8. Group-Transfer Polymerization, GTP

- **GTP** is a relatively new technique for the polymerization of acrylic monomers discovered by the scientists at DuPont in 1983.

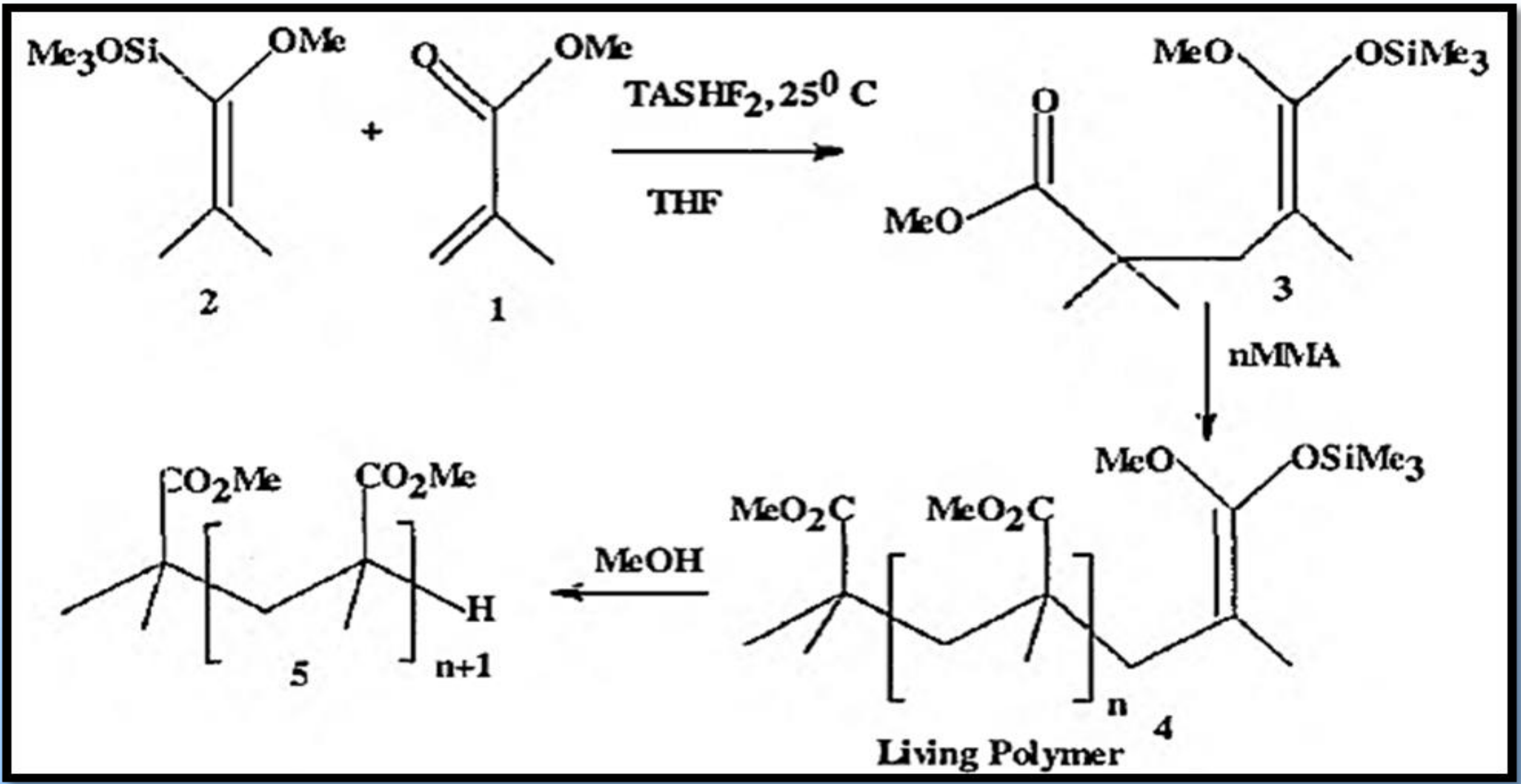
- The technique gives “living” polymers at room temperature or above.

- This is in distinct contrast to the anionic polymerization of (meth)acrylic monomers which can be performed satisfactory only at low temperatures (below -50°C).

