

Synthesis of Arborescent Polybutadiene

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Arborescent polymers are characterized by a tree-like architecture and a high branching functionality. This type of polymer can be synthesized by different techniques, but the ‘grafting onto’ method is attractive because it provides good control over the molecular weight of the graft polymer and the side-chains used as building blocks. This method was applied to the synthesis of arborescent polybutadienes, using cycles of epoxidation and anionic grafting reactions. The research focused on the optimization of the grafting yield. Additives useful as reactivity modifiers such as N,N,N',N'-tetramethylethylenediamine (TMEDA, a Lewis base) and Lewis acids were investigated to increase the yield of the grafting reaction. The influence of solvent polarity on the grafting yield was also examined. Preliminary results obtained show that the grafting reaction is successful on the basis of ^1H NMR spectroscopy and gel permeation chromatography analysis, and is sensitive to reaction parameters such as the substitution level of the epoxidized substrate and the presence of additives. Additionally, extended reaction times slightly increased the grafting yield.

Arborescent polymers were first synthesized by a ‘grafting onto’ method. This scheme starts from a linear polymer substrate that is functionalized with coupling sites. These functional groups are then reacted with living ionic polymers to yield a comb-branched polymer, also called a generation zero (G0) arborescent polymer, as represented in Figure 1. In the next step, the G0 polymer is further functionalized with coupling sites to serve as substrate for the preparation of an arborescent polymer of the first generation (G1). This represents the first generation of graft polymer with a dendritic (multi-level) branched architecture. Subsequent coupling reactions lead to arborescent polymers of generations G2, G3, etc.

This method does not provide very strict control over the polymer architecture, because the grafting sites are randomly distributed on the substrate. Ionic polymerization techniques do provide control over the molecular weight distribution (MWD) of the side-chains, however, and lead to arborescent polymer structures of uniform size. The multi-step sequence of Figure 1 is

best achieved if the grafting reaction proceeds in high yield and side reactions are minimized in the coupling reaction.

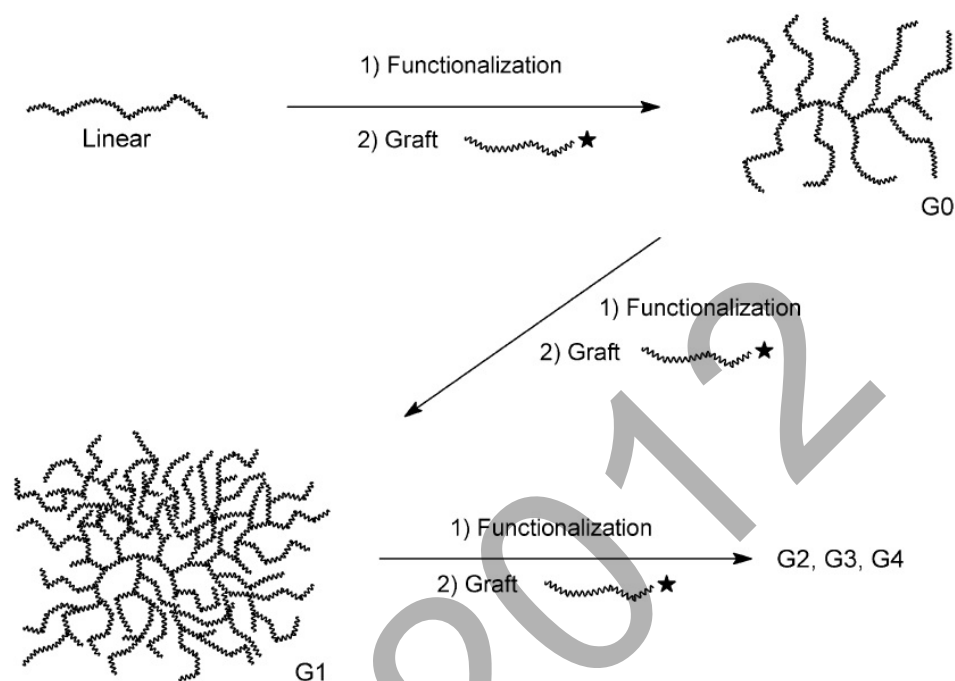


Figure 1. General 'grafting onto' scheme for the synthesis of dendrigraft polymers

The objective of the project is to synthesize arborescent polybutadienes while optimizing the grafting yield. Linear polybutadiene was successfully synthesized by anionic polymerization, by initiation with *sec*-Butyllithium in cyclohexane. The linear polymer had a number-average molecular weight $M_n=5000$ and a high 1,4-microstructure content (~94%). This type of microstructure can be functionalized by epoxidation to introduce coupling sites randomly on the polymer chain. Substitution levels above ~30 mol% lead to decreased solubility of the substrate in cyclohexane, however, and lower grafting yields as compared to substrates with 20-25 mol% substitution.

