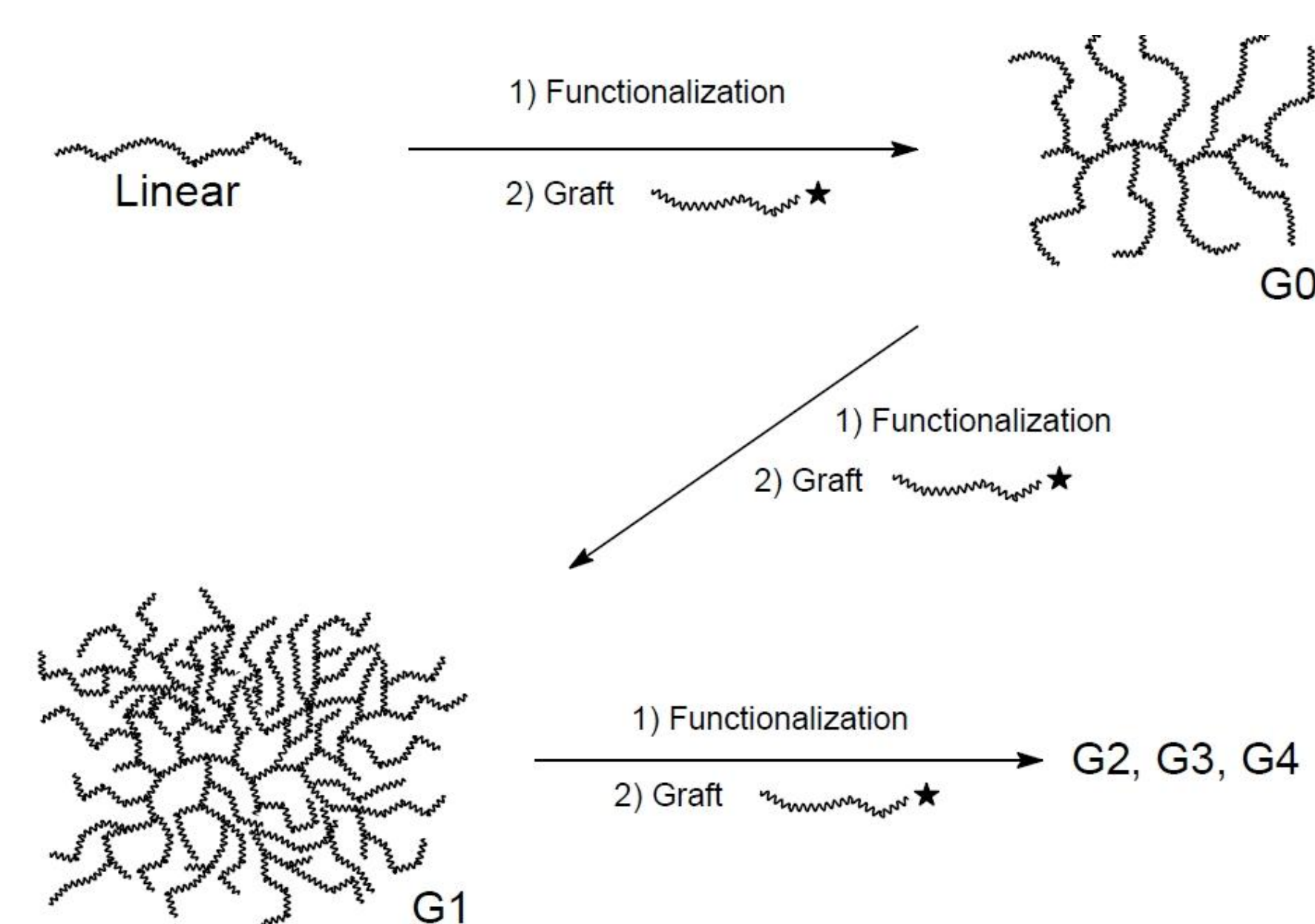


## Abstract

Living anionic polymerization techniques are applied to the synthesis of arborescent (dendritic) well-defined graft copolymers having a core-shell morphology, with a hydrophobic core and a hydrophilic shell. Cycles of polystyrene substrate acetylation and anionic grafting yield successive generations of arborescent polystyrenes. The anionic polymerization of styrene with *sec*-butyllithium gives polystyryllithium serving as side-chains. These are coupled with a linear acetylated polystyrene substrate to obtain a generation zero (Go) arborescent polymer. A Go hydroxyl-functionalized polystyrene core with hydroxyl end groups can be obtained by a variation of the same technique. In this case, a bifunctional organolithium initiator containing the hydroxyl functionality protected by a silyl ether group is used to generate the polystyrene side-chains. These are coupled with the linear acetylated polystyrene substrate and subjected to a deprotection reaction to give the Go polymer functionalized with hydroxyl groups at the chain ends. A similar procedure can be used to generate hydroxyl-functionalized arborescent polymers of generations G1-G3 from the corresponding Go-G2 acetylated polystyrene substrates, respectively. Polyglycidol chain segments are then grown from the hydroxyl-functionalized cores to form a hydrophilic shell around the hydrophobic core polymers.