- Although **GTP** works best for (meth)acrylates, other monomers such as acrylates, acrylonitrile, maleimide and vinyl ketone can also be polymerized.

- **GTP** appears to overcome some of the major disadvantages of other types of polymerization for preparation of well-defined functional block copolymers.

- **GTP** is an example of Michael addition of silyl ketene acetal to α, β-unsaturated carbonyl compound, scheme10.



- **GTP** initiator in presence of catalyst is very sensitive to protonic impurities (moisture, alcohol etc.).
- Presence of these impurities renders the initiator inactive and results in loss of molecular weight control.
- This is especially true when high molecular weight polymers are desired.
- Thus, ensuring that monomer, solvent and catalyst are pure and dry enables one to successfully prepare (meth)acrylate homo- and copolymers of desirable molecular weight.
- **GTP** requires either a nucleophilic or Lewis acid catalyst.

- Bifluoride and fluoride ions, supplied by soluble reagents such as tris(dimethylamino)-sulfonium bifluoride, $[(CH_3)_2N]_3SHF_2$, and $(n\text{-}C_4H_9)_4NF$, are the most effective nucleophilic catalysts.

- Although other nucleophiles (CN, acetate, p-nitrophenolate) are also useful.

- Zinc chloride, bromide, and iodide, and dialkylaluminum chloride have been used as Lewis acid (electrophilic) catalysts.

- Nucleophilic catalysts are effective at low concentrations (often 0.1 mol% relative to initiator).

- Much higher concentrations of Lewis acid catalysts are needed, 10 mol% or higher and this greatly limits the practical utility of electrophilic **GTP**.

- **GTP** requires the absence of materials such as water with active hydrogens, although **GTP** is not as sensitive to water as traditional anionic polymerization.

- Oxygen does not interfere with **GTP**. The range of solvents suitable for **GTP** is wider than for other anionic polymerizations.

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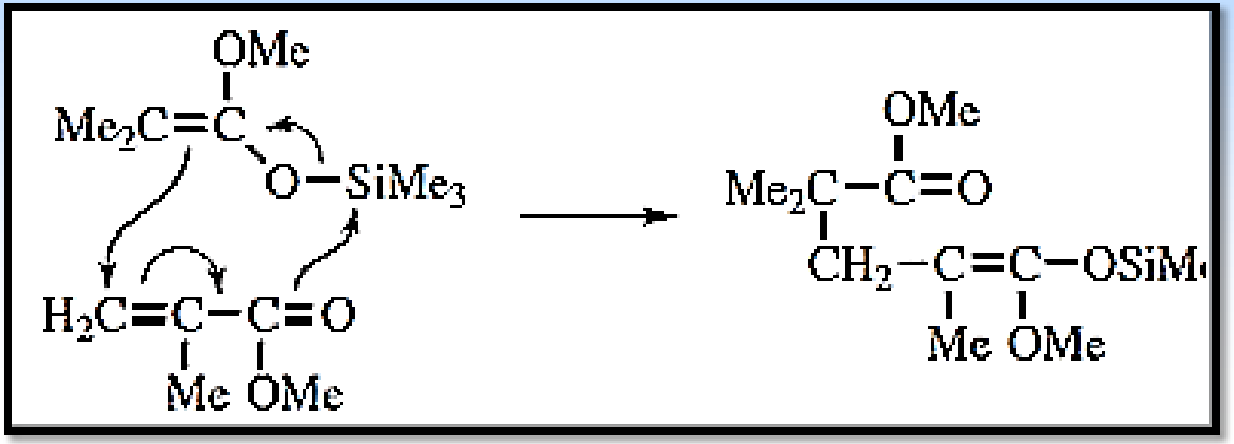
- DMF has been used with nucleophilic **GTP**, and chlorinated hydrocarbons as well as acetonitrile for electrophilic **GTP**.
- Although ethers such as THF and aromatics such as toluene are the most commonly used solvents.
- The mechanisms for nucleophilic **GTP** and electrophilic **GTP** are not the same.
- Electrophilic **GTP** proceeds by an associative or concerted mechanism that does not involve anionic propagating centers.

- Initiation involves a concerted addition of methyl trimethylsilyl dimethyl ketene acetal to monomer.

