Long-chain Hyperbranched Polystyrene Using Sulfoxide-functionalized ATRP

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Abstract

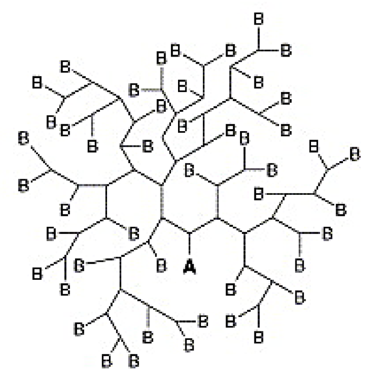
Traditional synthesis methods for hyperbranched polymers often suffer from poor architectural control, leading to random branching structures. To address this limitation, we introduce a novel one-pot synthesis approach based on sulfoxide chemistry to achieve precise control over branch lengths. In this method, linear polystyrene was initially synthesized at temperatures below 40°C. The reaction temperature was then increased to 100°C, triggering the deprotection of sulfoxide-protected vinyl groups into reactive methacrylate functionalities. These newly generated vinyl groups underwent further polymerization, forming well-defined hyperbranched polystyrene structures. This approach enabled precise control over branch-point spacing by tuning structural parameters during polymerization. We successfully synthesized hyperbranched polymers with branch lengths of 5k, 10k, and 20k by adjusting the molecular weight of the linear polystyrene precursor, demonstrating excellent control over branch length and distribution.

The rheological behavior of these hyperbranched polymers was characterized through Small Amplitude Oscillatory Shear (SAOS) tests for linear viscoelastic properties and Extensional Viscosity Fixture (EVF) tests for nonlinear viscoelastic behavior. Branch length had a significant impact on relaxation time and strain hardening effects, with more pronounced effects in the nonlinear viscoelastic regime. This comprehensive analysis provides valuable insights into the structure-property relationships of hyperbranched polymers. The versatile and efficient synthesis method, combined with detailed rheological analysis, paves the way for innovative applications in materials science.

Introduction

Hyperbranched Polymer

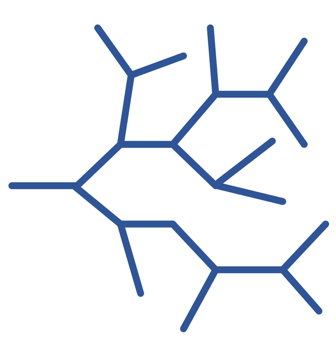
- ✓ A randomly branched structure
- ✓ Terminal functional groups ↑
- ✓ Low viscosity
- ✓ High solubility
- ✓ Weak entanglement



Fluid phase equilibria **2006** 241, 155-174

Introduction of long linear segments between branching points

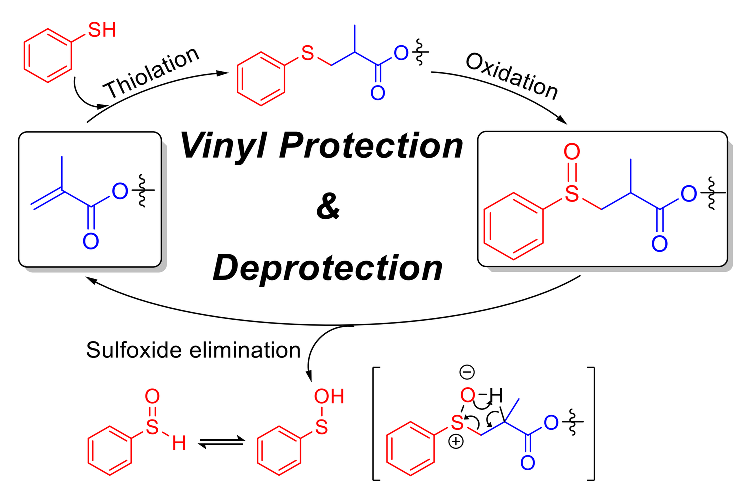
Long-chain Hyperbranched Polymer



- ✓ Terminal functional groups ↑
- ✓ Low viscosity
- ✓ High solubility
- ✓ Entanglement due to long branches
- ✓ Strain hardening
- ✓ Melt elasticity / strength ↑

