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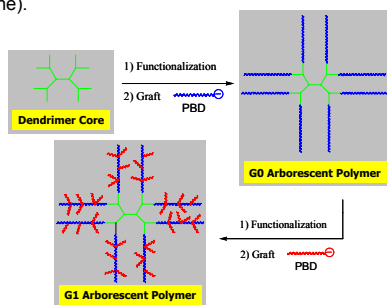
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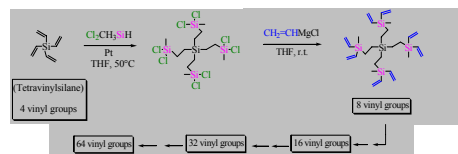
Introduction

Branched polymers are of interest, among others, because of their peculiar physical properties¹ and their potential usefulness as rheological modifiers for other polymers.² Star-branched³ and arborescent⁴ (dendrigrift) polymers are two families of branched polymers of particular importance because their controllable architecture enables fundamental investigations of structure-property relations. The physical properties of these materials can be fine-tuned through variations in parameters such as their side chain molecular weight and composition, branching functionality, the presence of functional end groups, etc. Their molecular weight distribution is very narrow, because their synthesis typically relies on living polymerization techniques. As a result, these polymers are ideal for the elucidation of the influence of structural parameters on the molecular (polymeric) and intermolecular (colloidal) properties of branched polymers.

A strategy combining carbosilane dendrimer substrates and arborescent polymer chemistry is presented for the synthesis of high branching functionality dendrimer-arborescent polybutadiene hybrid polymers. Carbosilane dendrimer substrates bearing 32, 64, or 128 peripheral Si-Cl functional groups are first coupled with short 1,2-polybutadienyllithium segments and hydrosilylated with dichloromethylsilane. The polyfunctional substrates are then reacted with polybutadienyllithium chains of different number-average molecular weights ($M_n = 1500, 5000, \text{ and } 30000$) with a high 1,4-microstructure content. This approach yields substrates with up to 2830 side chains, significantly higher than for the star-branched polymers reported previously. Interesting physical properties are expected for these polybutadiene arborescent hybrids, due to their very high branching functionality, compact structure, and the very low entanglement molecular weight of the PBD segments ($M_e = 1800$ for 1,4-polybutadiene).



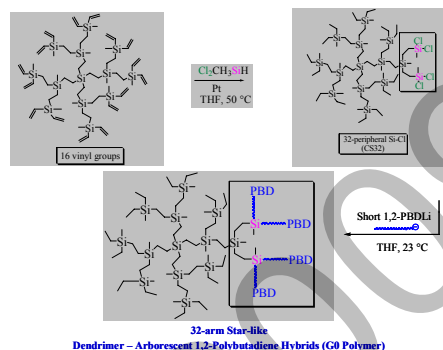
Synthesis of Carbosilane Dendrimer Core



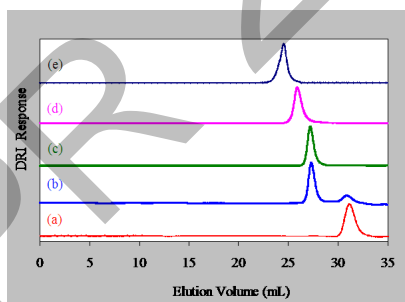
> All carbosilane substrates were synthesized by a modification of a procedure published by Zhou and Roovers, *Macromolecules* **1993**, 26, 963

— Adapted for high-vacuum techniques used in our laboratory (e.g. Gauthier et al. *Macromolecules* **1996**, 29, 519)

Synthesis of Star-like 1,2-Polybutadiene Hybrids



GPC Analysis: G0 Polymers



(a) 1,2-Polybutadiene side chains (b) Crude grafting product
(c) Fractionated CS32-mPBD1 (d) Fractionated CS64-mPBD1
(e) Fractionated CS128-mPBD1

Characterization: G0 Polymers

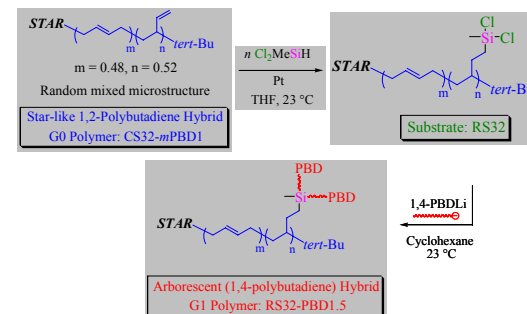
| Sample | Side Chains | | M_c | Star Polymer | | |
|----------------------|-------------|-----------|-------|-------------------|-----------|------------|
| | M_n | M_w/M_n | | M_n | M_w/M_n | f_n |
| CS32- <i>m</i> PBD1 | 540 | 1.13 | 2016 | 1.9×10^4 | 1.02 | 31 |
| CS64- <i>m</i> PBD1 | 1000 | 1.10 | 4288 | 6.1×10^4 | 1.03 | 57 |
| CS128- <i>m</i> PBD1 | 1200 | 1.10 | 8832 | 1.6×10^5 | 1.16 | 126 |

$$f_n = \frac{(M_n)_{star} - M_c}{(M_n)_{arm}}$$

> Branching functionality f_n , determined from the equation

— Branching functionalities comparable with the nominal values (except CS64: -8.8 %)

Synthesis of 1,4-Polybutadiene Hybrids



Characterization: G1 Polymers

| Sample | Side Chains | | M_c | Hybrid Polymers | | |
|--------------|-------------|-----------|--------|-------------------|-------------|-------------|
| | M_n | M_w/M_n | | M_n | M_w/M_n | f_n |
| RS32-PBD1.5 | 1200 | 1.10 | 26200 | 4.3×10^5 | 1.01 | 336 |
| RS32-PBD5 | 6500 | 1.11 | | 2.0×10^6 | 1.05 | 304 |
| RS32-PBD30 | 26000 | 1.08 | | 3.7×10^6 | 1.03 | 141 |
| RS64-PBD1.5 | 1270 | 1.11 | 85000 | 1.5×10^6 | 1.07 | 1114 |
| RS64-PBD5 | 4000 | 1.10 | | 3.8×10^6 | 1.03 | 929 |
| RS64-PBD30 | 29900 | 1.09 | | 4.9×10^6 | 1.03 | 161 |
| RS128-PBD1.5 | 1300 | 1.10 | 224000 | 3.9×10^6 | 1.13 | 2828 |
| RS128-PBD5 | 5800 | 1.13 | | 5.3×10^6 | 1.08 | 875 |
| RS128-PBD30 | 23000 | 1.06 | | 8.6×10^6 | 1.14 | 364 |

> Branching functionality f_n , determined from the equation

— Within the series f_n , lower than nominal values due to steric limitations

Related Publications

- 1) Masuda, T.; Ohta, Y.; Onogi, S. *Macromolecules* **1986**, 19, 2524.
- 2) Khadir, A.; Gauthier, M. *Polym. Mater. Sci. Eng.* **1997**, 77, 174.
- 3) Roovers, J. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed., Vol. 2; Kroschwitz, J. I. Ed.; Wiley: New York, 1985; p 478.
- 4) Gauthier, M. In *Ionic Polymerizations and Related Processes*; Puskas, J. E., Ed.; NATO ASI Series E359; Kluwer Academic: Dordrecht, 1999, p 239.

Acknowledgements

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