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Scale up Batch Reaction of Precision Polymers

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U.S. DEPARTMENT OF ENERGY

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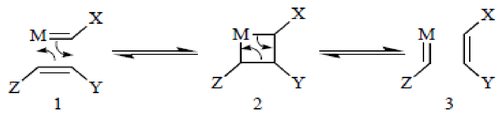
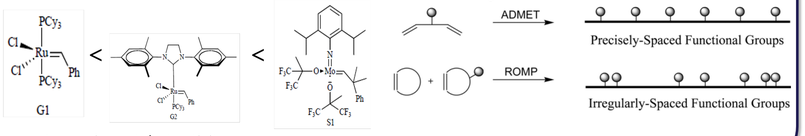
Introduction to ADMET



General mechanism of Olefin Metathesis

Olefin metathesis chemistry has been widely studied since the early 1960's by many oil companies and chemical industries such as Du Pont, Phillip's Petroleum, and Standard oil[1]Two types of metathesis have become popular, Ring Opening Metathesis Polymerization (ROMP) and Acyclic Diene Metathesis Polymerization (ADMET).

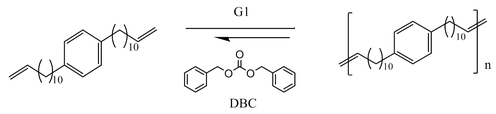
ADMET is a type of olefin metathesis which has the ability to form polymers from α,ω diene monomers, with evenly and precisely spaced functional groups along it's polymer backbone. This characteristic of ADMET is of interest to many material scientists because they can study the morphology of these polymers knowing that the functional group position can be predicted. As an ADMET polymerization is step growth in nature, it takes much longer time to achieve high conversion compared to ROMP. Also depicted is the mechanism for ROMP, which does not produce a precise polymer, but is chain growth in nature. Each type of metathesis uses a catalyst such as Grubbs (1st, 2nd, or 3rd generation), Schrock's catalyst as well as a few others based on the desired activity.



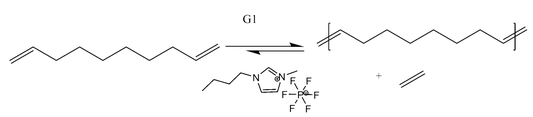
Increasing catalyst activity

Solvent Efficiency

Much of the ADMET polymerization has been done in bulk, with little research in useful solvents. This is because of the high vacuum conditions necessary to remove the ethylene formed from the forward equilibrium reaction. The removal of ethylene is an essential driving force to push these reactions to high conversion. The viscosity increases dramatically with degree of polymerization and has a limiting effect on the polymerization, as ethylene can no longer be removed efficiently, even under high vacuum.

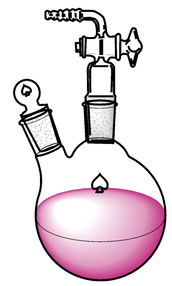


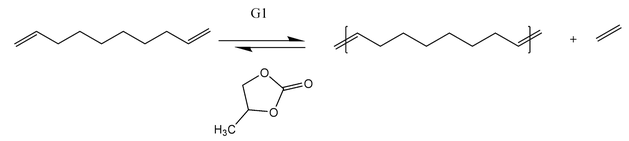
Expensive solvents such as ionic liquids,1-butyl-3-methyl imidazolium hexafluorophosphate ([bmim]PF6)[2], synthesized dibenzyl carbonate (DBC)[3] and 1,2 dichlorobenzene[4] prove to increase the degree of polymerization greatly. This is due to their elevated boiling points which is desired in a low vacuum environment. Sauty *et.al*. reports in increase in average molecular weight from 20,000 to 65,000 g/mol from bulk to solvent conditions using synthesized DCB of poly(p-phenylene alkylene)s. Using a cheap commercial, non hazardous, high boiling solvent within the reaction can improve the degree of polymerization, and be used in large scale reactions to produce precision polymers.



Experimental

A cheap and well studied monomer 1,9 decadiene, was used to study if propylene carbonate could be used as a solvent in a large batch reaction utilizing ADMET. Grubb's 1st generation catalyst was used because of its lower activity, resulting in low isomerization. Intermittent vacuum, followed by full vacuum of 100 mTorr was employed on a 5:1 solvent to monomer ratio, after the addition of 10 wt% G1 catalyst at 45°C.

