1. Introduction

One of the major goals of synthetic polymer chemistry is to prepare polymers with well-defined structures as well as adequate control over properties such as molecular weight, molecular weight distribution, copolymer composition and microstructure, tacticity, chain-end functionality, and branching. Ever since the first report of living polymerization by Szwarc, living/controlled polymerization techniques such as anionic, cationic, group transfer polymerization (GTP) and living/controlled free radical polymerization methods (atom-transfer polymerization (ATRP), stable free radical polymerization (SFRP), reversible addition fragmentation transfer (RAFT) and nitroxide mediated polymerization (NMP)) have emerged as powerful tools for the controlled synthesis of macromolecules. Living/controlled polymerization is an attractive technique offering opportunities to tailor-make model macromolecules with well-defined structures of technical interest such as graft, block, star, \(\alpha,\omega\)-functional polymers and macromonomers. Well-defined polymers possess diverse properties and are useful as elastomers, compatibilizers for polymer blends, additives for oil industry, general-purpose resins, adhesives, impact modifiers, processing aids in textiles, optical fibers, etc.

Each of the above methods offers specific advantages, depending on the nature of monomer and the desired polymer structure. Controlled polymerization of methyl methacrylate (MMA) can be achieved using techniques of living anionic, group transfer and atom transfer polymerization. A brief description of the salient features of these methods is given in the following paragraphs.

1.1 Controlled polymerization of (meth) acrylates

1.1.1. Living anionic polymerization (LAP)

Classical anionic initiators such as metal alkyls when used for alkyl (meth) acrylate monomers generally yield polymers with broad molecular weight distribution (MWD) and in low conversions. During polymerization the ester group of the monomer participates in the solvation of counterion. Thereby, it becomes more susceptible to nucleophilic-attack. Nucleophilic attack of the polar ester group can take place either during initiation or in
propagation. Many such secondary reactions are proposed by Schreiber\textsuperscript{11a} and Goode et al.\textsuperscript{11b,11c} these are shown in Scheme 1.1

Scheme 1.1. Secondary reactions in MMA polymerization

Controlled anionic polymerization of acrylates offers greater challenges than methacrylates because of higher reactivity of the carbonyl group towards nucleophiles and the presence of acidic hydrogen at the α-position to the carbonyl group\textsuperscript{12a-12c}.

The propagating centers in the anionic polymerization of alkyl (meth) acrylates are ester enolate anions, which in general, tend to stabilize through aggregation. The existence of ester enolates in equilibrium with aggregated form also poses a problem in controlling the living anionic polymerization of alkyl (meth) acrylates\textsuperscript{13a-c}. The influence of the aggregates in alkyl (meth) acrylate polymerization is very strong in controlling the MWD of the polymer\textsuperscript{13b}. It was observed that a slow exchange between aggregated and non-aggregated ion pairs leads to broadening of MWD\textsuperscript{13b}. Hence, controlling side reactions as well as aggregation-equilibrium dynamics assumes significant importance in achieving an ideal living anionic polymerization of alkyl (meth) acrylates.
In the mid 1970s Anderson conducted research on anionic polymerization of methacrylates to produce block polymer dispersing agents. Diphenylhexyl lithium was used as the initiator at -78 °C (Scheme 1.2). At these temperatures the bulky initiator does not react with the ester groups on the monomers and the backbiting reaction is absent. Molecular weight control and low MWDs ($M_n/M_w \leq 1.2$) were obtained and the products were excellent dispersing agents, but the purifying solvents and monomers and the need for refrigeration to cool reactors is too cost for commercialization the process.

Scheme 1.2. Anionic polymerization of MMA using $1.1'$-diphenylhexyllithium as initiator

The optimal condition for the anionic polymerization of alkyl (meth) acrylates is the use of bulky monofunctional initiator such as $1.1'$-diphenylhexyl, $1.1'$-diphenylmethyl, trityl, $\alpha$-methylstyryl salts or metalated esters with bulky counterion ($Cs^+ > K^+ > Na^+ > Li^+$) in polar solvent (DME>THF) at lower temperature ($<-65^\circ C$). Higher alkyl (meth) acrylates are insoluble at lower temperatures and require polymerization relatively at higher temperatures ($\geq -40^\circ C$).

Classical anionic polymerization strategies have been modified for better control with the help of ligands capable of coordinating with enolate ion pairs. Teyssie and Jerome have classified the coordination of ligands with enolate ion pairs into (i) $\sigma$-type coordination with crown ethers, cryptands, tertiary amines, (ii) $\mu$-type coordination with aluminum alkyls, alkali metal salts of alkoxide, halides, perchlorate, and (iii) $\sigma$, $\mu$-type coordination with alkoxalkoxides, aminoalkoxides and silanlates. Ballard et al. found that bulky dialkyl aluminum phenolate additives would improve the anionic polymerization of acrylic monomers (Scheme 1.3).

Scheme 1.3. Screened anionic polymerization of MMA with bulky dialkyl aluminum phenolate as additive
However, the use of appropriate additive/ligand in conjunction with initiator brings perfect control of the polymerization in both polar and non-polar solvents. Although, the efficiency of each additive/ligand is strongly dependent on the steric and electronic constraints with respect to its coordination to enolate, in general, the presence of various ligands/additives during the polymerization improves the living character to a greater extent. But, from a practical point of view, however, this may be unprofitable since it is not easy to remove the added salts/additive (for e.g. LiCl) from the resulting polymer-salt mixture, and residual salt, especially chlorine, may have an adverse influence upon coating as acrylics widely used as resin for paint and varnish.

Metal-free initiators are of great interest due to their low cost as well as their ability to polymerize primary acrylates at room temperature. Metal-free carbon nucleophiles, resonance stabilized tertiary carbanions with tetrabutylammonium ion as countercations, act as initiators for the controlled polymerization of alkyl acrylates. Reetz and coworkers$^{20,27}$ first used metal-free carbon as initiators (1a, Scheme 1.4) for the controlled anionic polymerization of nBA to get relatively narrow MWD at room temperature. Side reactions such as end group cyclization and Hoffmann elimination were observed$^{28}$.

Quirk and Bidinger$^{29}$ used Bu₄N⁺ salt of 9-methylfluorene (2c, Scheme 1.4) to initiate polymerization of MMA in THF at ambient temperature. At very low initiator concentration, they obtained PMMA with a broad MWD (Mw/Mn = 2.16) in low yield (24%). At higher initiator concentration (2b, Scheme 1.4), Reetz et. al.$^{30}$ observed a slow initiation at room temperature. The reason for a slow initiation was attributed to both aggregation and steric shielding of bulky non-metal cation. Muller et al.$^{31}$ performed anionic polymerization of methyl acrylate (MA), nBA, 1BA, and MMA using various carbanions with tetrabutylammonium counterion (1b, 2a, and 2b, Scheme 1.4) in THF at 30
°C. The initiator efficiency was low and polymers obtained were characterized by broad MWDs, which in some cases were bimodal.

Muller et al.\textsuperscript{31} also studied the effect of metal and non-metal counterions on the anionic polymerization of MMA in THF. They performed anionic polymerization of MMA in the presence of tetrabutylammonium, tetramethyldiethylguanidinium (initiator 3a, 3b, Scheme 1.4) and lithium counterion using 1,1'-diphenylhexyl anion as initiator at -40 °C. They reported that the polymerization in the presence of non-metal counterion is very fast and conversion is quantitative within 2 minutes, however, the obtained PMMAs had broad/bimodal distribution with low initiator efficiency.