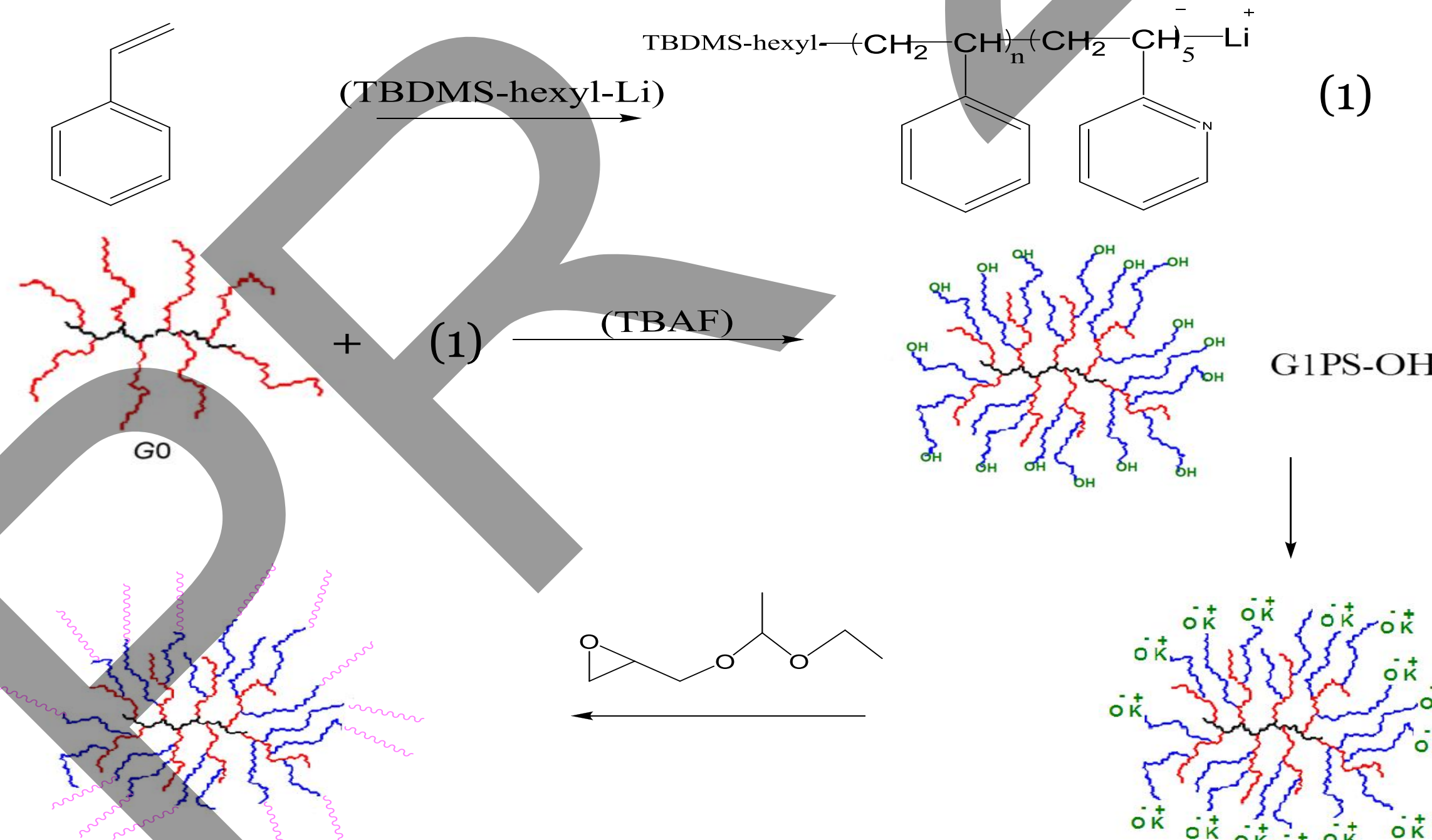
## Arborescent Polymers

Dendrigraft polymers, also called Comb-burst® polymers by Tomalia et al.<sup>1</sup> and arborescent polymers by Gauthier and Möller,<sup>2</sup> are highly branched molecules synthesized from polymeric building blocks. These are assembled according to a generation-based scheme analogous to dendrimers, which relies on cycles of substrate functionalization and grafting. In dendrigraft polymers the coupling sites are distributed randomly on the substrate, in contrast to dendrimers, where they are strictly located at the chain ends.<sup>3</sup> The reaction of a functionalized linear substrate with side-chains thus yields a generation zero (Go or comb-branched) polymer. Subsequent functionalization and grafting cycles result in arborescent polymers of generations G1, G2, and so on.<sup>4</sup> The tree-like architecture with multiple branching levels, characterizing arborescent polymers, results from the successive grafting cycles.<sup>5</sup> These polymers can be synthesized by both *grafting onto* and *grafting from* methods, although the *grafting onto* methods have been most widely applied.



## Arborescent Core-shell Copolymers

Gauthier et al.<sup>6</sup> also synthesized core-shell copolymers by a variation of the "graft-upon-graft" methodology, using a combination of *grafting onto* and *grafting from* techniques. The arborescent polystyrene substrates serving as