A Divergent Synthesis of Polyurethane Dendrimers

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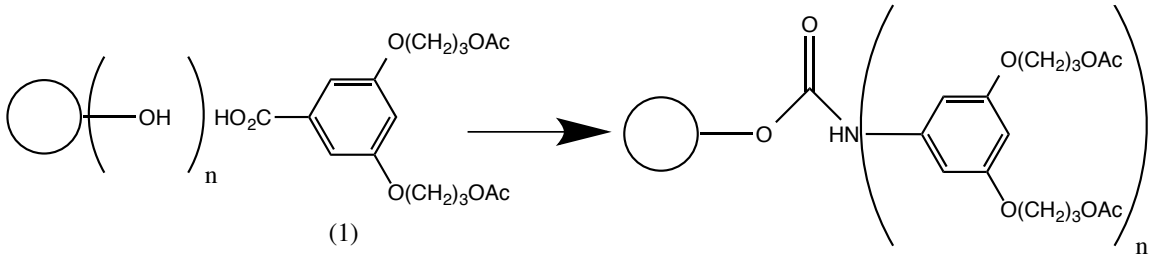
Previous work

- Convergent synthesis of polyurethane dendrimers using diphenylphosphoryl azide, alcohols and carboxylic acids
- Development of a polymer bound version of DPPA
- Richard T. Taylor and Uraiwan Puapaiboon, Tetrahedron Letters 39 (1998) 8005-8008
- Yuhua Lu and Richard T. Taylor, Tetrahedron. Lett., 2003, 44, 9267-9269.

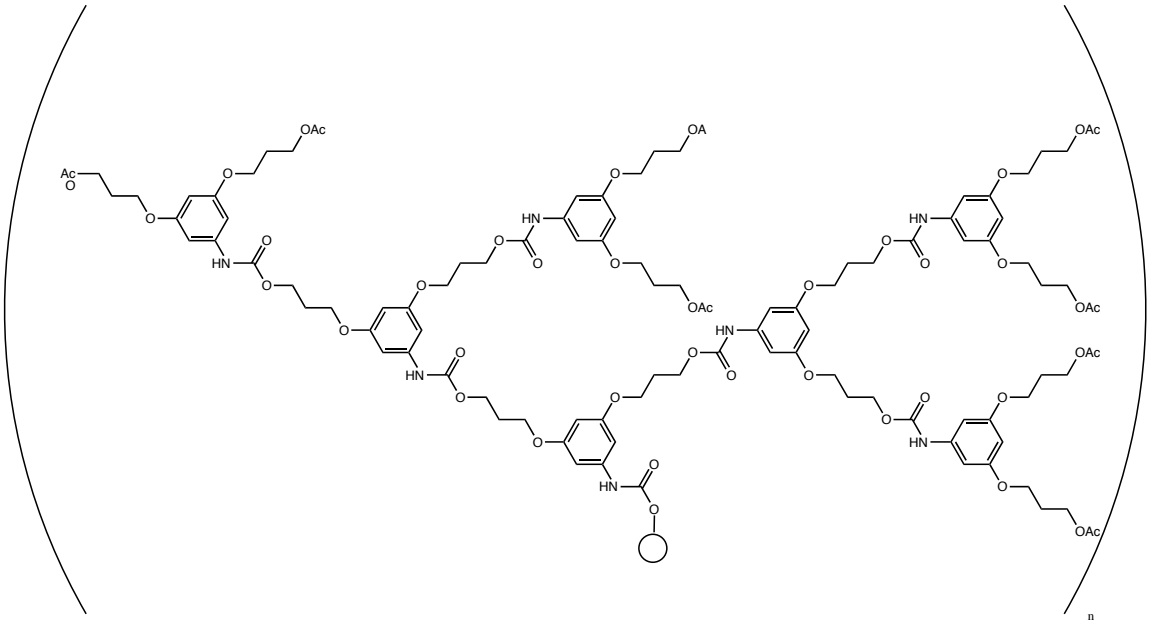
Present objective

- Use a similar strategy to prepare polyurethane dendrimers by starting with polyol core molecules
- Use polymer bound DPPA and a carboxylate with protected alcohols for each generation

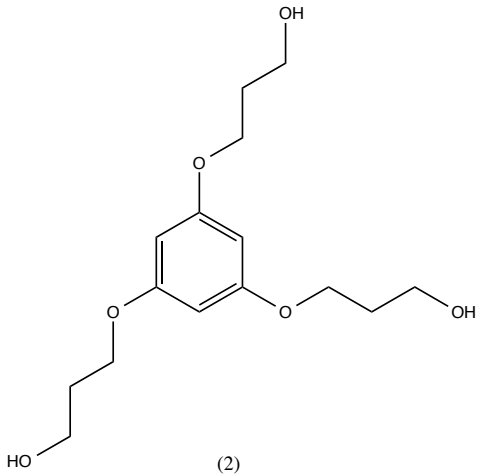
General strategy



General – three generations



Cores polyols and results



(2)

	Generation 1	Generation 2	Generation 3
Yield	83%	69%	57%
MALDI-TOF	Expt (calc)	Expt (calc)	Expt (calc)
M + Na	1376.45 (1376.54)	3231.98 (3231.27)	6940.70 (6940.72)
M + K	1392.43 (1392.52)	3247.96 (3247.24)	6957.19 (6956.70)

Flexible diols – diethylene and triethylene glycol

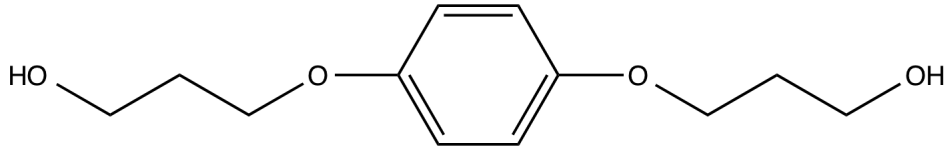
Diethylene glycol core

	Generation 1	Generation 2	Generation 3
Yield	100%	87%	64%
MALDI-TOF	Expt (calc)	Expt (calc)	Expt (calc)
M + Na	831.35 (831.32)	2067.47 (2067.80)	4542.09 (4542.78)
M + K	847.31 (847.29)	2083.63 (2083.78)	4558.94 (4558.75)

Triethylene glycol core

	Generation 1	Generation 2	Generation 3
Yield	87%	72%	60%
MALDI-TOF	Expt (calc)	Expt (calc)	Expt (calc)
M + Na	875.53 (875.34)	2111.80 (2111.83)	4584.51 (4584.80)
M + K	891.39 (891.32)	2127.77 (2127.80)	4600.35 (4600.77)

More rigid core



(3)

	Generation 1	Generation 2	Generation 3
Yield	75%	69%	54%
MALDI-TOF	Expt (calc)	Expt (calc)	Expt (calc)
M + Na	951.51 (951.37)	2187.60 (2187.86)	4660.75 (4660.83)
M + K	967.46 (967.35)	2203.60 (2203.83)	4676.76 (4676.80)

Conclusion

- The DPPA strategy is an effective way to build polyurethane dendrimers in a divergent strategy
- The polymeric version of DPPA is somewhat more effective in the reaction
- Further work and more cores and examination of groups at the periphery
- Acknowedgement – Miami University