Webster found\textsuperscript{32} that the size of the gegenion is more important than the fact that it is nonmetallic. Potassium dimethyl malonate/18-crown-6 polymerizes MMA at 25-60 °C to give quantitative yields of PMMA, with MWD 1.5-1.9. Excess malonate or methanol lowered the molecular weight of the PMMA but did not shut down the polymerization. They also postulated that a hydrogen-bonded version of the Quirk intermediate (in GTP) is stabilizing enolate ends (Scheme 1.5).

\begin{center}
\textbf{Scheme 1.5.} Hydrogen-bonded version of the stabilizing enolate ends
\end{center}

Seebach and Pietzonka\textsuperscript{33} used P$_4$ base (Scheme 1.6a) as an initiator for the anionic polymerization of MMA.

\begin{center}
\textbf{Scheme 1.6a.} Anionic polymerization of MMA with P$_4$ base as an initiator
\end{center}

Good control of molecular weight and MWDs are obtained at temperatures up to 60 °C. The process has the strange property of not proceeding at temperatures below -20°C (all other
anionic polymerizations of MMA work better at low temperatures). The experimental MWs are higher than those expected by the amount of P₄ base used. Muller and Baskaran⁴ confirmed these results using P₅ counterion at 20 °C (Scheme 1.6b).

\[
\begin{align*}
\text{P}^4 & \quad \text{MMMA} \\
\text{P}^5 & \quad \text{PMMA} \quad \text{M}_{w} / \text{M}_{n} = 1.20
\end{align*}
\]

Scheme 1.6b. Anionic polymerization of MMA with P₅ counterion

Muller et al used the related bis (triphenylphosphoranylidene) ammonium ion (PNP) as a counterion (Scheme 1.6c) for polymerization of MMA at 0 °C.

\[
\begin{align*}
P & \quad \text{PNP} \\
\text{PNP} & \quad \text{PMMA} \quad \text{M}_{w} / \text{M}_{n} = 1.20
\end{align*}
\]

Scheme 1.6c. Anionic polymerization of MMA with PNP counterion

Hogen-Esch and Zagata⁶ used a tetraphenylphosphonium gegenion for anionic polymerization of MMA, at low temperatures (-80 °C). However, Muller has shown that -20 to 20 °C is adequate.

The historical developments and strategies adapted by several research groups in the living anionic polymerization of alkyl (meth) acrylates with the objective of enhancing the living nature, and thus control, of the polymerization is discussed in detail in recent reviews.²ᵃᵇ

### 1.1.2. Group transfer polymerization (GTP)

GTP is a controlled conjugate addition of organosilicon compounds such as silyl ketene acetals (5) to acrylate monomers at ambient or elevated temperatures in the presence of either a nucleophilic or electrophilic catalyst. One of the most important characteristic features of GTP is the formation of isolable, well-characterized silyl ketene acetal ended polymers (6) (Scheme 1.7) whose reactive end groups can be converted into other functional groups. Addition of a new monomer at this point starts chain growth again to produce a block polymer or quenching with a proton source gives the silicon-free...
polymer. Since Webster et al., reported\textsuperscript{4} GTP of methyl methacrylate in 1983, a large variety of about one hundred different methacrylates-many of them specialty monomers have been employed for GTP to form polymers with narrow molecular weight distribution (MWD).

\[
\text{Me} \quad \text{O} \quad \text{Me} \\
\text{MMA (4)}
\]

\[
\text{Me} \quad \text{O} \quad \text{Me} \\
\text{MTS (5)}
\]

\[
\text{Me} \quad \text{O} \quad \text{Me} \\
\text{Silyl ketene acetal-ended PMMA (6)}
\]

Scheme 1.7. Nucleophile catalysed GTP of MMA

To obtain polymer with low MWDs in a living polymerization the rate of initiation must be faster or similar to rate of propagation ($k_i \geq k_p$). This can suitably be accomplished if the structure of the initiator is the same as that of the growing chain end. The preferred initiator for GTP is 1-Methoxy-2-methyl-1-propenoxy trimethylsilane (MTS, 5). MTS, 5 is prepared by addition of trimethylsilane\textsuperscript{4} to MMA 4 (Scheme 1.8) and, although it is commercially available, it is relatively expensive.

\[
\text{Me} \quad \text{O} \quad \text{Me} \\
\text{MMA (4)}
\]

\[
\text{Me} \quad \text{O} \quad \text{Me} \\
\text{MTS (5)}
\]

Scheme 1.8. Preparation of 1-methoxy-2-methyl-1-propenoxy trimethylsilane (MTS)

Bandermann and Witkowski synthesized\textsuperscript{18} functional silyl ketene acetal and used it to prepare macromonomers. The initiator that contains vinyl group is not reactive to GTP conditions.

Two main mechanistic routes for base catalyzed GTP\textsuperscript{4} under consideration are the associative pathway (Scheme 1.9) and the dissociative pathway (Scheme 1.10). In the associative mechanism the silyl ketene acetal group is activated by complexation with catalyst for addition to monomer. The silyl group transfers to incoming monomer and remains on the same polymer chain during the polymerization step. The well-documented silyl end group exchange would be occurring by some unknown process. The equilibrium
rate for catalyst complex formation must be fast to insure molecular weight control and low MWD.

**Scheme 1.9. Associative mechanism in GTP**

In the dissociative route the nucleophilic catalyst complexes with the silyl ketene acetate end groups and in a reversible cleavage step generates a reactive enolate end that adds monomer.

**Scheme 1.10. Dissociative mechanism in GTP**

The enolate end groups are then capped by R,SiNu to regenerate silyl ketene acetate ends. Since low MWD and controlled molecular weight polymer is obtained at low catalyst concentrations, the equilibrium generating enolate ends must be much faster than the rate of polymerization.

In associative mechanism increasing the amount of catalyst should merely increase the rate of reaction. However, in the dissociative mechanism increasing the amount of catalyst may generate more enolate than can be stabilized through complexation with the existing silyl ketene acetate end groups. In the associative process the catalyst should merely complex reversibly with the MTS and not destroy it. At less than 1:1 ratios considerable isomerization of the ketene acetate to its C-silyl isomer occurs. At low concentrations of
catalyst compared to initiator, the small amount of ester enolate generated would be
stabilized by the presence of large amounts of MTS. Therefore the catalyst and initiator can
be combined before the addition of monomer.

However, studies by Quirk and coworkers\textsuperscript{44} have shown that significant amounts (~ 40%) of silyl group exchange are observed during the polymerization, which is inconsistent with initially proposed mechanism and GTP criterion. A mechanism involving an enolate anionic propagating species reversibly complexed with the silyl ketene chain-end has been proposed as shown in Scheme 1.11. Also, this ester enolate anion reacts with monomer to produce polymer. This supports the presence of enolate anions as active center in GTP as well as ester enolates operate as both initiators and catalysts for GTP.

![Scheme 1.11. Intermolecular equilibrium of dissociated enolate anion with silyl ketene acetal](image)

Except for the low temperature exchange studies, no other evidence supports the associative mechanism. Based on the lack of exchange of added silyl fluoride with silyl ketene acetal ends it looks as though fluoride and bifluoride catalysts operate by irreversible generation of ester enolate chain ends. On the other hand carboxylate catalysts appear to operate by reversible generation of ester enolate ends as evidenced by rapid exchange of silyl acetate with silyl ketene acetal ends. Kinetics of GTP has been studied by Brittain\textsuperscript{41} using stopped flow FT-IR, by Mai and Muller\textsuperscript{42} using gravimetry, and by Bandermann and coworkers\textsuperscript{43} using dilatometry.