Different procedures were also examined to increase the grafting yield in the G0 polymer synthesis. Table 1 summarizes four methods examined, and the grafting yields achieved in each case after different reaction times. These data were obtained for different reactions in the G0 polymer synthesis from a ~25 mol% epoxidized substrate.

Table 1. The grafting yield attained by different procedures and reaction times

Reaction conditions	Grafting yield %	Grafting yield %
	1 Day	1 Week
Pure cyclohexane	70	74
Cyclohexane in the presence of TMEDA	73	75
Cyclohexane:THF 3:1 mixture	78	80
Cyclohexane:THF 3:1 mixture, with LiBr 6:1 ratio LiBr:living ends	82	85

The grafting yield for the G1 and G2 polymers was also optimized. Based on the grafting yield obtained from a 1:1 molar ratio of coupling sites and living chains after one week, the amount of substrate was increased to enhance grafting. The modified ratios were calculated theoretically to reach 100% grafting yield on the basis of the results obtained using a 1:1 coupling site : living end ratio, and thus depend on the generation number (Table 2).

Table 2. Influence of the molar ratio of coupling sites : living ends on the grafting yield

ratios	G0	G1	G2
1 : 1	85	80	78
1.17 : 1	87	—	—
1.25 : 1	—	84	—
1.28 : 1	—	—	81

References:

- Tomalia D.A., Fréchet J.M.J. In *Dendrimers and Other Dendritic Polymers*, Fréchet J.M.J., Tomalia D.A., editors. Wiley: New York, 2001. p 14.
- Tomalia D.A., Naylor A.M., Goddard III W.A. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 138-75.
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Synthesis of Arborescent Polybutadiene

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Presented by *Ala Alturk*

Advised by Prof. Mario Gauthier

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Outline







1. Introduction
2. Objectives
3. Experimental Procedures and Results
4. Conclusions
5. Future Work
6. Acknowledgements

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1 - Introduction

- Synthetic polymers can be divided on the basis of their molecular architecture:

I. Linear	II. Cross-linked	III. Branched	IV. Dendritic
			<div style="display: flex; justify-content: space-around;"> <div style="text-align: center;">(a)  Random Hyperbranched</div> <div style="text-align: center;">(b)  Dendrigrafts</div> <div style="text-align: center;">(c)  Dendrimers</div> </div>

↑
This Project

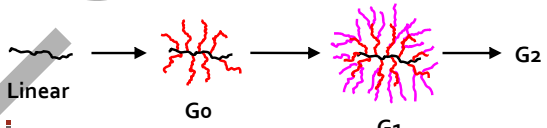
□ Tomalia, D. A., and Fréchet, J. M. J., *J. Polym. Sci. Part A: Polym. Chem.* **2002**, 40, 2719.

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1.1 Dendrigraft (Arborescent) Polymers

- Arborescent = tree like
- Derived from successive grafting reactions



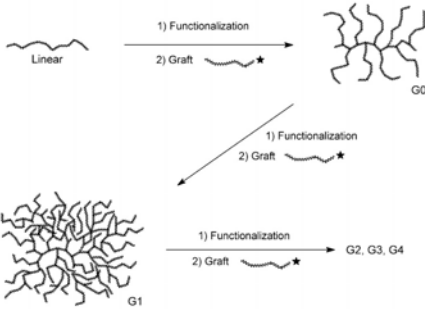
Linear → G₀ → G₁ → G₂

- Generation-based scheme, geometric increase in
 - M_n (number-average molecular weight)
 - f_n (number-average branching functionality)
- Narrow size distribution

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1.2 'Grafting onto' method



□ Steven J. Teertstra, Mario Gauthier, *Prog. Polym. Sci.* **2004**, 29, 277.

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2 - Objectives

- 1) Synthesis reported before, but not enough information provided and reaction not systematically optimized
- 2) Synthesize arborescent polymers from polybutadiene building blocks (G₀, G₁ and G₂)
- 3) Optimize the reaction for low molecular weight side-chains ($M_n = 5000$)
- 4) Influence of substrate substitution level on grafting (G₀)
- 5) Optimize grafting through different reaction procedures
- 6) Investigate the optimal ratio of side chains and coupling sites (G₀, G₁ and G₂)
- 7) Influence of reaction time on grafting yield