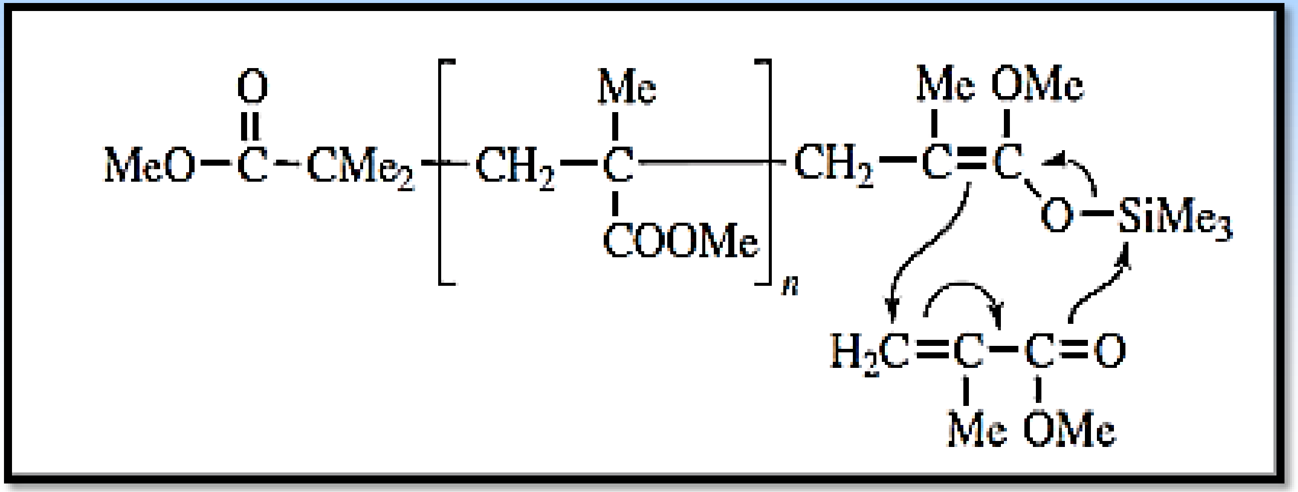


Scheme 11: Addition of methyl trimethylsilyl dimethyl ketene acetal to monomer

- The overall effect is to transfer the silyl ketene acetal center from initiator to monomer.

- Propagation proceeds in a similar manner, with the ketene acetal double bond acting as the propagating center.

- Both initiation and propagation involve nucleophilic attack of the π-electrons of the ketene acetal on monomer.

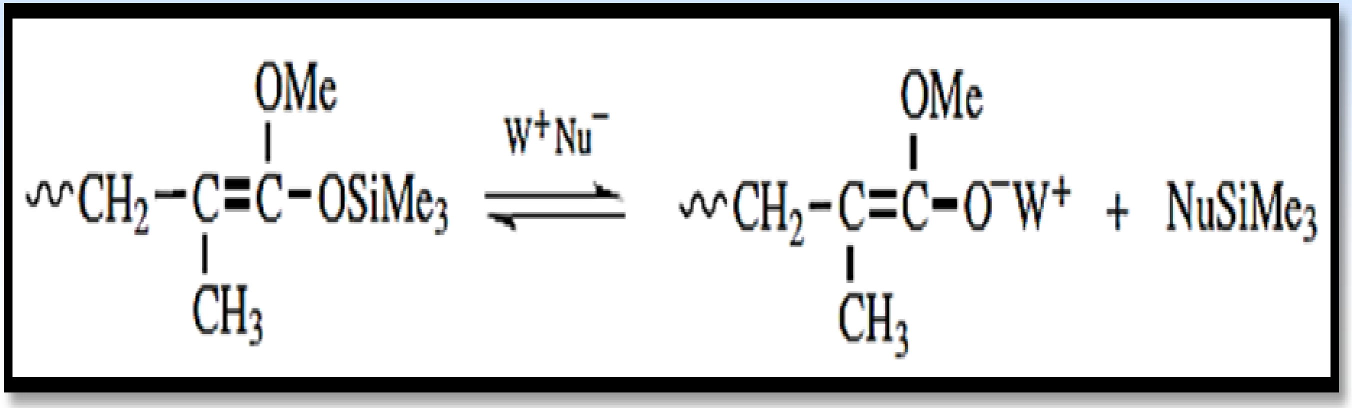


Scheme 12: nucleophilic attack of the π-electrons of the ketene acetal on monomer**.**

- Electrophilic catalysts probably function by coordination with the carbonyl oxygen of monomer to increase the electrophilicity of the double bond, rendering it more prone to nucleophilic attack.