Nucleophile assisted GTP inevitably involves participation of enolate anion as intermediate during propagation except in associative mechanism. The most active catalysts are fluorides and bifluorides. At above ambient temperatures, carboxylates and bicarboxylates are preferred\textsuperscript{44}. However, the relative efficiency of a catalyst strongly depends on the
corresponding acidity (pKₐ value) of the carbon acids from which it is derived. The
efficiency increases with increasing nucleophilicity of the catalyst. In general, bifluoride is
more reactive than oxyanions, which are more reactive than bioxyanions. Banderman and
Sitz have studied the effect of catalyst concentration on GTP. A large counter ion is
required for maximum efficiency.

The catalysts are very likely reacting irreversibly with the initiators to produce products that
are involved in the polymerization. TAS fluoride makes ester enolate plus silyl fluoride plus
methyl isobutyrate. TBA bibenzoate makes silyly benzoate plus TBA benzoate. Brittain
has found that the rate of polymerization to be 50 times slower for bibenzaote than for
benzoate catalysis.

Backbiting reaction (cyclization) is major termination pathway in GTP. Banderman and
Sitz. found that the polydispersity of PMMA obtained in the nucleophile catalyzed GTP
increases with increasing concentration of catalyst. The termination reaction in GTP
becomes insignificant when catalyst concentration was kept low, but it dominates at higher
catalyst concentration. If one assumes a dissociative mechanism, the large unreactive
counterion may work better by slowing down the rate of backbiting termination and
formation of ketenes from ester enolate ends. In addition in the dissociative process the
large counterions would foster complex formation of enolate polymer ends with silyl ketene
acetal ends. The Backbiting termination reaction is more pronounced for stronger
nucleophilic catalysts than for weaker ones. The concentration and nature of catalyst
strongly determine the 'living character' of GTP, possibly because of the participation of
enolate anions in the propagation.

Molecular weights in the 20,000 ranges are easily obtained but preparation of higher
molecular weight polymer is relatively more difficult. As in other living systems the
molecular weight is controlled by the monomer/initiator ratio and the MWDs are narrow.
During polymerization, especially at higher temperatures the resulting polymer will contain
up to 30% dead ends, as a consequence of backbiting reaction of enolate chain ends and/or reaction with protic impurities\textsuperscript{48}. Brittain and Dicker\textsuperscript{47} found that at the trimer stage (DP=3) the rate of backbiting is ten times higher than at DP>3. Thus one should start GTP with more than three equivalents of monomer to by-pass the trimer stage quickly.

Acrylates polymerize two orders of magnitude faster than methacrylates by anion catalysed GTP. However, the polymerization dies after reaching a molecular weight of about 10,000. During the anion catalysed polymerization of acrylates the silyl ketene acetal end groups migrate to internal positions. These ketene acetals are too hindered to act as initiators for branch formation\textsuperscript{49}. Also, due to presence of $\alpha$-hydrogen in these monomers, side reaction occurs. The living polymerization of acrylates by GTP does proceed under lewis acid catalysis\textsuperscript{50}. ZnCl\textsubscript{2} or ZnBr\textsubscript{2} are effective but require concentrations of catalyst at a level of 10\% based on monomer. R\textsubscript{2}AlCl works at lower levels. However, HgCl\textsubscript{2} activated by TMS iodide is the best lewis acid system and gives living acrylate polymers at low catalyst level\textsuperscript{51}. Lewis acids are believed to activate monomers by coordination with carbonyl oxygen of acrylates.

Recently, Webster reported\textsuperscript{44} that GTP operates at 80 °C in solvents so that the heat of polymerization could be removed by cooling with a reflux condenser. One of the reasons for proposing an associative GTP over a dissociative GTP was that an associative process would involve stable silyl ketene acetal groups as key intermediates in the formation of polymer. On the other hand the dissociative process would involve free ester enolate, known to be unstable at 80 °C. A closer look at the whole system however reveals why GTP works at above ambient temperatures, while classical anionic polymerization does not.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Scheme_1.12.png}
\caption{Backbiting termination reaction in MMA polymerization}
\end{figure}
In GTP the backbiting termination reaction turns into a chain transfer process. The backbiting reaction of chain ends produces a cyclohexanone derivative and methoxide. In classical anionic polymerization this terminates the chain. In GTP the methoxide can react with the latent silyl ketene acetal ends to regenerate enolate ends for further polymerization (Scheme 1.12).

For acrylate polymerization by GTP the cyclohexanone that results from backbiting is a \(\alpha\)-ketoester with active hydrogen that reacts with the methoxide, thus, preventing it from regenerating the enolate ion as in the case of methyl methacrylate (Scheme 1.13).

![Scheme 1.13. Termination reaction in acrylate polymerization via chain end cyclization (backbiting)](image)

In view of the “living” nature of GTP, the method is amenable for the synthesis of well-defined random, block copolymers including amphiphilic block copolymers containing poly methacrylic acid (PMAA) segments by using protected monomers, graft, and star-branched polymers, networks as well as macromonomers, functional polymers including end-functionalized polymers, and telechelics. Hyper-branched methacrylates were also synthesized by self-condensing group transfer polymerization (SCGTP). Also, GTP can be advantageously carried out in bulk to prepare linear polymers and randomly cross-linked networks. Very recently GTP has also been performed in ionic liquids.

Known anionic initiators (ester enolates) for MMA can act as catalysts for GTP. Other factors such as, the need for large unreactive counterions, induction periods, use of living enhancing agents, etc. support the dissociative process in GTP. Living anionic polymerization works better at very low temperature (-78°C) where as GTP works at ambient or elevated temperatures. The ‘living nature’ of GTP depends on the nature and
Scheme 1.14. Dynamic equilibrium between active species and dormant species

Table 1.1. Comparison of characteristic parameters of GTP and anionic polymerization of MMA in THF