➢ Tunable properties between linear and hyperbranched polymers

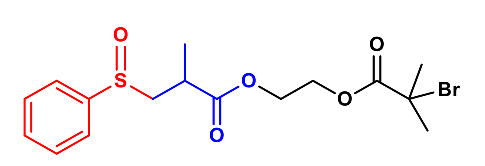
Sulfoxide Chemistry



Macromolecules, **2021**, 54, 17, 7716-7723

- ➢ Generation of vinyl groups on demand
- ➢ Tunable branch lengths

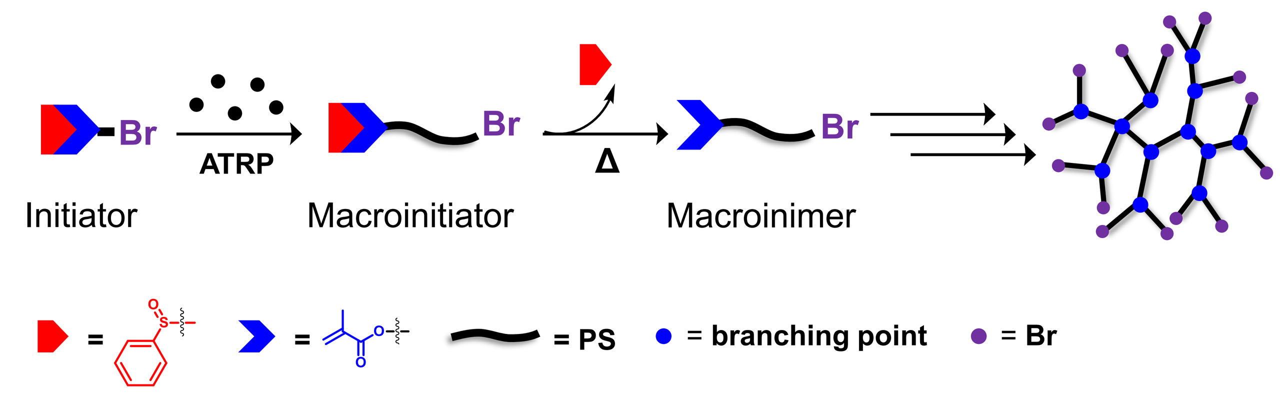
Sulfoxide-protected ATRP Initiator



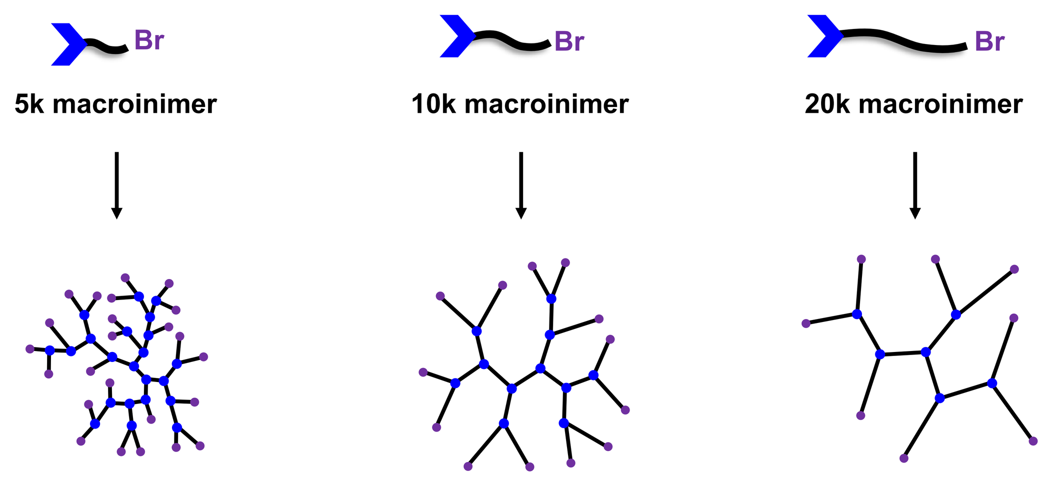
sMAc

sMAc: 2-((2-Bromo-2-methylpropanoyl)oxy)ethyl 2-methyl-3-(phenylsulfinyl)-propanoate

Overall Scheme



" Long-chain Hyperbranched PS with Branch Length Control "

