Effects of Various Leaving Groups on Chain Growth Condensation Mechanism by Computational Methods

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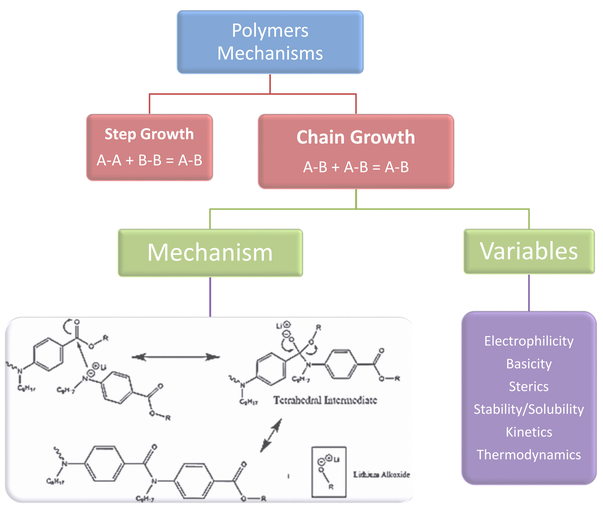
Abstract

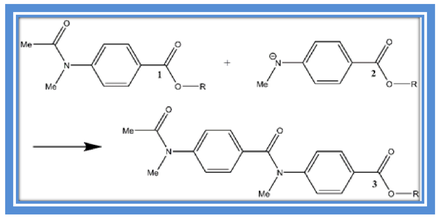
Optimizing polymer mechanisms is a popular area of study and one such mechanism that is still not fully understood is the chain growth condensation. A systematic study of the behavior of different leaving groups on an ester-based monomer was performed for the chain-growth condensation of N-octyl benzamide. Quantum mechanical calculations were performed to determine the energies and charges of each step of the reaction for each of the leaving groups, ranging from extremely electron withdrawing to extremely electron donating. The leaving groups are phenyl oxides with functional groups that were placed in both the para and meta positions on the ring. In both the meta and para positions the functional groups that are electron withdrawing tend to increase reactivity with the exception of the halogens. The halogens tendency to be electron donating through resonance makes them slightly more reactive in the meta position.

Background



Computational Methods

- Optimizations and frequency calculations performed with a 2006 Minnesota functional (M06-2X) and 6-31g(d) basis sets level of theory
- Implicit solvation using a polarizable continuum model (iefpcm) in a tetrahydrofuran solvent
- Gausian09 Software



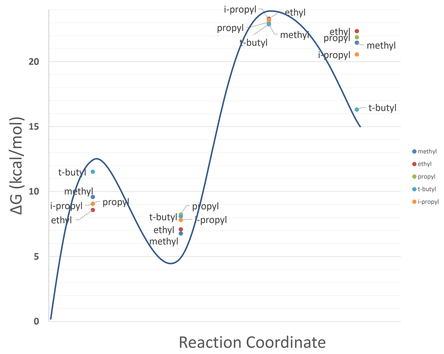
Alkoxides

Alkoxides are bad leaving groups due to:

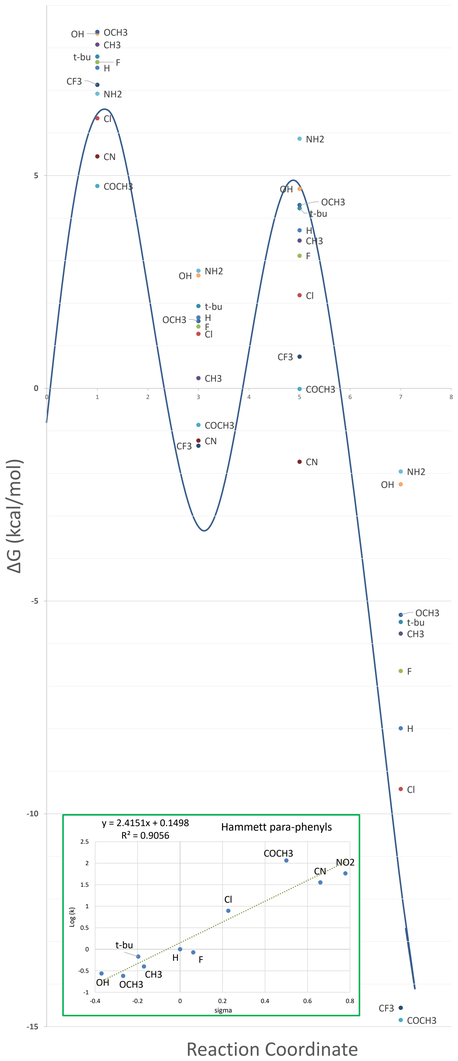
- **Poor solubility during polymerization**
  - N-alkyl alkoxides insoluble
  - Branched alkoxides soluble
- **Steric hinderance**
  - Branched alkoxides hinder Td formation
  - Prevents polymerization
- **Basicity of leaving group**
  - High pK_a of conjugate acid hinders aminolysis
  - Prevents polymerization from occurring

Table X: pKa values of conjugate acids corresponding to the lithium alkoxides produced as by-products.