<table>
<thead>
<tr>
<th>Entry</th>
<th>Parameter</th>
<th>GTP</th>
<th>Anionic</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Chain life times (sec)</td>
<td>$10^{-10}^{\circ}$</td>
<td>$10^{-10}^{\circ}$</td>
<td>66</td>
</tr>
<tr>
<td>2</td>
<td>$k_p/k_i$ (mol/L)</td>
<td>250</td>
<td>8</td>
<td>47</td>
</tr>
<tr>
<td>3</td>
<td>Termination reaction</td>
<td>Backbiting</td>
<td>Backbiting</td>
<td>47,67</td>
</tr>
<tr>
<td>4</td>
<td>Chain transfer reaction</td>
<td>With carbon acids of $16 &lt; \text{pK}_a &lt; 25$</td>
<td>With carbon acids of $16 &lt; \text{pK}_a &lt; 25$</td>
<td>68</td>
</tr>
<tr>
<td>5</td>
<td>Activation energy, $E_a$ (kJ/mol)</td>
<td>$16.9$ (TASHF$_2$)</td>
<td>$19.5$ (Cs$^+$)</td>
<td>69,42</td>
</tr>
<tr>
<td>6</td>
<td>Syndiotacticity of PMMA</td>
<td>($\sim 56%$ (TASHF$_2$); $\sim 54%$ (N$^+$Bu$_4$); $\sim 35%$ (Cs$^+$))</td>
<td>($\sim 61%$ (Li$^+$); $\sim 56%$ (N$^+$Bu$_4$); $\sim 57%$ (P$^+$Ph$_3$); $\sim 34-38%$ (Cs$^+$))</td>
<td>70,71</td>
</tr>
<tr>
<td>7</td>
<td>Frequency exponent, $\log A$</td>
<td>$6.8$ (TASHF$_2$)</td>
<td>$7.3$ (Cs$^+$)</td>
<td>69, 42(c), 42(a)</td>
</tr>
<tr>
<td>8</td>
<td>Reactivity ratios</td>
<td>MMA/$^1$BMA: 4.59:0.16</td>
<td>MMA/$^1$BMA: 35:0.43</td>
<td>42(c), 4(b), 72-74</td>
</tr>
</tbody>
</table>
concentration of catalyst, possibly because of the participation of enolate anions in the propagation. Several kinetic and mechanistic studies that are currently available convincingly suggest that the nucleophile catalyzed GTP of alkyl (meth) acrylate is merely a hypervalent silicon mediated anionic polymerization. Scheme 1.14 shows the dynamic equilibrium between active species and dormant species in GTP as well as in living anionic polymerization. Several experimental evidences suggest that GTP is a sub-set of anionic polymerization, with similar active centers (ester enolates) and differ only with respect to the relative concentration of active centers (table 1.1).

1.1.3. Atom transfer radical polymerization (ATRP)

Atom transfer radical polymerization (ATRP) is a rapidly emerging method since its discovery a decade ago by Matyjaszewski and Sawamoto for obtaining pseudo-living polymerization of vinyl monomers with controlled M_n and MWD. In ATRP, the transition metal catalyst (M^n/L, where M^n is the transition metal in the lower oxidation state n complexed with an appropriate ligand L) reacts reversibly with the added initiator molecule and generates an oxidized transition metal halide complex (X-M^{n+}/L) and a radical (R*). This radical propagates, adding monomer (M), and is rapidly deactivated by reaction with the oxidized transition metal halide complex to reform the initial transition metal catalyst and an oligomeric X-terminated chain (P_X) (Scheme 1.15).

![Scheme 1.15. Transition-metal-catalyzed atom transfer radical polymerization](image)

This sequence can repeat itself, until desired consumption of the monomer is reached, resulting in the synthesis of polymers with predetermined molecular weights (DP_n = [M]_o/[RX]_o) and low polydispersities (M_w/M_n < 1.5).
The equilibrium is attenuated by the choice of the ligand and ligand also increases the solubility of the catalyst complex in the polymerization medium. Additionally, when the concentration of propagating radicals is sufficiently low in comparison with dormant chains, the proportion of terminated chains can be often neglected (<5%). This may enable the preparation of highly functional polymers (>95%). Care has to be taken to reduce the amount of dissolved oxygen in the system since that will oxidize the catalyst complex forming the redox conjugate, or persistent radical, and reduce the rate of reaction.78

In his early work Sawamoto used carbon tetrachloride77 as initiator and Matyjaszewski, α-halo esters75 (Scheme 1.16 (i), (ii)). Percec79 discovered that sulfonyl chlorides provided advantages over the other initiators and has used these initiators extensively in his research (Scheme 1.16 (iii)).

$$\text{Cl} \rightarrow \text{CO}_2 \text{Me} + \text{CuCl} \quad \text{MMA} \rightarrow \text{PMMA} \ldots \ldots (i)$$

$$\text{CCl}_4 + \text{RuCl}_2 \rightarrow \text{MMA} \rightarrow \text{MeA}[\text{ODBP}]_2 \rightarrow \text{Cl} \rightarrow \text{CO}_2 \text{Me} \quad \text{MMA} \rightarrow \text{PMMA} \ldots \ldots (ii)$$

$$\text{ODBP} = \text{ortho-di-tert-butylphenoxy}$$

$$\text{SO}_2 \text{Cl} + \text{CuCl} \quad \text{MMA} \rightarrow \text{PMMA} \ldots \ldots (iii)$$

Scheme 1.16. ATRP of methyl methacrylate using different initiators

ATRP of methyl methacrylate (MMA) has been reported using ruthenium,77 copper,80 nickel,81 iron,82 palladium,81 and rhodium84 catalytic systems. The facile polymerizability of MMA and the large range of available catalysts for the ATRP reaction are due to the relative ease of activation of the dormant species and the high values of the ATRP equilibrium constants.

By using functional initiator, functionalities such as vinyl, hydroxyl, epoxide, cyano and other groups have been incorporated at one chain end, while other chain end remains an alkyl halide. The polymer can be dehalogenated in a one-pot process or the halogen end
groups can be transformed to other functionalities using nucleophilic substitution reactions or electrophilic addition reactions. Moreover, utilizing the ability of the halogen chain end reactivated, radical addition reactions can be used to incorporate allyl end groups, insert one less reactive monomer unit at the chain end, or to end-cap the polymer chain. Haddleton reported hydroxyl functional alkyl bromide initiator leads to α-hydroxyl functional PMMA with controlled Mn and PDI < 1.20 without the use of protecting group chemistry. With ATRP, functionality, and architecture can be combined resulting in multifunctional polymers of different compositions and shapes such as block copolymers, multiarmed stars or hyperbranched polymers.

For industrial use, residual halides and metals in the product would be a problem for electronic device uses. As a multicomponent system, ATRP is composed of the monomer, an initiator with a transferable (pseudo) halogen, and a catalyst (composed of a transition metal species with any suitable ligand). Sometimes an additive is used. For a successful ATRP, other factors, such as solvent and temperature, must also be taken into consideration. All these parameters were discussed in detail in recent review.

1.2. End-functional poly (methyl methacrylate)s by GTP

In living polymerization methods like anionic and GTP, end-functional polymers and macromonomers synthesis can be achieved by two different strategies, i.e. either by deactivation of the living species with a suitable electrophile or by initiation of the living process with an organic anionic species that bears either the protected functional group, or the polymerizable double bond respectively. The use of functional initiators in living polymerization methods like GTP and anionic technique ensures that each polymer chain contains one functional group. However, initiators of this type are limited. Some of the functional groups such as hydroxyl, amino, carbonyl are not compatible with the chain ends of living polymers. To overcome this obstacle, the concept of protective groups into anionic polymerization and GTP was introduced. Anionic initiators often exhibit limited solubility in hydrocarbon solvents where as GTP initiators are readily soluble in all solvents used in GTP.

A disadvantage of the termination route to prepare end-functional polymers is that any polymer chain that has been terminated during the propagation will not react with the
electrophile, thereby, impairing quantitative functionalization. If such conventional procedures are not available, end-functional polymer can, however, be obtained in high yields by appropriate chemical modification of a preexisting reactive functional group. In any event, the functionalization with a functional group or with a double bond must be as quantitative as possible to be a useful synthetic strategy. One of the challenges facing the field of functional polymers is the relative complexity of synthesis and difficulties in characterizing the chain end functionalities.

### 1.2.1. Use of functional initiators

Polymers with terminal hydroxyl (9) or carboxyl groups (10) are readily prepared by using the functionalized initiators [(2-methyl-1-[2-(trimethylsiloxy)ethoxy]-1-propenyl)oxy] trimethylsilane (7), 1,1’-bis(trimethylsiloxy)-2-methylpropene-1 (8), followed by hydrolysis of the resulting polymer in refluxing methanolic tetrabutyl ammonium fluoride (Scheme 1.17). The high degree of monofunctionality of the resulting polymer was determined using HPLC.

