

Synthesis of arborescent polystyrene from epoxidized substrates

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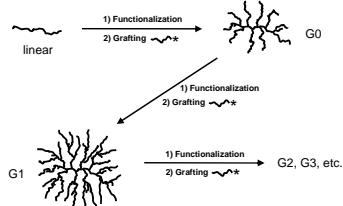
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Introduction

Arborescent polymers are a class of highly branched molecules belonging to the dendritic polymers family.¹ Prepared by ionic polymerization and grafting, they combine the features of dendrimers (generation-based scheme) and hyperbranched polymers (random nature of the grafting process). The *grafting onto* method has been mostly employed for the synthesis of arborescent polystyrene. This involves the introduction of coupling sites onto a polymeric substrate, followed by grafting with ionic polymer chains. Chloromethyl^{1(a)} and acetyl² functionalities have been previously used to prepare arborescent polystyrenes. With the goal to gain in practicality and efficiency, epoxide functionalities have now been tested for the synthesis of arborescent polystyrene.

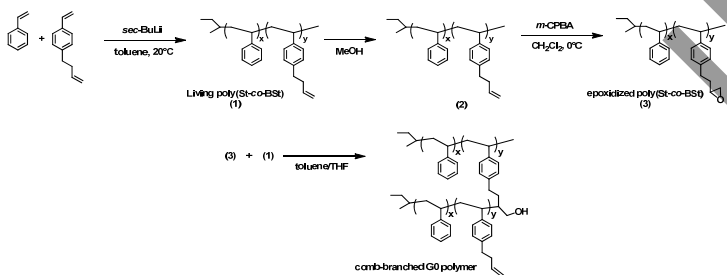
Arborescent polymers



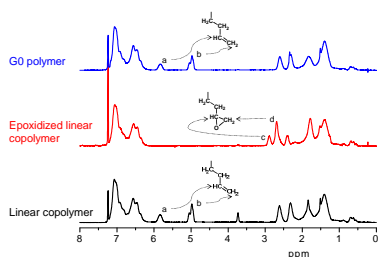
□ Grafting of ionic polymeric chains onto a polymer backbone functionalized with coupling sites

□ Highly branched polymers with a controllable architecture can be prepared

Grafting reaction



Synthesis of comb-branched (G0) polystyrene: ¹H NMR characterization



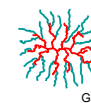
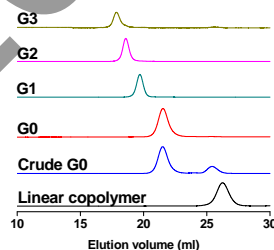
Synthesis of successive generations of graft polymers: Molecular weight characterization data and SEC curves



Series 1: Poly(st-co-BSt) side-chains added in each grafting cycle

Sample	M_w (SC) ^b	Grafting yield (%) ^c	M_w/M_n ^d	$10^{-3} M_w$ (SEC) ^e	$10^{-3} M_w$ (TD) ^d	f_w^f
G0	4.5	76	1.07	37	62	14
G1	4.9	62	1.05	131	473	84
G2	4.9	39	1.03	306	2,920	499
G3	4.9	25	1.02	602	10,190	1484

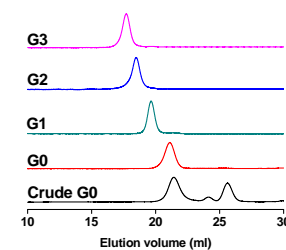
^a Linear substrate with $M_w = 4000$ and $M_w/M_n = 1.05$ used for the preparation of the G0 polymer; all reactions used a living end : epoxide ratio = 1, 4/1 v/v toluene/THF solvent mixtures, and a 25% epoxidation level
^b Absolute molecular weight of the side-chains
^c Grafting yield from relative peak areas
^d Absolute values from Triple Detection (TD)
^e Apparent values from SEC analysis with a refractometer detector and a linear polystyrene standards calibration curve
^f Number of side-chains added in the last grafting reaction



Series 2: PS side-chains added in the last grafting cycle

Sample	M_w (SC) ^b	Grafting yield (%) ^c	M_w/M_n ^d	$10^{-3} M_w$ (SEC) ^e	$10^{-3} M_w$ (TD) ^d	f_w^f
G0	5.6	63	1.15	45	65	11
G1	5.6	21	1.12	134	395	69
G2	4.7	26	1.05	415	1,800	282
G3	4.4	6	1.07	762	9,470	1783

^a Linear substrate with $M_w = 4000$ and $M_w/M_n = 1.05$ used for the preparation of the G0 polymer; all reactions used a living end : epoxide ratio = 1, 4/1 v/v toluene/THF solvent mixtures, and a 25% epoxidation level
^b Absolute molecular weight of the side-chains
^c Grafting yield from relative peak areas
^d Absolute values from Triple Detection (TD)
^e Apparent values from SEC analysis with a refractometer detector and a linear polystyrene standards calibration curve
^f Number of side-chains added in the last grafting reaction

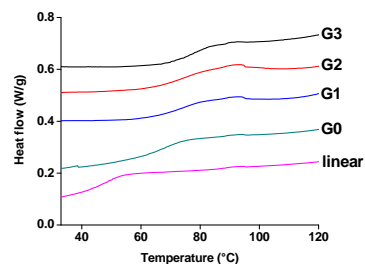


- Non-grafted side chains were easily removed by precipitation fractionation.
- The molecular weight distribution of the arborescent polymers is monomodal and narrow
- They have a compact structure as demonstrated by $M_w^{TD} > M_w^{SEC}$

Thermal analysis



Series 1



- Increase in T_g with increase in branching functionality
- Broad transition due to sample heterogeneity
- Lower T_g for copolymers with poly(st-co-BSt) side-chains than for polymers with pure PS side chains: Strong plasticizing effect of the butenyl substituents

Conclusions

- The epoxide functionality is suitable as a coupling site for the synthesis of arborescent polystyrene
- 2 series of arborescent polymers up to G3 have been prepared
- Narrow molecular weight distribution, controllable branch size

References

- (a) Gauthier, M.; Möller, M. *Macromolecules* **1991**, *24*, 4548; (b) Teertstra, S. J.; Gauthier, M. *Prog. Polym. Sci.* **2004**, *29*, 277.
- Li, J.; Gauthier, M. *Macromolecules* **2001**, *34*, 8918.