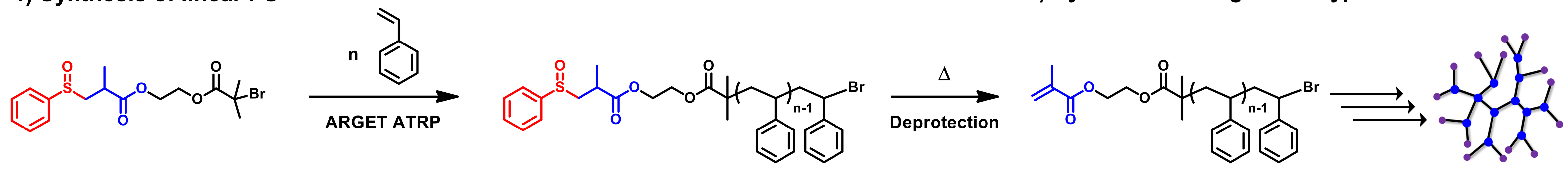


Result & Discussion

Synthesis of LCHPs

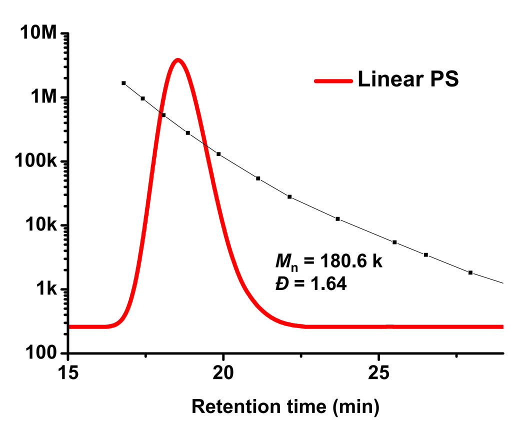
1) Synthesis of linear PS

2) Synthesis of long-chain hyperbranched PS

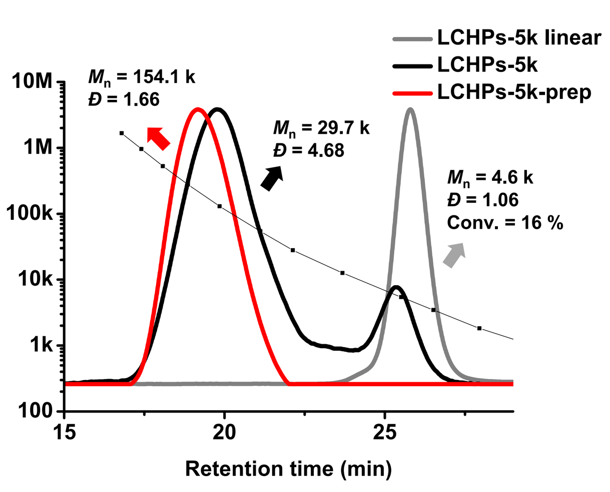


❖ **SEC**

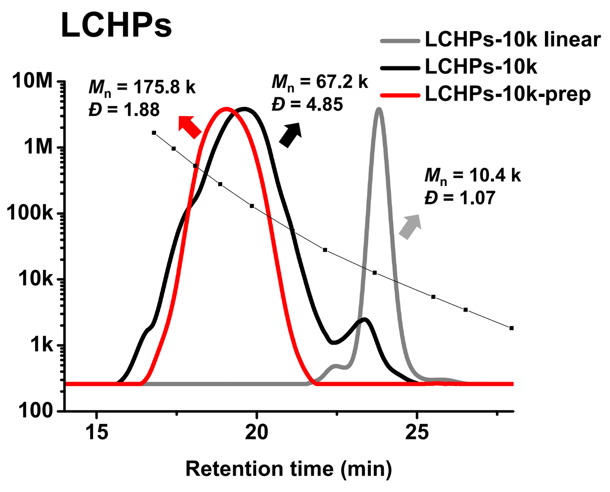
▪ **Linear PS**



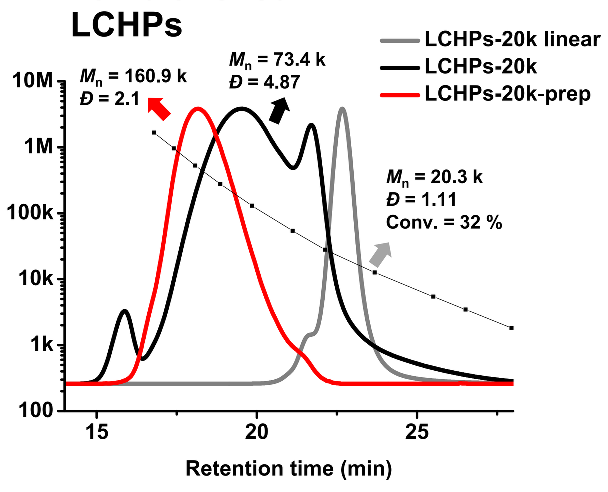
▪ **5k branched LCHPs**



▪ **10k branched LCHPs**



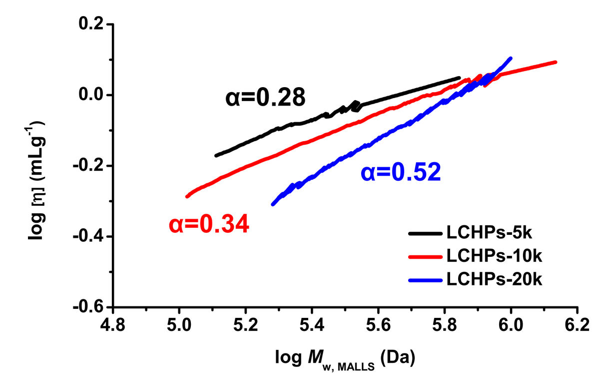
▪ **20k branched LCHPs**



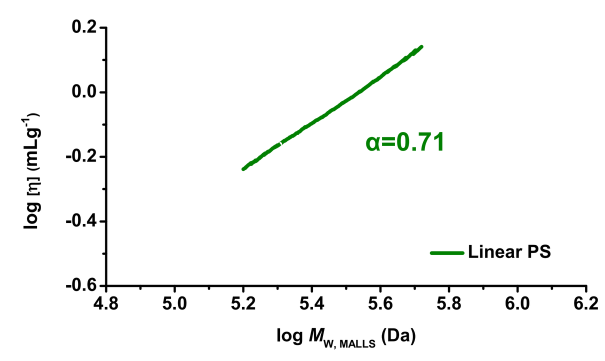