![Scheme 1.17. Hydroxyl and carboxyl end-functional poly (methyl methacrylate)s](image)

To prepare epoxy functional meth (acrylate) s an epoxy functional initiator (11, table 1.2) was used. The epoxy-group can be reacted with conventional epoxy-based resins to make branched or triblock polymers.

A variety of phosphorous-terminated polymers were synthesized by the use of phosphorous containing silyl ketene acetals (12, table 1.2) These initiators initiated the GTP of MMA in the presence of TASHF2 to give functional PMMA with low polydispersity. Usually high levels of catalyst (4-11% on initiator) were required for these polymerizations due to coordination of catalyst with phosphonate group. Polymers containing a terminal silyl phosphonate group are easily converted into a terminal phosphoric acid group by hydrolyzing with dilute HCl or methanolic TBAF.
Shen et al. prepared phosphonium containing silyl ketene acetals (13, table 1.2), which was used to initiate GTP of acrylic monomers, which formed polymers with terminal phosphonium cations. The phosphonium cation was post reacted to make functional polymers. Polydispersities of the polymers were higher because the reactivity for a nucleophilic attack was reduced in the initiators substituted by the triphenylphosphonium group with electron withdrawing property. The macromolecular phosphonium salts could be converted with sodium ethanolate into the corresponding macromolecular ylides and by a subsequent Wittig reaction with an aldehyde into a macromonomer.

A variety of initiators bearing functional groups such as vinyl, allyl, styrenyl etc. that are not reactive under GTP conditions have been used to prepare acrylic macromonomers. Functional initiators (14, 15 table 1.2) initiated GTP of MMA in THF using TPSHF or TBACN with quantitative conversions\(^9\) \(^{92}\). The polydispersities were broader (1.2-1.7) than those expected from a truly living system.

Attempts have been made to prepare\(^9\) \(^{92}\) vinyl group substitution at the alkoxy group of silyl ketene acetals (16, table 1.2) but their activity in GTP has not been examined in detail. A variety of allyl group containing initiators has been used by Hertler et al.\(^9\) \(^2\). The rate of initiation of MMA with silyl poly (enolate) s (17-21, table 1.2) was found to be faster than with silyl ketene acetals. A summary of end-functional PMMA’s prepared by GTP using functional initiators is given in table 1.2.

“Macromonomer” is defined as a polymer or oligomer having a polymerizable functional group (double bond, heterocycle) at one chain end or at both chain ends, not only for vinyl polymerization, but also for polycondensation, polyaddition or ring-opening polymerization occurring at the chain end. Macromonomers for soft contact lens materials is used, (22) as macromonomer and HEMA as comonomer were used in soft contact lens materials\(^9\) \(^4\).
Table 1.2. End-Functional Poly (methyl methacrylate)$^*$ using Different Functional Initiators

<table>
<thead>
<tr>
<th>Entry</th>
<th>Initiator</th>
<th>Catalyst</th>
<th>$M_n \times 10^3$ (Theory)</th>
<th>$M_n \times 10^3$ (SEC)</th>
<th>$M_n/M_n$</th>
<th>Functionality</th>
<th>Ref.</th>
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<td><img src="image2" alt="Structure 2" /></td>
<td>TASHF$_2$</td>
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<td>21.0</td>
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<td>-COOH</td>
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<td>3</td>
<td><img src="image3" alt="Structure 3" /></td>
<td>CsHF$_2$</td>
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<td>4</td>
<td><img src="image4" alt="Structure 4" /></td>
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<td>92</td>
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<td><img src="image1.png" alt="Image" /></td>
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<td>Allyl</td>
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<td>Allyl</td>
<td>92</td>
</tr>
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<td><img src="image3.png" alt="Image" /></td>
<td>TBABB</td>
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<td><img src="image4.png" alt="Image" /></td>
<td>TBAmCB</td>
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<td>19.0</td>
<td>1.34</td>
<td>Allyl</td>
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</tr>
<tr>
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<td><img src="image5.png" alt="Image" /></td>
<td>TBABB</td>
<td>10.1</td>
<td>9.76</td>
<td>1.46</td>
<td>Allyl</td>
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</tr>
<tr>
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<td><img src="image6.png" alt="Image" /></td>
<td>TBABB</td>
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<td>Allyl</td>
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<tr>
<td>12</td>
<td><img src="image7.png" alt="Image" /></td>
<td>TASHF₂</td>
<td>3.1</td>
<td>3.91</td>
<td>1.17</td>
<td>Allyl</td>
<td>92</td>
</tr>
<tr>
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<td><img src="image8.png" alt="Image" /></td>
<td>TBABB</td>
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<td>20.1</td>
<td>1.12</td>
<td>Allyl</td>
<td>92</td>
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<tr>
<td></td>
<td><img src="image9.png" alt="Image" /></td>
<td>TBAmCB</td>
<td>5.12</td>
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<td>1.15</td>
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</tr>
</tbody>
</table>

a: In none of the cases, information on degree of functionality is available in the literature
Macromonomer can be used to make rheology control agents, adhesives, elastomers, water dispersible polymers, inks, toners, etc. One of the end uses of macromonomers is in the synthesis of Non-Aqueous Dispersions (NAD’s), which are used for rheology control, and reinforcement of coatings. Because GTP macromonomers have all of their polymerizable groups located at the end of every chain, they make superior stabilizers for NAD’s. In the case of macromonomer by initiator method, polymerizable functional group (double bond, heterocycle) will be present on initiator moiety and is inert under GTP conditions.

Asami used vinylphenylketentrimethylsilylacetal (VPKMTMSA, 23, entry 1, table 1.3) as the initiator, the macromonomer with a styryl group (which is inert toward GTP) at the initiating end was synthesized using catalyst TASF$_2$SiMe$_3$ at room temperature as well as at 0°C in THF with $M_n$ 3,600-11400 g/mol ($M_n/M_w = 1.09 - 1.10$)

Asami et al. also prepared oxazoline ring-terminated macromonomers (entry 2, table 1.3) by GTP of methyl methacrylate by employing trimethylsilyl group-containing oxazoline initiators trimethylsilyl-2-methyl-2-oxazoline or trimethylsilyl-2-ethyl-2-oxazoline (24, table 1.3) and tris (dimethylamino) sulfonium difluorotrimethylsilicate as a catalyst, at room temperature or at -78°C. The oxazoline-terminated macromonomer obtained had a broad molecular weight distribution, and the initiating efficiency was low. However, the high functionality of the end oxazoline group was supported by the formation of the graft copolymer after cationic copolymerization with 2-methyl-2-oxazoline. This prepolymer can be used not only as a macromonomer, but also as a reactive polymer for the synthesis of functional polymers by exploiting the reactivity of the end oxazoline group toward carboxyl groups.