hydrophobic cores were synthesized by the *grafting onto* method described above, and hydroxyl chain ends were introduced on the outside of the molecules in the final grafting reaction through a bifunctional initiator containing a protected hydroxyl group. After deprotection, the end groups were titrated with potassium naphthalide to generate potassium alcoholate functionalities, and ethylene oxide was added to grow hydrophilic poly(ethylene oxide) segments from the chain ends. A similar procedure will be used in the current project to grow a polyglycidol shell (Scheme 2).



Scheme 2

## Synthesis

- Synthesis of linear and arborescent polystyrene substrates by cycles of acetylation and grafting
- Synthesis of hydroxyl-functionalized Go-G3 cores using a bifunctional initiator
- Synthesis of glycidol acetal
- Growth of poly(glycidol acetal) chains from hydroxyl-functionalized cores to form a shell
- Deprotection of the acetal to obtain a shell of hydrophilic polyglycidol segments

## Results

A linear polystyrene sample with a narrow MWD ( $M_n = 4770$  g/mol,  $M_w/M_n = 1.04$ ) with an acetylation level of 19 mole % as determined by <sup>1</sup>H NMR spectroscopy analysis (Figure below) served as substrate for the synthesis of the Go polymer. The introduction of the acetyl group causes two new resonances at  $\delta$  2.52 ppm (methyl protons of the acetyl group) and  $\delta$  7.59 ppm (phenyl protons ortho to the acetyl group).

