

Group Transfer Polymerization

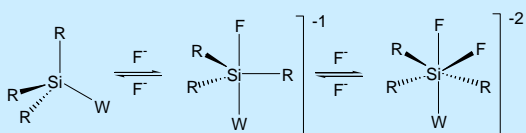
Concept
Getting to know your Silicon

	13 III A	14 IV A	15 V A	16 VI A	17 VII A	2 He 4.003
	5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
12 II B	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
2B	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90
						36 Kr 83.80

Group Transfer Polymerization

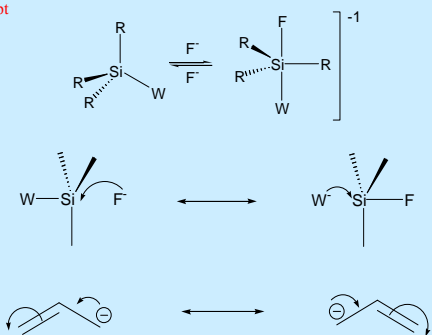
Concept

Getting to know your Silicon



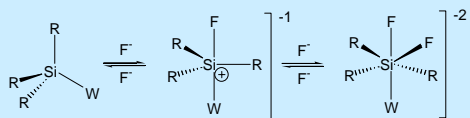
Group Transfer Polymerization

Concept



Group Transfer Polymerization

Concept

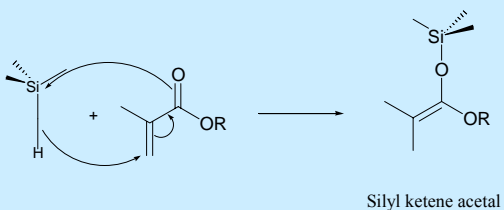


Five coordinate Silicon has greater Lewis acidity

- Because of charge or
- Because of greater resonance stabilization of six coordinate silicon

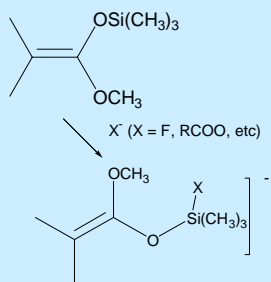
Group Transfer Polymerization

Initiator



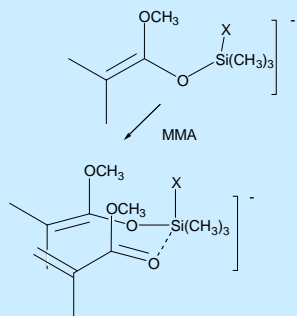
Group Transfer Polymerization

Mechanism: Propagation



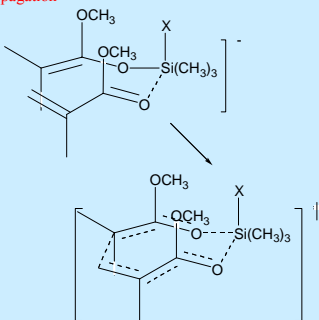
Group Transfer Polymerization

Mechanism: Propagation



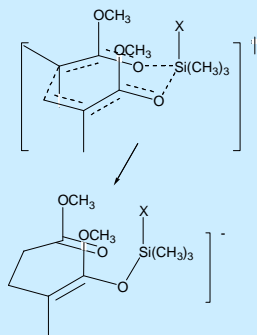
Group Transfer Polymerization

Mechanism: Propagation



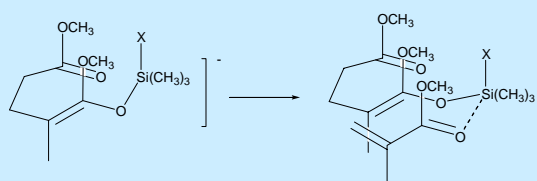
Group Transfer Polymerization

Mechanism: Propagation



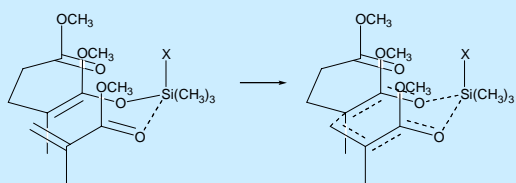
Group Transfer Polymerization

Mechanism: Propagation



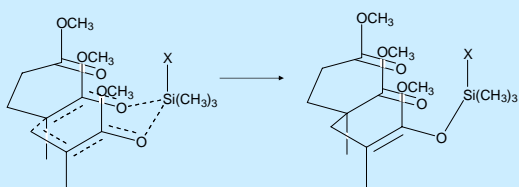
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Mechanism: Propagation



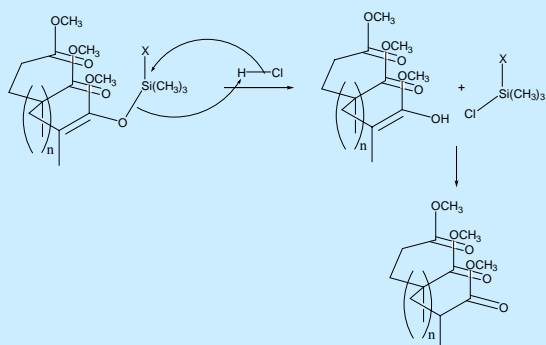
Group Transfer Polymerization

Mechanism: Propagation



Group Transfer Polymerization

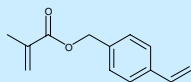
Mechanism: Termination



Group Transfer Polymerization

Advantages of GTP

1. Living (PDI \rightarrow 1)
2. Can do this reaction at room temperature (ionic requires low temp)
3. Can make telechelic polymers
4. Obtain random copolymers (reactivity ratios less of a consideration)
5. Air stable (but not water stable)
6. Can use DMF as solvent
7. Tolerant of other functional groups, especially vinyl side chains that would polymerize during radical polymerizations. Can't use acids (MAA)



Group Transfer Polymerization

Disadvantages of GTP

1. Only use for acrylate or methacrylate monomers (or aldehyde as discussed next)
2. More expensive than radical,
3. Requires water free conditions (pure reagents)

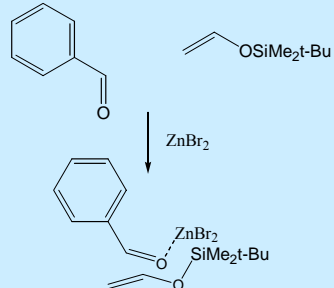
Group Transfer Polymerization

Aldol GTP: Things to know

1. Should use less than 5% anionic catalyst (F^- , or CH_3COO^-) to avoid total catalyst displacement
2. Rates slower than radical polym. (by approx an order of magnitude)
3. Can get competing radical polymerization.

Group Transfer Polymerization

Aldol GTP-Initiation



Group Transfer Polymerization

Aldol GTP: Initiation and Propagation