1-methoxy-2-methyl-1-trimethylsiloxy-1, 3-butadiene (MTB 25, table 1.3) cannot be radically homopolymerized in bulk presumably due to the stability of the conjugated π-electron system towards a radical attack. Because of substituents -OCH$_3$ and -OSiMe$_3$, MTB has more character of a polar compound, not able to stabilize a radical as active center in a free radical polymerization. It is also impossible to polymerize macromonomers of MMA from MTB by AIBN. Again, olefinic double bond at the end of each macromonomer seems to be less reactive in an addition step to a 1-cyano-1-methylethyl radical.
Table 1.3. Functional initiators for PMMA macromonomer synthesis via initiator method in GTP

<table>
<thead>
<tr>
<th>Entry</th>
<th>Initiators</th>
<th>Catalyst</th>
<th>$M_n$ (Theory)</th>
<th>$M_n$ (SEC)</th>
<th>$M_n$/M_n</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>1</td>
<td>VPKMTMSA 23</td>
<td>TAS$_2$SiMe$_3$</td>
<td>3000</td>
<td>3600</td>
<td>1.09</td>
<td>97, 99</td>
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<tr>
<td></td>
<td></td>
<td>TBACN</td>
<td>7500</td>
<td>6900</td>
<td>1.55</td>
<td></td>
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<tr>
<td>2</td>
<td>Trimethylsilyl-2-methyl-2-oxazoline 24</td>
<td>TAS$_2$SiMe$_3$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>98</td>
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<tr>
<td>3</td>
<td>MTB 25</td>
<td>TPSHF$_2$</td>
<td>15000</td>
<td>12400</td>
<td>1.69</td>
<td>99</td>
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<tr>
<td>4</td>
<td>MTPD 26</td>
<td>TPSHF$_2$</td>
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<td>1.55</td>
<td>99</td>
</tr>
<tr>
<td>5</td>
<td>MTBD 27</td>
<td>TBACN</td>
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<td>1.25</td>
<td>99</td>
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<tr>
<td>6</td>
<td>28</td>
<td>NBu$_4$OAc</td>
<td>1990</td>
<td>3520</td>
<td>1.09</td>
<td>101</td>
</tr>
</tbody>
</table>

: In none of the cases, information on degree of functionality is available in the literature.

Bandermann also observed no reactivity of these macromonomers in a free-radical copolymerization with styrene. They obtained similar results\(^9\) with initiator 1-methoxy-2-methyl-1-trimethylsilyl-1, 4-pentadiene MTPD.

In contrast to initiators MTB and MTPD (25, 26, table 1.3), the two other initiators, 1-methoxy-2-methyl-4-methylene-1-trimethylsilyloxy-1, 5-hexadiene MTBD (27, table 1.3) and VPKMTMSA (23, table 1.3), can be homopolymerized by AIBN. However, there is a severe restrictions. By $^1$H NMR measurements they found that the silyl ketene acetal groups in the system of a free-radical polymerization give side reactions. Both PMMA
macromonomers from MTBD and VPKMTMSA could be homopolymerized by AIBN in benzene. In the former case both 1,4- and 1,2-addition of butadienyl groups had happened.

Bandermann prepared graft copolymers from styrene and four PMMA macromonomers derived from initiator VPKMTMSA using AIBN at 60°C in benzene for 120 h. They separated all possible products: homopolystyrene, macromonomer and poly(macromonomer), and poly(styrene-g-MMA), the graft copolymer, according to procedure published by Kuhn.

GTP of MMA in THF with initiator 28 (entry 6, table 1.3) afforded the $\alpha$-silylketene acetal of $\alpha$-[2,5-bis(trimethylsilyloxy) phenyl] poly(methyl methacrylate) 29. The polymerization was carried out under solvent reflux conditions. Tetrabutylammonium acetate, oxyanion catalyst for GTP, was used as catalyst, in order to avoid cleavage of the phenolic TMS protective groups by the well-known fluoride or bifluoride catalysts (Scheme 1.18). The living end of 29 was quenched with methanol to give the TMS-protected macromonomer 30 with 76% yield ($M_n = 3520 - 16100$ g/mol, $M_w/M_n = 1.09-1.49$).

Scheme 1.18. Poly (methyl methacrylate) s macromonomers with phenolic functionality
However, a proof for the attachment of the “end group” to the polymer backbone was achieved by using its specific UV-absorption at 291 nm. Desilylation with fluoride and workup in air gave partially oxidized 31 with $M_n = 3780$ and $M_w/M_n = 1.25$

Slow or discontinuous monomer addition resulted in a broadening of the MWD. This means that some deactivation reactions are present in the monomer-deficient system and thus, this system is not living in the common sense\textsuperscript{101}. This was shown by an experiment in which the monomer feed was paused for seven minutes, which caused the reaction temperature to drop from 65 to 46°C. SEC analysis of the isolated polymer revealed a bimodal MWD indicating that more than 80% of the active chain ends had died during the seven minutes when monomer addition was paused. Resuming the monomer feed, the temperature rose to 54°C. Five minutes after the end of monomer addition the reaction was quenched with benzoyl fluoride to give a benzoyl end-group. Additionally, the presence of fluoride liberated from the benzoyl fluoride caused a desilylation-esterification reaction of the hydroquinone moiety to give a polymer 32 with a 2, 5-bis (benzoyloxy) phenyl end-group\textsuperscript{101}.

Reactivity of the macromonomers in condensation reactions was demonstrated by the synthesis of aromatic polyester 33 (PES-graft-PMMA) and a polycarbonate 35 (PC-graft-PMMA). Thus, the macromonomers were used as comonomers in polycondensations with tert-butylhydroquinone and 2-bromoterephthalic acid (Scheme 1.19) and 4,4'-isopropylidenediphenol 34 and bis (trichloromethyl) carbonate (Triphosgene) (Scheme 1.20), respectively. The use of lateral substituents on the acid and the codiol allows easy characterization of the respective homopolyester 36. The cocondensation gave a higher-molecular-weight product with 96% yield for the reaction carried out in solution at ambient temperature using a base as an HCl acceptor than for the reaction carried out in the melt. Melt condensation gave only a limited yield (58%) and a homopolyester portion could be separated from the product\textsuperscript{101}.

Scheme 1.19. PES-graft-PMMA by condensation reaction
A copolycarbonate of 31 and 34 was prepared by the base-catalyzed condensation reaction with triphosgene in CH2Cl2 to give 35 in a 65% yield (Scheme 1.20).

Scheme 1.20. PC-graft-PMMA by condensation reaction

No peak corresponding to residual unreacted macromonomer was detected in GPC. The maximum in the elution curve of the product (corresponding to a molecular weight of 11 400) was found at a higher elution volume than the one for a polycarbonate 37 from 34 (molecular weight at GPC peak M_p = 6780) synthesized by the same method (Scheme 1.21).

Scheme 1.21. Homopolyester and polycarbonate by condensation reaction

1.2.2. Chain end functionalization by electrophilic termination

The reactivity of the silyl ketene acetal group of polymers prepared by GTP provides an opportunity for chain end functionalization by end-capping reactions or coupling of polymer chains by reaction with polyfunctional terminating agents.

Sogah et al. reported the termination of silyl ketene acetal-ended PMMA with benzaldehyde using TASHF2 catalyst at room temperature gives, after desilylation using
TBAF/MeOH, a PMMA with a terminal benzhydryl alcohol group (Scheme 1.22). MMA was polymerized in THF using 1-(2-(trimethylsiloxy) ethoxy)-1-(trimethylsiloxy)-2-methyl-1-propene as initiator and TASHF₂ as catalyst at room temperature. After 2 h, the polymer was terminated with benzaldehyde using additional TASHF₂ catalyst and reacted overnight. After desilylation with TBAF/MeOH at reflux temperature for 1.5 h, a quantitative yield of hydroxy-PMMA was obtained with Mn = 3200 g/mol (Mw/Mn = 1.18).

