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Dynamics of hyperbranched polymers derived from acrylated epoxidized soybean oil

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ABSTRACT

In this article we demonstrate the role of chain architecture on the relaxation dynamics of poly(acrylated epoxidized soybean oil) (PAESO), a hyperbranched polymer, with a particular focus on the role played by intramolecular loops. PAESO is produced by reversible addition-fragmentation chain transfer (RAFT) polymerization from acrylated epoxidized soybean oil (AESO) containing an average of 2.6 polymerizable acrylic moieties per trigylceride. By adjusting the relative concentrations of solvent, monomer, and RAFT chain transfer agent, PAESO undergoes a series of both inter-molecular and intra-molecular reactions such that both molecular weight and chain architecture vary throughout the reaction. While intermolecular reactions are responsible for branching, *intra*molecular reactions introduce loops to the structure with altogether different consequences on chain conformations and segmental dynamics. Using dynamic shear rheology in the linear viscoelastic regime we find that Rouse/Zimm-like dynamics persist to molecular weights as high as 390 kDa and that the primary influence of looping is to strongly suppress the number of Zimm relaxation modes.

1. Introduction

Hyperbranched polymers (HP) are polymers with chain architectures comprised of many tree-like branches. They are a member of a family of branched polymers that express unique physical properties due to a variety of branch configurations [1,2]. In order to understand the effect of branches on main chain relaxation, researchers have investigated a number of polymer topologies with different branch densities, including (from the least to the highest branch density): stars [3–5], H-shapes (or “miktoarm star”) [6,7], combs [8–10], bottle brushes [11–13] and dendrimers [14–16].

Both experimental and theoretical studies are available that describe the rheological behavior of these various well-defined polymer topologies [8,13,17–20]. It is well accepted that branched polymers follow “hierarchical relaxation dynamics” [21–24]; that is, several relaxation processes can be observed with a hierarchy of characteristic times. Shorter relaxation times are associated with branches and arms, while larger components such as the primary chain have longer relaxation times, with the macro-chain relaxation time being the longest. However, the interactions of branches and arms with the primary chain are highly dependent on the overall chain topology. For star polymers, even though branch points provide hindrance to relaxation, macro-chains still follow the reptation model that applies to linear polymers: chain entanglements can form when the arm length exceeds the critical and entanglement molecular weights ($M_{n,arm} > M_c > M_e$). As the number of branch points increases, however, entanglement becomes less achievable. For example, comb polymers consist of a linear chain backbone with multiple randomly distributed side chain pendants of nearly equal length. As the pendant (branch) density increases, the backbone conformational degrees of freedom become increasingly suppressed. Beyond a critical branch density this suppression is essentially complete, meriting a distinct class: the bottle brush polymer. In this chain architecture the side chain interactions strongly hinder the flexibility of the backbone, precluding the evolution of reptation dynamics even as the backbone molecular weight far exceeds M_c. For this reason bottle brush polymers tend to be well described by Rouse or Zimm models, which was originally applied only to small linear polymers and solutions thereof. Hu et al. [20] have pointed out that even with short side chains ($M_{n,\text{side chain}}/M_e \approx 0.2$) and a long backbone ($\approx$800 repeat units), no backbone entanglement is observed and Rouse dynamics well-account for the melt rheology. When increasing side chain length to$M_{n,\text{side chain}}/M_e = 1.0$, arm

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entanglement can also be observed. In Dalsin et' al.s work [13], the side chain length was further increased to$M_{n,\text{side chain}}/M_e \sim 3.5$. While reptation dynamics corresponding to the side chain relaxation were observed, Zimm dynamics best accounted for the backbone relaxation. Dalsin et al. proposed that in this system the side chains isolated the backbone analogously to solvent molecules in polymer solution, providing Zimm-like hydrodynamic interactions in the polymer melt at time scales longer than the side chain relaxation. As in other studies, the main effect of the side chains was to act as a "dilution factor"; that is, the cooperative motion of the side chains attached backbone "dilutes" the model representation of the backbone into a fewer number of active beads. This action causes the backbone dynamics to mimic those associated with much shorter chains.

Like comb and bottle brush polymers, hyperbranched polymers consist of a primary chain backbone with a statistical distribution of pendant chains. In this topology, however, the pendant chains are themselves further branched in a recursive or fractal-like pattern. The pendant chains, therefore, affect the rheological properties by the degree of branching [25–27] and end-group properties [28–30]. Among the previous studies, polycondensation, chain-walking polymerization or radical polymerization with low amounts of crosslinkers were selected to avoid crosslinking. The rheological behavior of hyperbranched polymers produced via one-pot radical polymerization is thus unknown.