- ✓ Initial polymerization at <40 ℃ yielded linear polystyrene, followed by further reaction at 100 ℃ to produce long-chain hyperbranched polystyrene.
- ✓ Long-chain hyperbranched polystyrene was fractionated by preparative liquid chromatography after polymerization for rheological characterization.

❖ ***Intrinsic viscosity*** $[\eta] = KM^{\alpha}$

▪ *Long-chain hyperbranched PS*



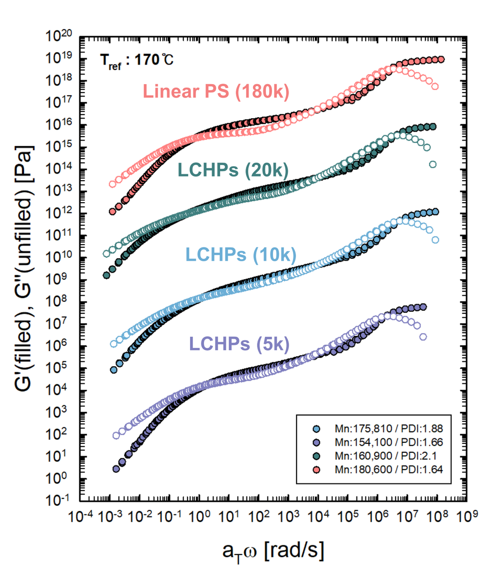
▪ *Linear PS*

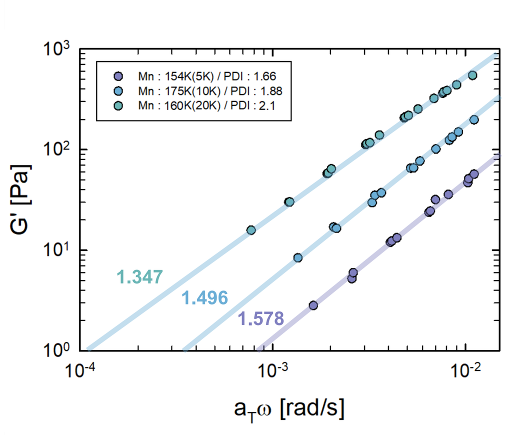


✓ Lower α values for LCHPs reflect a more compact molecular structure compared to linear PS, consistent with increased branching and reduced hydrodynamic volume.