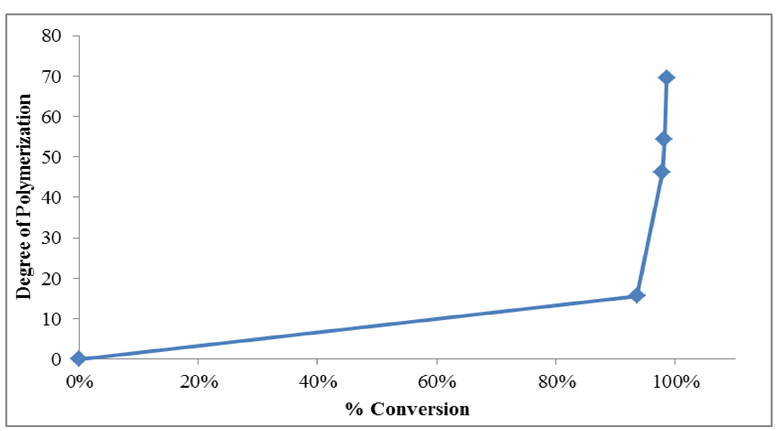


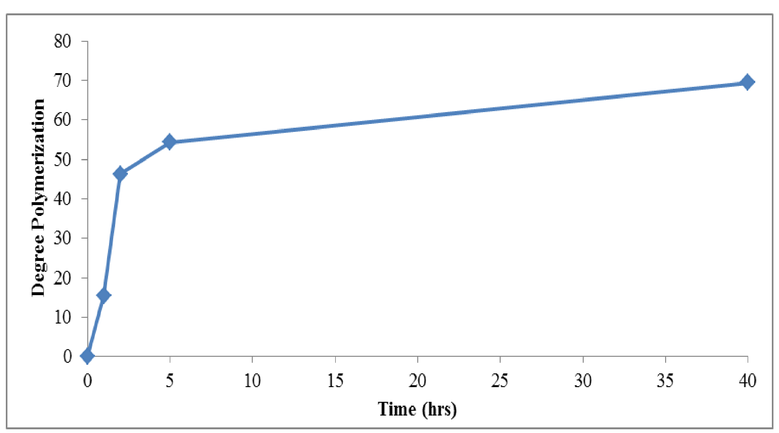


. The reaction scheme and mechanism is illustrated above, with a total volume of 30 mL. 250 µL aliquots were taken from the reaction, to study how the conversion changed with time. The figures within the results section show the degree of polymerization as a function of time, as well as percent conversion as a function of degree of polymerization. A 98 % conversion is achieved, but limited; due to the low solubility after 5 hours.

Results of Experiment

Aliquot	Time (hrs)	Mn (g/mol)	PDI	DP	% Conversion
1	1	2150	2.22	15.6	93.6%
2	2	6400	2.39	46.3	97.8%
3	5	7500	2.03	54.2	98.2%
4	40	9600	3.1	69.4	98.6%





Conclusion and Future Work

- GPC analysis of the large scale polymerization of the 1,9 decadiene in propylene carbonate gave a M_n = 96,000 g/mol after about 40 hours under high vacuum.
- The polymerization was limited by the solubility of the polymer.
- The large scale polymerization was successful yielding a high conversion, and there fore a high number average molecular weight poly(1,9 decadiene).
- The use of propylene carbonate did not work to keep the polymer in solution during synthesis.
- Future work will include experiments using Diethyl phthalate as a solvent due to its plasticizing abilities and very high boiling point of 295°C.
- Using other Grubbs catalysts will also be explored.

References:

[1] Simocko, Chester, Pascale Atallah, and Kenneth Wagener. "A Brief Examination of the Latest ADMET Chemistry." *Current Organic Chemistry COC* 17.22 (2013): 2749-763. Web. 10 Oct. 2015.

[2] Simocko, Chester, Yong Yang, Timothy M. Swager, and Kenneth B. Wagener. "Metathesis Step-Growth Polymerizations in Ionic Liquid." *ACS Macro Lett. ACS Macro Letters* 2.12 (2013): 1061-064. Web. 10 Oct. 2015.

[3]] Sauty, Nicolas F., Lucas Caire Da Silva, Caitlyn Gallagher, Robert Graf, and Kenneth B. Wagener. "Unveiling the Hyperbolic Thermal Behaviour of Poly(p-phenylene Alkylene)s." *Polym. Chem.* 6.33 (2015): 6073-082. Web. 20 Oct. 2015.

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[5] Baughman, Travis W., Christopher D. Chan, Karen I. Winey, and Kenneth B. Wagener. "Synthesis and Morphology of Well-Defined Poly(ethylene- Co -acrylic Acid) Copolymers." *Macromolecules* 40.18 (2007): 6564-571. Web. 10 Oct. 2015.

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