Conjugate Acid	pKa[a] @25°C
tert-butanol	19.2
isopropanol	17.1
n-butanol	16.1
n-propanol	16.1
ethanol	16.0
methanol	15.5



PARA-phenoxides



Average Activation Energies		
	TS#1	TS#2
PARA	7.125	2.780
META	7.354	2.683

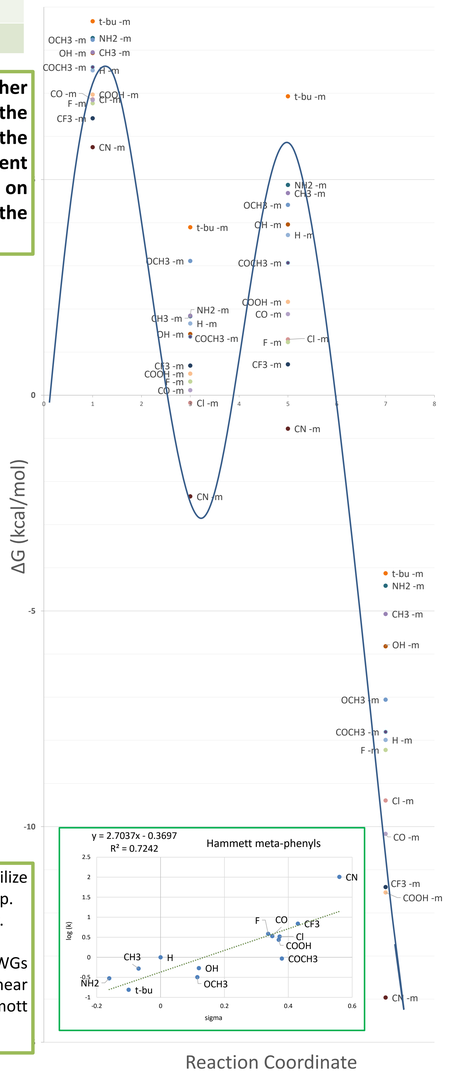
Standard deviation is higher for TS#2 than TS#1 due to the electronic nature of the leaving group substituent having a greater impact on decomposition of the intermediate.

Standard Deviations		
	TS#1	TS#2
PARA	1.180	2.273
META	0.815	2.222

Electron Donating
NH_2
OH
$NHCOCH_3$
$OCOCH_3$
CH_3
t-bu
H (no group)
Cl
F
CO
$COCH_3$
CF_3
CN
NO_2
Election Withdrawing

- EWGs tend to stabilize intermediate and leaving group.
- EDGs have the opposite effect.
- Rate of polymerizations for EWGs and EDGs have fairly linear correlation as shown in Hammott Plots.

META-phenoxides



Electrophilicity

Relative charge distribution and stabilization of the ester substituents effects both TS#1 and TS#2.

- EWGs increase Electrophilicity
- EDGs decrease Electrophilicity

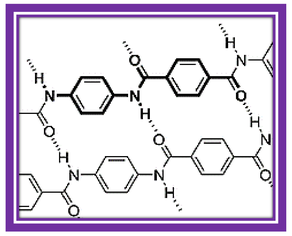
Reaction Coordinate	ATOM	para		meta			alkyl	
		coch3	OH	CN	t-bu	NH2	butyl	methyl
TS#1	**O**=C-O	-0.735	-0.755	-0.736	-0.752	-0.748	-0.804	-0.802
	O=**C**-O	0.813	0.817	0.815	0.816	0.818	0.815	0.813
	O=C-**O**	-0.581	-0.592	-0.583	-0.591	-0.590	-0.636	-0.636
Td Inter	**O**=C-O	-0.865	-0.876	-0.866	-0.878	-0.880	-0.902	-0.902
	O=**C**-O	0.760	0.758	0.760	0.760	0.761	0.763	0.762
	O=C-**O**	-0.626	-0.652	-0.632	-0.640	-0.634	-0.672	-0.674
TS#2	**O**=C-O	-0.801	-0.759	-0.796	-0.757	-0.761	-0.688	-0.682
	O=**C**-O	0.759	0.744	0.758	0.758	0.758	0.761	0.761
	O=C-**O**	-0.681	-0.763	-0.696	-0.753	-0.745	-0.954	-0.975

Conclusions and Future Work

1. **EWGs on the phenyl ring have lower reaction energetics and are favorable in both the para and meta positions.**
2. The energy required for the attack of the carbonyl is consistent for all the phenoxides and alkoxides.
3. Decomposition of the tetrahedral intermediate is shown to be the driving force for CGC polymerization.

Future work:

1. **Experimental chemists will synthesize** what were determined to be the ideal polymers for these specific applications.
2. Protecting groups will be studied to determine those that can easily be replaced with hydrogen t**o make Kevlar-like materials**.



References

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3. F. C. Prehn and S. G. Boyes, *Macromolecules*, 2015, **48**, 4269-4280.

Acknowledgments

Thank you to HPC at Mines for supercomputer resources, NSF for funding, the polymer REU program.