Rheological properties of LCHPs

❖ ***Small Amplitude Oscillatory Shear Test***

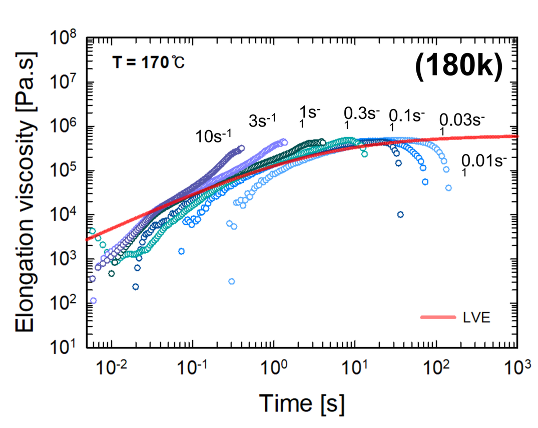




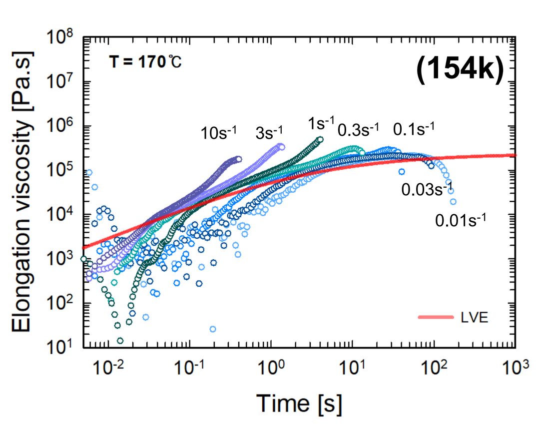
✓ As the branch length of LCHPs increases, enhanced entanglement leads to slower relaxation dynamics, evidenced by reduced terminal slopes and extended viscoelastic response.

❖ ***Extensional Viscosity Fixture Test***

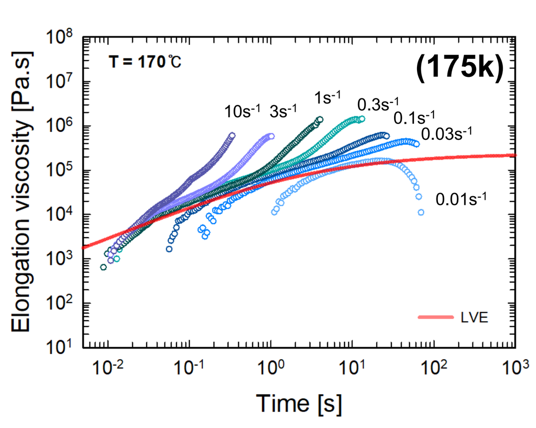
▪ **Linear PS**



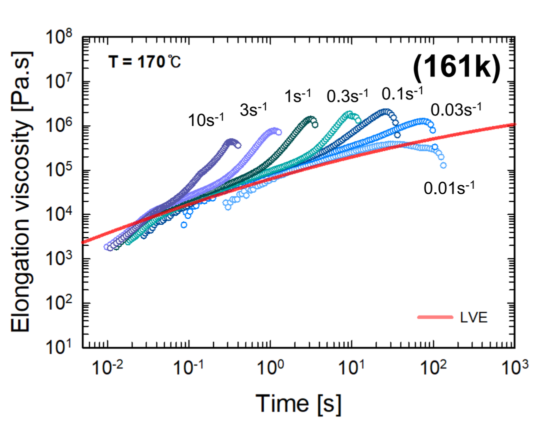
▪ **5k branched LCHPs**



▪ **10k branched LCHPs**



▪ **20k branched LCHPs**



✓ Longer branched structures exhibit enhanced strain hardening behavior, indicating that increased branch length leads to greater resistance to extensional flow due to more effective entanglement and molecular stretching.

Conclusion

- ✓ A **one-pot sulfoxide-based method** was developed to synthesize **long-chain hyperbranched polystyrene** with tunable branch lengths (5k, 10k, 20k), paving the way for broad applications in advanced material systems.
- ✓ Variations in **branch length** caused changes in the **branching degree**, which in turn affected the intrinsic viscosity.
- ✓ **Branch length** plays a key role in viscoelastic behavior: longer branches → **slower relaxation**, **stronger strain hardening**.

Acknowledgements

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