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2.1 Synthesis of Arborescent Polybutadiene

$$\text{CH}_2=\text{CH}=\text{CH}-\text{CH}_2 \xrightarrow[\text{Cyclohexane}]{\text{sec-BuLi}} \text{H}_3\text{C}-\text{CH}(\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2)_n-\text{Li}^+$$

$$\xrightarrow{\text{Methanol/HCl}} \text{H}_3\text{C}-\text{CH}(\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2)_n-\text{H}$$

- Anionic polymerization of 1,3-butadiene initiated with *sec*-BuLi in cyclohexane at room temperature
 - High 1,4-microstructure content (~95%)

2.1 Synthesis of Arborescent Polybutadiene (Cont'd)

- Partial epoxidation of 1,4-butadiene units
- Coupling with polybutadienyllithium side-chains
- Epoxidation and grafting repeated to obtain upper generation (G1, G2...) arborescent polymers

2.2 Optimization of the Grafting Yield

$$G_y = \frac{A_1}{A_1 + A_2} \times 100\%$$

- Fraction of side-chains attached to the substrate
- Sample purification (fractionation) simplified for higher grafting yields

Solvent Polarity

- Synthesis of arborescent polybutadiene reported in cyclohexane (non-polar solvent)
 - Zhang et al., *Macromolecules* **2009**, *42*, 5073
- Influence of solvent polarity and other reaction parameters not investigated

$$\text{wavy line}^{\ominus}\text{Li}^{\oplus} \xrightleftharpoons[\text{Cyclohexane}]{\text{THF}} \text{wavy line}^{\ominus} + \text{Li}^{\oplus}$$

Ion pairs (Low reactivity) vs. Free ions (High reactivity)

Reactivity Modifiers

- Synthesis in the presence of N,N,N',N'-tetramethylethylenediamine (TMEDA)
- Enhances chain end dissociation

$$\text{wavy line}^{\ominus}\text{Li}^{\oplus} \xrightleftharpoons[\text{Cyclohexane}]{\text{TMEDA}} \text{wavy line}^{\ominus} + \text{TMEDA}\cdot\text{Li}^{\oplus}$$

Ion pairs (Low reactivity) vs. Free ions (High reactivity)

- Complexing agent for lithium counterions

Reactivity Modifiers (Cont'd)

- Synthesis in the presence of LiBr in THF
- Suppresses chain end dissociation

$$\text{wavy line}^{\ominus}\text{Li}^{\oplus} \xrightleftharpoons[\text{LiBr}]{\text{THF}} \text{wavy line}^{\ominus} + \text{Li}^{\oplus}$$

Ion pairs (Low reactivity) vs. Free ions (High reactivity)

- Increases the reactivity of epoxide groups

3 – Experimental Procedures and Results

1. Synthesis of linear polybutadiene
2. Epoxidation of polybutadiene
3. Grafting reactions (G0, G1 and G2)
4. Reaction time influence

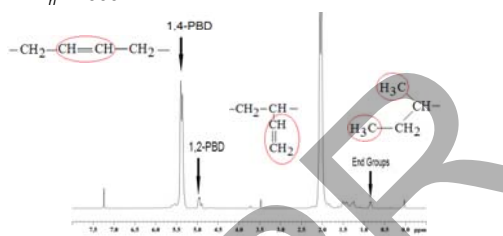
3.1 Synthesis of Linear Polybutadiene



- Monomer and solvent purification necessary
- Initiation by *sec*-butyllithium
- Polymerization in cyclohexane under N_2 , room temperature
- 'Living' polymer terminated with acidified methanol
- Product recovered by precipitation in methanol, dried under vacuum, stored at $-80\text{ }^\circ\text{C}$

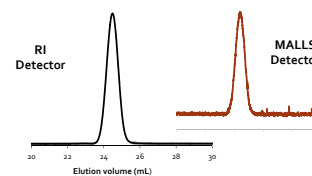
3.1 Synthesis of Linear Polybutadiene (Cont'd)

- ^1H NMR analysis:
 - Major microstructure: 95% 1,4-butadiene units
 - Minor microstructure: 5% 1,2-butadiene units
 - $M_n = 4900$



3.1 Synthesis of Linear Polybutadiene (Cont'd)

- GPC analysis (MALLS detector):
 - $M_n = 5000$
 - Polydispersity index PDI (M_w/M_n) = 1.05

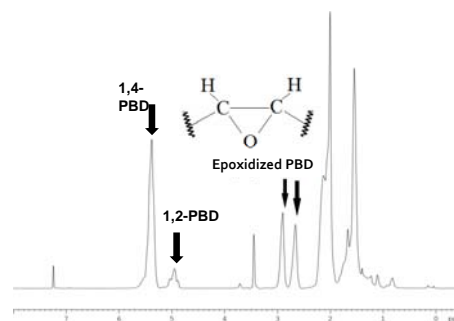


3.2 Epoxidation of Polybutadiene



- *m*-CPBA in dichloromethane (homogenous reaction)
- Epoxidation level easily controlled by stoichiometry, reaction time.
- Same technique applied for G0 and G1 epoxidation
- GPC analysis: PDI unchanged (1.05)
- Product analyzed by ^1H NMR spectroscopy

