Arborescent poly(ε-caprolactone) copolymers: Synthesis and characterization

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Introduction

Arborescent polymers are a class of highly branched molecules belonging to the dendritic polymers family. Poly(ε-caprolactone) is a biodegradable, biocompatible material that has found multiple applications in the medical and pharmaceutical fields. Highly branched polycaprolactones may have new interesting physical properties as compared to traditional PCL, which among others degrades very slowly due to its high degree of crystallinity. The goal of this project is to synthesize and characterize polyisoprene-*graft*-poly(ε-caprolactone) copolymers with a dendritic architecture by a combination of addition and ring-opening polymerization. The molecules will have a polyisoprene core and a poly(ε-caprolactone) shell.
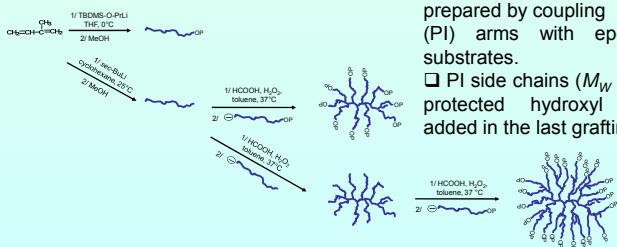
Arborescent polymers
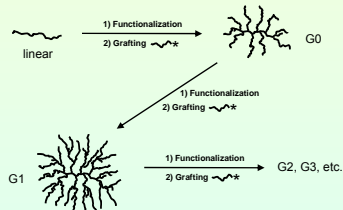
❑ Grafting of ionic polymeric chains onto a polymer backbone functionalized with coupling sites.
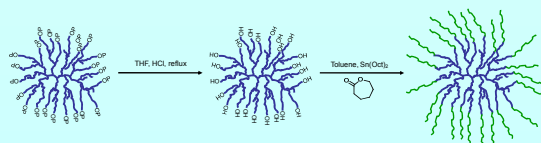❑ Highly branched polymers with controllable architecture can be produced.

Synthesis

The core: arborescent polyisoprene

❑ Arborescent isoprene polymers prepared by coupling polyisoprene (PI) arms with epoxidized PI substrates.
❑ PI side chains (M_W = 2.5 K) with protected hydroxyl end-groups added in the last grafting cycle

Arborescent poly(ε-caprolactone)

❑ Protecting groups at side chain ends removed under acidic conditions.
❑ The ring opening polymerization (ROP) of ε-caprolactone is initiated from the hydroxyl groups.

Characterization

Polyisoprene core[a,b]

Sample	Side chains		Graft homopolymer			
	M_w^{TD}	PDI	M_w^{SEC}	M_w^{TD}	PDI	Number of branches f_w
PI(linear)-5K	5000	1.18	-	-	-	-
PI(G0)-2.5K [c]	2100	1.17	37500	39000	1.07	16
PI(G1)-2.5K [d]	2800	1.23	197000	491000	1.09	144

[a] M_w^{TD} determined by Triple detection method
[b] M_w^{SEC} determined with a PS standards calibration curve
[c] PI (M_w 5400, PDI 1.05, epoxidation level 23%) used as a linear precursor
[d] PI-G0 (M_w 87 000, PDI 1.10, epoxidation level 26%) used as a G0 grafting precursor

❑ Three structures with different branching levels prepared with controlled architectures.
❑ The graft homopolymers have a compact structure as demonstrated by $M_w^{TD} > M_w^{SEC}$

Arborescent poly(ε-caprolactone)

| Substrates	Arborescent poly(ε -CL)				
	M_w (SEC)	M_w/M_n	poly(ε –CL) content[e] (mol %)	Thermal properties	
				T_c (°C)	ΔH_c (J/g)
PI(linear)-5K	12 400	1.18	29	49.6	40.0
	16 400	1.10	38	54.1	46.1
	30 700	1.12	65	55.1	59.8
PI(G0)-2.5K	70 300	1.19	26	53.0	1.6
	76 800	1.10	33	n.d.	n.d.
	220 400	1.09	76	55.4	48.3
PI(G1)-2.5K	417 200	1.08	59	54.6	34.5
	563 300	1.15	60	54.5	43.3

[e] determined by ^{1}H NMR

❑ After removal of the protecting group at the side chain ends, the isoprene homopolymers served as macroinitiators for the ROP of ε-CL.
❑ The linear sample was used to ascertain the living character of the ROP.
❑ Copolymers with different poly(ε-CL) content prepared.
❑ The materials are semicrystalline as determined by DSC.

^{1}H NMR spectroscopy
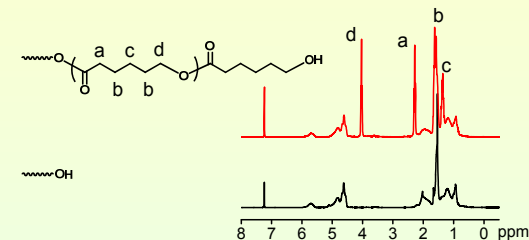
❑ Characteristic signals for ε-CL repeating units appear after the ROP of ε-CL.

GPC analysis
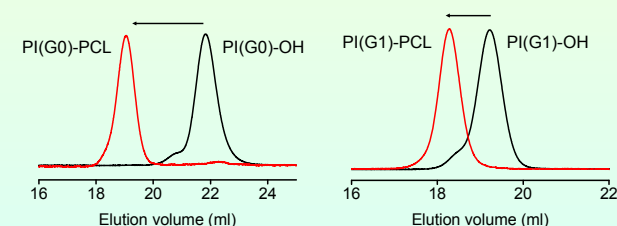
❑ Peak shift to higher elution volumes indicates that the G0 and G1 polyisoprene substrates are effective macroinitiators for the ROP of ε-CL
❑ Low molecular weight PεCL contaminants removed by semi-prep GPC
❑ Low polydispersity maintained after the ROP of ε-CL.

Conclusions

❑ Highly branched hydroxytelechelic polyisoprenes with narrow molecular weight distribution and controllable branch size successfully synthesized.
❑ Effective as substrates for the Sn(Oct)₂-catalyzed Ring Opening Polymerization of ε-CL.
❑ Graft copolymers with low polydispersity can be produced.
❑ Rate of polymerization of ε-CL decreases as branching functionality (generation number) increases.

References

[1] (a) Gauthier, M.; Möller, M. *Macromolecules* **1991**, *24*, 4548; (b) Teertstra, S. J.; Gauthier, M. *Prog. Polym. Sci.* **2004**, *29*, 277.
[2] Yuan, Z.; Gauthier M. *Macromolecules* **2005**, *38,* 4124.