- Nucleophilic **GTP** proceeds by a dissociative mechanism in which the propagating centers are ionic-similar to other anionic polymerizations.

- The anionic propagating species is generated in low concentrations by nucleophilic displacement of the trimethylsilyl group by the nucleophilic catalyst (W+Nu-):



$$\sim CH_2-\underset{CH_3}{\underset{|}{C}}=\overset{OMe}{\overset{|}{C}}-OSiMe_3 \overset{W^+Nu^-}{\rightleftharpoons} \sim CH_2-\underset{CH_3}{\underset{|}{C}}=\overset{OMe}{\overset{|}{C}}-O^-W^+ + NuSiMe_3$$

Scheme 13: The generation of the anionic propagating species.

- Control of the side reactions is achieved through two factors:

1. reversible complexation of the anionic propagating species by the silyl ketene acetal polymer chain ends maintains the concentration of the anionic propagating species at a low concentration; and

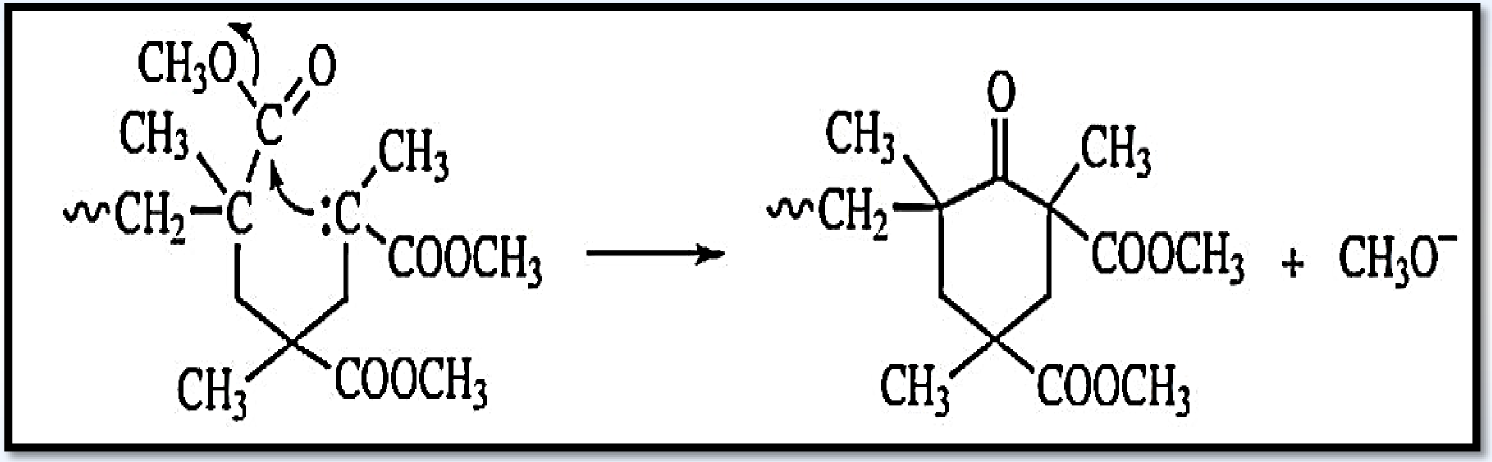
2. the bulky counter ion (e.g., tetra-n-butylammonium, tris(dimethylamino)sulfonium) decreases the reactivity of the anionic propagating centers toward the terminating side reactions.

- Living polymerizations of methacrylates with narrow **PDI**, generally 1.2–1.3 with some lower, are achieved by nucleophilic (dissociative) **GTP** at temperatures of 0–80ºC.

- However, the maximum molecular weights that can be achieved with narrow **PDI** are limited to about 20,000–30,000.

- Two factors limit the molecular weights-termination

1. by cyclization (scheme 14), although suppressed, is always present, and



Scheme 14: GTP cyclization.

2. by complexation of silyl ketene acetal ended polymer.