^1H NMR Analysis of Epoxidized Polybutadiene

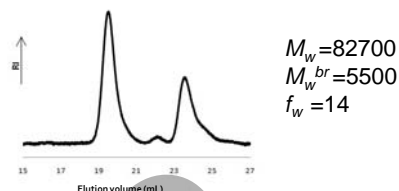


3.3 Grafting Reaction

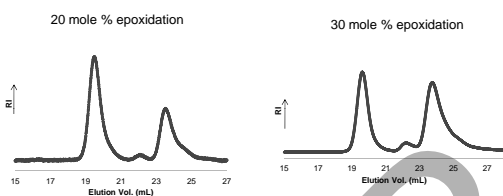
- Living polybutadiene chains synthesized by anionic polymerization in cyclohexane
- All reactions with 1:1 ratio of living ends : epoxide groups
- Grafting in pure cyclohexane
- Grafting in pure cyclohexane with TMEDA
- Grafting in mixture of cyclohexane and THF
- Grafting in mixture of cyclohexane and THF with LiBr

Grafting Reaction in Cyclohexane

- Grafting yield from GPC analysis: 63% when using a 20 mol% epoxidized substrate



Grafting Reaction: Influence of Epoxidation Level



- Substrate with higher epoxidation level (30 mol%) led to lower grafting yield due to steric crowding

Grafting Reaction: G0

- 24-26 mole % epoxidation for the linear substrate
- 1:1 ratio coupling sites : living ends
- Short vs. long reaction time

Reaction conditions	Grafting yield % 1 Day	Grafting yield % 1 Week
Pure cyclohexane	70	74
Cyclohexane with TMEDA, 6:1 ratio TMEDA:living ends	73	75
3:1 Mixture of cyclohexane:THF	78	80
3:1 Mixture cyclohexane:THF, with LiBr 6:1 ratio LiBr:living ends	82	85

Grafting Reaction: G0, G1 and G2

- Optimized the ratio of coupling sites : living ends based on one week reaction time
- Grafting reaction in mixture of 3:1 cyclohexane : THF with 6:1 ratio LiBr : living ends

	G0	G1	G2
1:1	85	80	78
1.17:1	87		
1.25:1		84	
1.28:1			81

4 - Conclusions

- Conditions reported in the literature for the synthesis of arborescent polybutadiene are not optimal
 - Very low M_n side chains used
 - No systematic optimization
- Lower epoxidation level substrates (~25 mole%) are preferable
- A mixture of cyclohexane and THF in the presence of LiBr is preferred for the grafting reaction
- The grafting yield increased slightly with time (~2-4 % from 1 day to 1 week)
- The grafting yield only increased slightly when using a larger excess of substrate

5 - Future Work

- Investigate the synthesis of the G3 polymer under the same conditions
- Re-investigate the synthesis of G0-G3 for longer side-chains ($M_n = 30K, 50K$ or $80K$)
- Reaction time and conditions must be re-examined for long side-chains
- Investigate the rheological properties of the materials prepared

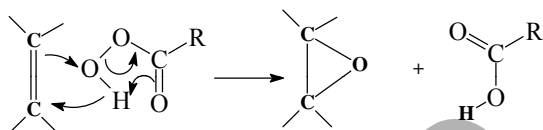
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5 - Acknowledgements

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 - Taibah University, Madina, Saudi Arabia
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Epoxidation Mechanism



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Calculations

- x : mole fraction of 1,2 PBD units
- x' : mole fraction of 1,4 PBD units = $(1-x)$

$$\frac{3x}{(1-x)^2} = \frac{I_{1,2-PBD}}{I_{1,4-PBD}}$$

- y : Epoxidation level (mole fraction of epoxydized 1,4 PBD units)

$$\frac{2y}{2x' - 2y} = \frac{I_{\text{Epoxydized PBD}}}{I_{1,4-PBD}}$$

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Calculations (cont'd)

- Degree of Polymerization

$$\frac{I_{1,4-PBD} + I_{1,2-PBD}}{2+3} = \frac{I_{\text{End group}}}{6}$$

- f_w : weight- average branching functionality

$$f_w^{(G)} = \frac{M_w(G) - M_w(G-1)}{M_w^{br}}$$

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