Webster et al. also reported the termination of GTP living chain end with bromine to produce PMMA-Br. Eastmond also prepared bromine terminated PMMA and utilized in the formation of block copolymers comprised of blocks of PMMA with a narrow molecular weight distribution and blocks of polystyrene with broader distribution. GTP of MMA was achieved by using MTS as initiator and potassium bifluoride in acetonitrile and polymerization was terminated with excess bromine to yield quantitative PMMA-Br with Mn = 12,790 g/mol and Mₙ/Mₚ = 1.2 (Scheme 1.22).

Scheme 1.22. Bromo and hydroxyl end-functional PMMA via electrophilic termination

The PMMA-Br was used to initiate styrene polymerization by free radical polymerization to form block copolymers (ABA and AB type) using dimanganese decacarbonyl under vacuum, and irradiated with light (λ = 436 nm) from an ME/D high-pressure mercury arc for 30 min. Under the reaction conditions employed only a small fraction of the PMMA-Br would have reacted to form radicals.

GTP of simple acrylates using a bifluoride catalyst generally leads to polymers with a broader molecular weight distribution than is observed in GTP of the corresponding methacrylate or GTP of acrylates using Lewis acid catalysts. Thus, polymerization of butyl
acrylate in THF at 0 °C gave poly (butyl acrylate) with $M_n = 27,200$ and $D = 2.16$ (theoretical $M_n = 26,100$).

To obtain insight into the causes of the molecular weight broadening, living ethyl acrylate oligomer (degree of polymerization DP = 4) prepared by TASF-catalyzed GTP was treated with p-nitrobenzyl bromide at -78 °C. Chromatographic purification gave 60% yield of the benzylated product containing both internal and terminal p-nitrobenzyl groups in the ratio of 9:1 (Scheme 1.23). These results suggest that the trimethylsilyl group is capable of isomerizing to an internal position of the poly (acrylate) chain. However, $^{13}$C NMR studies of GTP poly (ethyl acrylate) gave no evidence of branching, suggesting that the internal ketene silyl acetal, while capable of reacting with a benzyl halide, is too sterically hindered to initiate a branch point. Webster provided no evidence to indicate whether or not O- or C-silyl intermediates are formed.

Scheme 1.23. p-Nitrobenzyl end-functional poly (ethyl acrylate) s

Isomerization is presumably slower than chain propagation so that poly (acrylates) remains living, but the decrease in the concentration of “useful” living ends caused by the isomerization may be accountable for the observed broadening of molecular weight distribution. The problems encountered in the anion-catalyzed GTP of acrylates may be avoided by using Lewis acid catalysts.
Quirk and coworkers\textsuperscript{104} developed a functionalization method for GTP using sterically hindered monomers analogous to the substituted 1,1-diphenylethylene chemistry, which has been utilized for anionic polymerization. The monomers used for functionalization were methyl-2-phenylpropenoate (MPHA), ethyl-2-phenyl-2-butenoate (EPB), ethyl-2-methyl-2-butenoate (EMB) and methyl-\(E\)-3-(2-dimethyl aminophenyl)-2-phenyl acrylate (AMPA) (Scheme 1.24). Various functional groups such as \(-\text{NR}_2\), \(-\text{OMe}\), \(-X\) (Br, I, Cl), \(-\text{COOMe}\) etc. could be introduced into poly (alkyl methacrylates) via substituents on the aromatic ring.

![Scheme 1.24. Sterically hindered monomers for functionalization of GTP](image)

The functionalization reactions of MPHA with living PMMA prepared by GTP were investigated under a variety of reaction conditions and stoichiometries. The functionalized polymer was characterized by SEC, VPO, NMR and UV spectroscopy. All of the results were consistent with only monoaddition of MPA to the living silyl ketene acetal chain end at room temperature, even when two molar equivalents of MPHA were present. No evidence for oliomerization was obtained. However, when the addition of MPHA was carried out at \(-78^\circ\text{C}\) with two molar equivalents of MPHA, diaddition to the chain end was observed. This is consistent with the predictions based on the reported ceiling temperature of \(-40^\circ\text{C}\) for MPHA.

The polymerizations were carried using, silyl ketene acetal-ended PMMA with monomers (EPB, EMB and MPB) at room temperature\textsuperscript{104} for 0.5 h using TASHF\(_2\) as catalyst. In the case of EPB, high functionalization efficiency of 95\% (by \(F_n = M_n\) (VPO) / \(M_n\) (NMR), was observed when one molar equivalent of EPB is used. Surprisingly, the functionalization efficiency decreased to 0.6 when functionalizations were carried out with two molar equivalents of EPB. This fact suggested the incursion of a non-living process. It was considered that several variables, such as catalyst activity, temperature etc. could influence the functionalization efficiency. Nucleophilic catalysts promote chain termination as well as propagation, and at sufficiently low monomer concentrations the chain termination rate is
faster than that of propagation. In order to obtain high functionality and to minimize chain termination, catalyst levels should be kept as low as possible. Therefore, a catalyst concentrating of 0.1 mol% based on initiator was used. Temperatures between 0 to 60°C do not have significant effect on the functionalization efficiency (0.92 to 0.87). However, it is reasonable to conclude that functionalization reactions will be favored at lower temperature since chain termination should be minimized at lower temperatures.

EPB could function as a chain transfer agent and that this process would correspond to chain transfer to monomer. When two molar equivalents of EPB was added to the living silyl ketene acetal-ended PMMA in the presence of 0.1 mol% of TASHF<sub>2</sub> catalyst with respect to initiator, it was recognized that a possible non-living process which would lower the functionality due to chain transfer reactions of the living polymer chain ends with the allylic hydrogens in EPB. This result suggests that the functionalization reaction is reversible since the functionality decreases upon addition of a second equivalent of functionalizing monomer. A possible mechanism to explain these results is shown in Scheme 1.25.

Similarly, it was reported<sup>44</sup> that methyl 2-phenyl-2-butenoate (MPB) as well as ethyl 2-methyl-2-butenoate (EMB) acts as chain transfer agent.

The stoichiometric addition reaction<sup>44a</sup> of 1,4-butanediol diphenylacrylate (2-phenylpropenoic acid, 1,4-butanediyl ester (DBPA) (1.2 mmol) with living trimethylsilylketene acetal-ended PMMA (2 mmol, M<sub>n</sub> = 2.1 x 10<sup>3</sup> g/mol, M<sub>n</sub>/M<sub>n</sub> = 1.07) in 20 ml of THF (Scheme 1.26) was carried out for an hour and no unreacted DBPA was detected in the final product by SiO<sub>2</sub> TLC analysis (ethyl acetate/hexane, 1.4 (V/V)). The
molecular weight of the product ($M_n = 3.9 \times 10^3$ g/mol; $M_w/M_n = 1.06$) corresponds closely to the molecular weight expected for dimerization by simple monoaddition of one living chain-end to each acrylate unit in DBPA with coupling efficiency of 94%.

Polymeric materials containing amino groups are important because of the chemical versatility of the amino function. The reaction of methyl-$E$-3-(2-dimethylaminophenyl)-2-phenyl acrylate (AMPA) with living trimethylsilylketene acetal-ended PMMA$^{104a}$ (2 mmol, $M_n = 2.1 \times 10^3$ g/mol, $M_w/M_n = 1.07$) in THF for an hour was investigated as shown in Scheme 1.27. The polymer solution turned slightly yellow on addition of AMPA and the color faded when the reaction was quenched with methanol.

