STUDY OF THE SYNTHESIS OF POLYALDEHYDES VIA ORGANOCATALYTIC ANIONIC POLYMERIZATION

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ABSTRACT

Polyaldehydes (PA), in particular poly(phthalaldehyde) (PPA), are an interesting class of selfimmolative polymers.¹ PAs have very low ceiling temperatures (T_c); e.g. for PPA, $T_c = -40$ °C, hence PAs have to be stabilized by end-capping to be stable above room temperature and enable one to process the polymer materials.^{2,3}. PAs depolymerize completely in response to a specific stimulus, either chemical or physical, which removes the end-caps.¹ Due to this PAs are interesting responsive materials, with a range of applications, including as responsive materials.^{1,4} PAs can be synthesized via anionic, cationic and coordinative mechanisms.⁵⁻⁷ Strategies which utilize organometallic catalysts are least popular because of possible contamination from residual metal ions. Recent studies utilizing metal-free phosphazene bases, have been successful, enabling access to PAs, with good agreement between theoretical and experimental molar masses.^{2,5} However, *D* values are often high,² and specialized conditions, e.g. use of glove box, are always required. There is a need therefore to further enhance the appeal of these materials by elaborating simple synthesis strategies for accessing PAs. Towards this goal we have carried out a detailed study, on the synthesis of the PAs, by anionic polymerization, using a range of organic superbases,^{8,9} assessing the effect of each base on predictability of molar mass, *D*, as well as the effects of solvent polarity and monomer concentration, on the polymerization.

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<u>References</u>:

- ²DiLauro, A. M.; Robbins, J. S.; Phillips, S. T. *Macromolecules* **2013**, *46*, 2963.
- ³Esser-Kahn, A. P.; Odom, S. A.; Sottos, N. R.; White, S. R.; Moore, J. S. Macromolecules 2011, 44, 5539.
- ⁴DiLauro, A. M.; Zhang, H.; Baker, M. S.; Wong, F.; Sen, A.; Phillips, S. T. *Macromolecules* **2013**, *46*, 7257.
- ⁵De Winter, J.; Dove, A. P.; Knoll, A.; Gerbaux, P.; Dubois, P.; Coulembier, O. Polym. Chem. 2014, 5, 706.
- ⁶Ito, H.; Schwalm, R. J. Electrochem. Soc. 1989, 136, 241.
- ⁷Yasuda, H.; Tani, H. Macromolecules 1973, 6, 303.
- ⁸Boileau, S.; Illy, N. Prog. Polym. Sci. 2011, 36, 1132.
- ⁹Kaljurand, I.; Kütt, A.; Sooväli, L.; Rodima, T.; Mäemets, V.; Leito, I.; Koppel, I. A. J. Org. Chem. 2005, 70, 1019.

¹Peterson, G. I.; Larsen, M. B.; Boydston, A. J. Macromolecules 2012, 45, 7317.