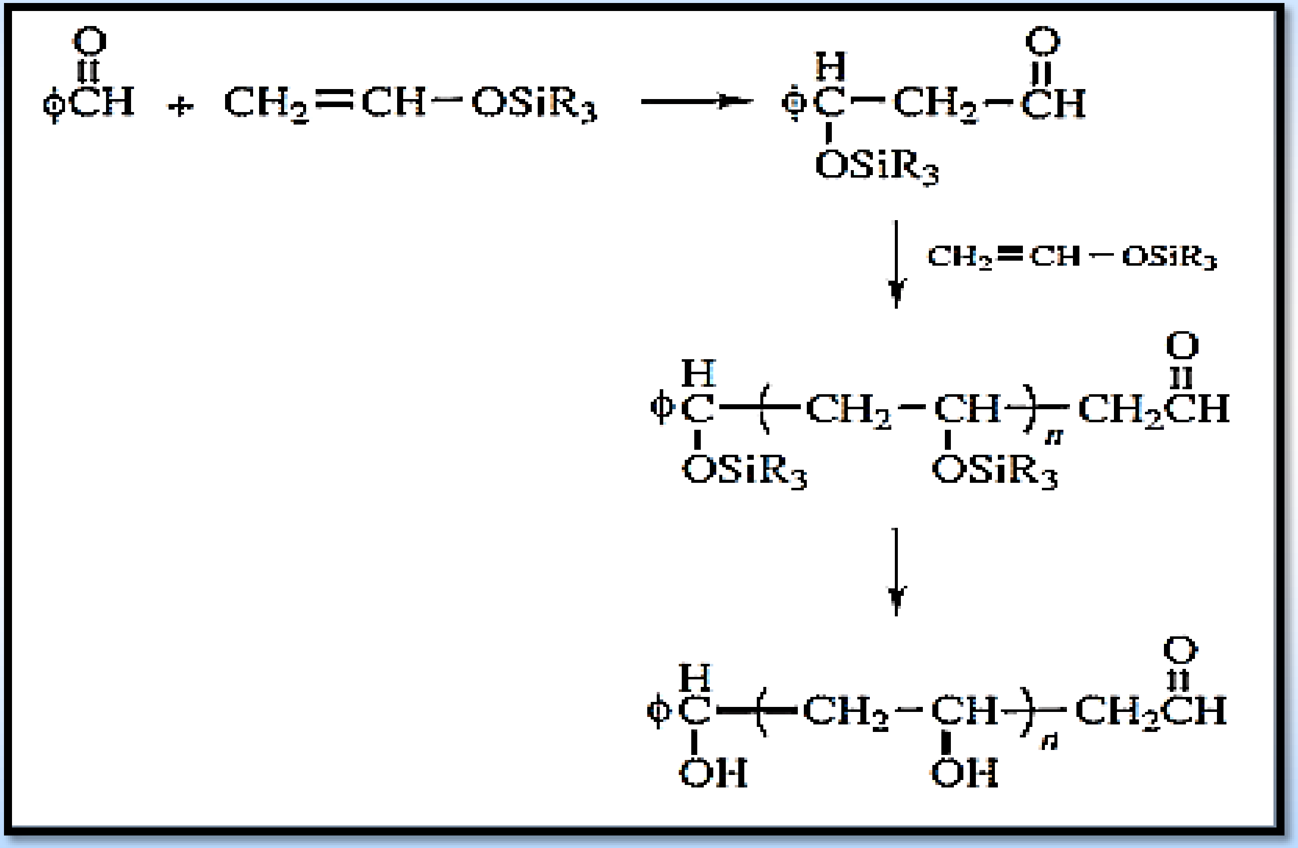
- **GTP** of acrylates is not as successful. Lower temperatures are required and there is substantial **PDI** broadening even at 0ºC.

- Better results for acrylates are achieved by electrophilic (associative) **GTP** using $HgCl_2$ and trimethylsilyl iodide at 20ºC.

- A variation of **GTP**, referred to as aldol **GTP**, involves polymerization of a silyl vinyl ether initiated by an aldehyde.

- Both initiation and propagation involve nucleophilic addition of the vinyl ether to the aldehyde carbonyl group with transfer of the trialkyl silyl group from vinyl ether to the carbonyl oxygen.

- The reaction has similar characteristics as **GTP**. The product is a silated poly(vinyl alcohol) (PVA), which can be hydrolyzed by acid to PVA.



Scheme 15: Aldol GTP