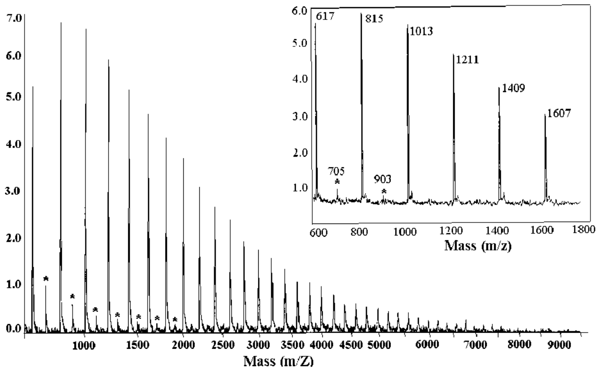

Figure 1. MALDI mass spectrum of the hyperbranched PEGDMA. The major peaks in the inset correspond to the [M + Na] for the trimer, tetramer, pentamer, hexamer, heptamer, and octamer.

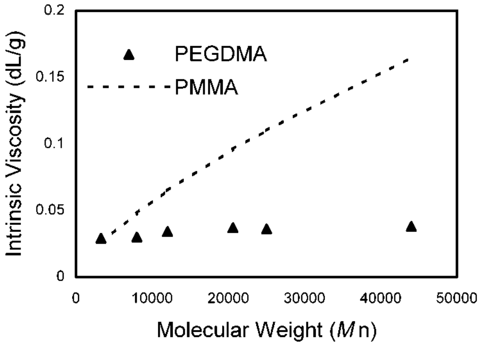

Figure 2. Intrinsic viscosity versus molecular weight for PEGDMA and PMMA.[10]

up to 70%. On the contrary, **3** forms gel instantaneously in regular free radical polymerization without **1**.

The chemical structure of the hyperbranched polymers (PEGDMA) was confirmed by nuclear magnetic resonance (NMR) analyses. The ratio of [external methacrylate]/[internal vinylidene] was calculated from ^{1}H NMR to be about 1.0, which clearly supports the hyperbranched structure of the polymer (Supporting Information). The molecular weights of the PEGDMAs were characterized by SEC and matrix assisted laser desorption ionization (MALDI) mass spectrometry. The MALDI spectrum of one sample is shown in Figure 1 for which the number-averaged molecular weight (M_n) measured by MALDI ($M_n = 2408$) agrees reasonably well with the value obtained from SEC ($M_n = 2500$). The MALDI spectra show that the polymers were clean with the mass of each peak matching exactly the molar mass of that specific oligomer calculated on the basis of the structure shown in Scheme 1. The major set of peaks corresponds to polymer chains that were initiated by the cobalt hydride species generated in the catalytic cycle. The minor set of peaks (labeled with $*$) is due to polymer chains that were initiated by the primary alkyl radicals formed from decomposition of the initiator **2** in the beginning of the polymerization.

The hyperbranched polymers exhibit interesting solution properties. The intrinsic viscosities ([η]) of the hyperbranched PEGDMAs are much lower compared to that of linear poly(methylmethacrylate) (PMMA) having the same molecular weight. For example, the [η] of a hyperbranched PEGDMA having M_n of 25 000 is only 0.036 dL/g, while for a linear PMMA with the same M_n, the [η] is 0.11 dL/g.[10] Another unique feature is that there is essentially no dependence of the [η] on molecular weight (Figure 2). For linear polymers in good solvent, the [η] increases monotonically with the molecular weight following the Mark−Houwink equation with the coefficient α around 0.7.[11] It has been reported, however, that dendrimers and hyperbranched polymers exhibit unusual solution viscosity behavior.[12] For example, the [η] of some dendrimers increases initially and then decreases after a maximum is reached at certain generation.[12b] The [η] of star and hyperbranched polymers generally has much less dependence on molecular weight than that of the corresponding linear polymers, and the relationship is system-dependent.[12c] Very small dependence of [η] on molecular weight has been observed for star-shaped polystyrenes with the Mark−Houwink coefficient, α, being about 0.18.[12d] We are currently further investigating this unusual solution behavior of the hyperbranched PEGDMA.

In conclusion, a novel approach is demonstrated for polymer topology control using transition-metal catalysis, in which a cobalt catalyst was used to control the PEGDMA branching topology by regulating the competition between propagation and chain transfer. The hyperbranched polymers formed have interesting properties such as high surface functionality and low solution viscosity. These unique features, combined with the commercial availability of many divinyl monomers and the robustness of free radical polymerization, will make this new approach attractive for the preparation of new functional materials.

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Supporting Information Available: Polymerization procedure and data, SEC and MALDI characterization, NMR analyses of the hyperbranched polymers (PDF). This information is available free of charge via the Internet at http://pubs.acs.org.

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(10) The viscosity data are summarized in Table 1 in the Supporting Information. The intrinsic viscosity of PMMA was calculated from the Mark−Houwink equation: $[\eta] = KM^{\alpha}$, using $K = 7.5 \times 10^{-5}$ dL/g and $\alpha = 0.72$ which were measured for PMMA in THF at room temperature (see reference: Grubisic, Z.; Rempp, P. and Benoit, H. *J. Polym. Sci.* **1967**, *B5*, 753).
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