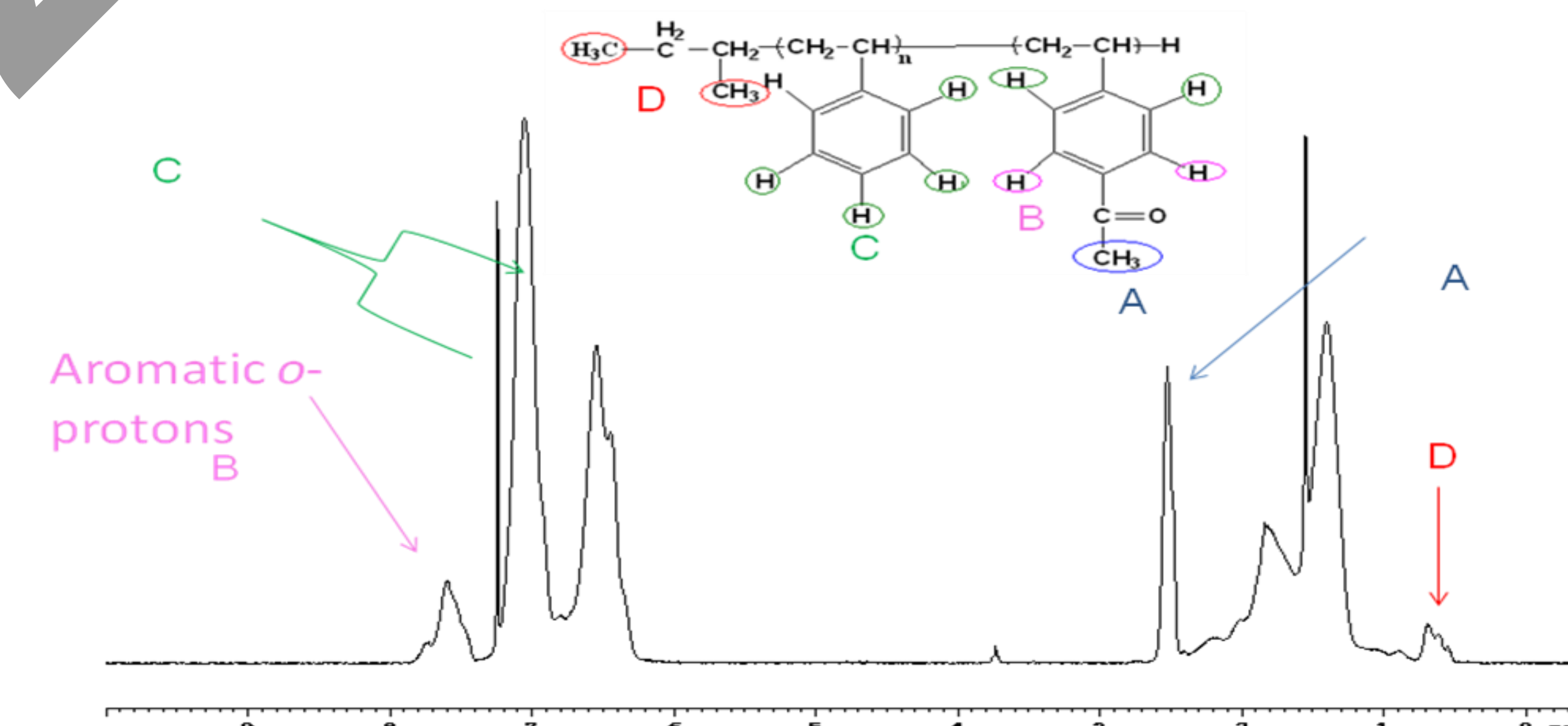
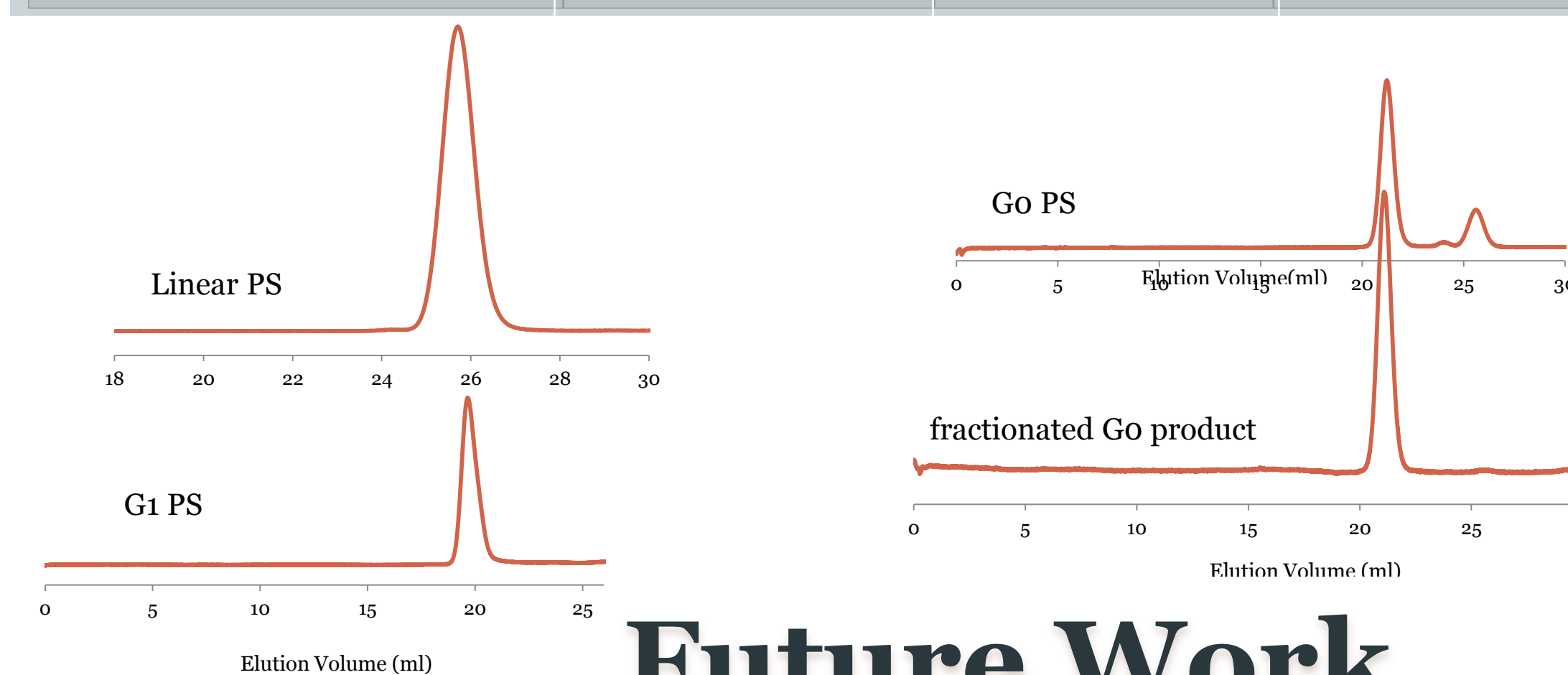


Table 1. Characteristics of Arborescent Polystyrene of Successive Generations

Polymer	Side chains		Graft polymer	
	$M_n$ (g/mol)	$M_w/M_n$	$M_n$ (g/mol)	$M_w/M_n$
Arborescent Go PS	5800	1.05	105,000	1.08
Arborescent G1 PS	4200	1.02	733,000	1.06
Arborescent Go-OH PS	6100	1.06	95,800	1.1
Arborescent G1-OH PS	4300	1.09	501,000	1.2



## Future Work

- Synthesis of glycidol acetal
- Growth of poly(glycidol acetal) chains from the hydroxyl-functionalized cores to form a shell

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