As mentioned above, one of the biggest challenges of HP synthesis, which requires the introduction of multifunctional monomers, is the tendency to abruptly crosslink in the early stages of polymerization, complicating the study of entanglement dynamics due to the attendant low molecular weight. That is, HP materials rapidly transition from oligomers/low molecular weight structures to a pervasive infinite network. According to Flory-Stockmayer theory [31,32], a small primary chain length can effectively limit crosslinking; consequently, most of known HPs in the literature are low molecular weight materials ($M \approx 2$–10 kDa $\ll M_e$) [33–38]. Additionally, intramolecular loops or cyclings are unavoidable aspects of the chain architecture. In view of reaction kinetics, intramolecular reactions are evidently favorable, since they play a major role in the suppression of crosslinking [39]. These architectural features may be expected then to also strongly influence the chain relaxation dynamics and rheological properties of HPs [40].

In our previous kinetic study [41], we reported the synthesis of poly(acrylated epoxidized soybean oil) (PAESO), a HP produced from acrylated epoxidized soybean oil containing 2.6 acrylic groups per monomer. In this study we found that by using reversible addition-fragmentation chain transfer (RAFT) polymerization, the polymerization of AESO can easily exceed 50% monomer conversion with resultant molecular weights greater than 100 kDa prior to the gel point. Moreover, we demonstrated that the reaction conditions, especially the monomer molarity, govern the balance of inter- and intra-molecular reactions. Intramolecular reactions were found to be prevalent at lower monomer concentration; in this regime macro-gelation was essentially eliminated, although the polymers so-produced presented a more heterogeneous chain architecture with significant looping. In contrast, in more concentrated systems macrogelation occurred at increasingly small conversions, while intramolecular reactions became substantially less frequent. Interestingly, this implies that the chain architecture, and thus the properties, of these polymers is a strong function of the manner in which they are produced. For example, the intrinsic viscosity of PAESO produced at low monomer concentration was much less than a PAESO originating from a high monomer concentration due to the comparatively compact chain architecture.

In this work, a variety of PAESO materials with molecular weight of $M_n \in$ [49 kDa, 390 kDa] have been synthesized. The ability to produce high molecular weight PAESOs affords a new opportunity to investigate the role of chain architecture in HP dynamics. Different primary chain lengths have been selected based on previous work [41] to obtain a wide range of inter/intra molecular reactions. In particular, we seek to illustrate how intra-molecular reactions, which cause loops to form in the hyperbranched architecture, influence the main chain relaxation. We apply dynamic shear rheology to measure the linear viscoelastic properties, and interpret the data with the Zimm and Rouse models.

2. Experiment

2.1. Materials

Acrylated epoxidized soybean oil (AESO, inhibited with MEHQ to 4000 ppm), Sigma-Aldrich) was de-inhibited and dried by passage over silica gel and inhibitor removers. The acrylic content is 2.6 acrylate groups per molecule. The fatty acid profile of the soybean oil precursor is 50% linoleic acid, 24% oleic acid, and 7% linolenic acid), corresponding to an average unsaturation of 4.6 alkene units per molecule. Azobisisobutyronitrile (AIBN, 98% Sigma-Aldrich) was used as the free radical initiator; it was purified via recrystallization in methanol (ACS grade, Fisher Scientific). Hydroquinone (99%, Fisher Scientific) and 1,4-dioxane (Fisher Scientific) were used as received. The RAFT chain transfer agent (CTA) was ethyl 2-(ethoxycarbonothioylthio)-2-methylpropanoate (ETMP), which was synthesized according to procedures published elsewhere [41–43].

2.2. RAFT polymerization

The polymerization of AESO via RAFT was as follows: Monomer-to-CTA molar ratios ranging from 208 to 832 were used to target number average molecular weights from 250 to 200 kDa, respectively. AIBN concentration was such that its molar ratio with the CTA was 0.2. 1,4-dioxane was used as the solvent in a 4:1 volumetric ratio with the monomer, consistent with the conditions identified in our previous study [41]. Detailed quantities are listed in Table 1. All polymerizations were conducted at 80 °C under argon atmosphere. Reaction times were chosen to correspond to roughly 15%, 25%, and 35% vinyl conversion.

2.3. Characterization

Size exclusion chromatography (SEC) provided the molecular weight distribution, molecular weight averages and polydispersity index (PDI). Chloroform at room temperature was used as the solvent at 1 mL/min. An RI detector (Wyatt Technology, Optilab T-rEX) and a dual detector assembly with light scattering and viscometer (Malvern, Viscotek 270 Dual Detector) were used to characterize the eluent. Molecular weight calibration was achieved through polystyrene standards (molecular weight ranging from 2.6 to 821 kDa, Malvern Instruments).

The extent of reaction was measured using proton nuclear magnetic resonance spectroscopy (Bruker AVII, 600 MHz) in deuterated chloroform according to the method used in our earlier report [41]. Thermal characteristics including the glass transition temperature were assessed using differential scanning calorimetry (DSC, TA Instrument Q2000) in hermetically sealed pans (Tzero). Specimens were first held at to 90 °C for 5 min and then at −20 °C for 2 min to erase thermal history. Next, scanning at 10 °C/min, the temperature was cycled three times to 90 °C and back to −20 °C. The second and third cycles were nearly identical; T_g values were reported from the second cycle.