The efficiency of this functionalization reaction$^{104a}$ ($F_n = 0.90-0.93$) was also determined by titrating the dimethylamino groups in the polymer with HClO$_4$ in acetic acid with methylene blue as indicator. Analyses of the resulting amine functionalized polymer by SEC, VPO, $^1$H NMR and end-group titration were all consistent with monoaddition of this non-polymerizable monomer (AMPA) to the living GTP chain-end.
In the case of macromonomer, the method involves termination of living chain end with an electrophile, which contains polymerizable functional group (double bond, heterocycle). Asami first reported\(^{107}\) poly (methyl methacrylate) macromonomer with quantitative styryl terminal functional groups by termination method. As shown in Scheme 1.28 the living PMMA prepared by the polymerization of MMA with the MTS in THF using HF\(_2\) catalyst at room temperature were reacted with vinylbenzyl bromide (or tosylate) using TASF\(_2\)SiMe\(_3\) as catalyst. The styryl terminal PMMA macromonomer obtained were shown to be highly monodisperse (M\(_w\)/M\(_n\) = 1.07 to 1.06 with M\(_n\) = 3250 to 4380 g/mol).

When one equivalent catalyst to the living end is used the functionality (F\(_n\)) determined by UV spectroscopy is high and under experimental conditions the F\(_n\) was found in the range 25 to 83\%. Asami anticipated that less than quantitative functionalization could be due to either a loss of living ends of the PMMA formed by GTP or side reactions in the coupling reaction with vinyl benzyl derivatives.

A summary of end-functional PMMA’s prepared by GTP using functional terminators given in table 1.2. Spinelli reported\(^{105}\) that macromonomers are formed by polymerization of methacrylates with initiators having protected hydroxyl group, followed by deprotection and then by the reaction with (meth) acrylic acid, (meth) acryloyl chloride, isocyanatoethyl methacrylate, trimellitic anhydride. Such macromonomers are suitable for paints in non-aqueous media and in particular for rheology control.

\(\omega\)-Trimethylsiloxy PMMA (38, Scheme 1.29) was prepared by GTP of MMA in THF at 20\(^\circ\)C using TETMP as a functionalized initiator and TBABB as the catalyst. Several procedures were used to convert the resulting \(\omega\)-Trimethylsiloxy PMMA (38, Scheme 1.29) to \(\omega\)-methacryloyl-PMMA (40, Scheme 1.29). \(\omega\)-Trimethylsiloxy PMMA 38 was either directly reacted with methacryloyl fluoride/TBAF\(^{106a}\) or hydrolyzed with subsequent reaction of the resulting \(\omega\)-hydroxy PMMA (39, Scheme 1.29) with methacryloyl...
chloride/trimethylamine\textsuperscript{106b} or methacrylic acid/dicyclohexylcarbodiimide (DCC) (Scheme 1.29).

Table 1.4. Functional terminators for GTP

<table>
<thead>
<tr>
<th>Entry</th>
<th>Terminators</th>
<th>Catalyst/Solvent</th>
<th>$M_w$ (Theory)</th>
<th>$M_w$ (SEC)</th>
<th>$M_w/M_n$</th>
<th>Functional group</th>
<th>$F_n$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Benzaldehyde</td>
<td>TASHF$_2$/THF</td>
<td>3300</td>
<td>2800</td>
<td>1.04</td>
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<td>-</td>
<td>87</td>
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<td>12790</td>
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<td>-Br</td>
<td>-</td>
<td>103</td>
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<td>3250</td>
<td>1.07</td>
<td>Styril</td>
<td>0.83 (by UV)</td>
<td>97</td>
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<td>TASHF$_2$/SiMe$_2$/THF</td>
<td>3000</td>
<td>4380</td>
<td>1.06</td>
<td>Styril</td>
<td>0.73</td>
<td>97</td>
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<td>2100</td>
<td>3600</td>
<td>1.05</td>
<td>$-$C$_6$H$_5$</td>
<td>1.05 (a)</td>
<td>104</td>
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<td>6</td>
<td>EPB</td>
<td>TASHF$_2$/THF</td>
<td>2100</td>
<td>1900</td>
<td>1.03</td>
<td>$-$C$_6$H$_5$</td>
<td>0.94 (b)</td>
<td>104</td>
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<tr>
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<td>TASHF$_2$/THF</td>
<td>2100</td>
<td>2200</td>
<td>1.06</td>
<td>$-$C$_6$H$_5$NMe$_2$</td>
<td>0.93 (by titration)</td>
<td>104 (a)</td>
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The functionality of the macromonomers was determined by $^1$H NMR, using ratio of the signals at $\delta = 5.2-6.2$ (vinyl protons) to $\delta = 4.1-4.4$ (ethyl protons of initiator). It was poorly reproducible for the methacryloyl chloride method, ca. 75% for methacrylic acid/DCC and 80-100% for methacryloyl fluoride (Scheme 1.29). The fraction of unfunctionalized polymer was taken into account for the determination of macromonomer conversion.

Cohen reported\textsuperscript{106b} macromonomers of $M_n = 3000-40,000$, with up to 95% terminal vinyl functionality (where as methacryloyl chloride gave only 4% terminal vinyl functionality), were prepared by extending the acylation chemistry to PMMA silyl ethers and thereby avoiding the need to hydrolyze them to PMMA-OH. Silyl ether was chosen for reaction with methacryloyl fluoride (MAF) because the silyl ketene acetal-end of PMMA failed to
give the desired product. It needs about 50-500 times more catalyst than SKA (5-15 mol% F⁻ or carboxylate, depending on polymer molecular weight), or else acylation is limited or negligible. Polycondensations (Cl⁻ catalyzed) using aryl silyl ether and acid chloride generally occur at 200-300 °C.

Scheme 1.29. Synthesis of methacryloyl-terminated PMMA macromonomer by GTP

The macromonomer technique is the only method available to prepare well-defined graft polymers containing nearly monodisperse branches of controlled molecular weight. McGrath and co-workers synthesized¹⁰⁶b a novel all-PMMA comb polymer by a combination of GTP and anionic polymerization (Scheme 1.30).

Scheme 1.30. Comb-shaped poly (methyl methacrylate) s by a combination of GTP and anionic polymerization

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The resulting comb had a Mn = 2,48,6000, with an average of 14 grafted PMMA chains per molecule. The grafted PMMA chain had a Mₙ = 6300 and Mₙ/Mₚ = 1.11. Additional examples of comb-grafted polymers via GTP have been reported by Heitz and Webster, Hertler et al., and Jenkins et al.

1.3 Comparative efficiencies of chain end functionalization of PMMA’s by LAP, GTP and ATRP

End-functional polymers synthesized via LAP, GTP and ATRP have the advantage of narrow molecular-weight distribution and high number average degree of functionality (Fₙ). In this section we provide a comparative evaluation of chain end-functionalization of (meth)acrylates using LAP, GTP and ATRP techniques.

1. GTP and LRP can be performed at room temperature or above, whereas, LAP requires low temperatures (-78°C).

2. GTP and LRP can be performed in solvents like toluene and even in bulk. However, LAP works best only in THF.

3. LRP is more tolerant of reactive functional groups in the monomer. GTP, and LAP requires protection of reactive functionalities prior to polymerization.

4. Functional groups can be introduced in the polymer through use of either functional initiators or suitable terminating agent in case of GTP and LAP. In case of LRP, use of functional initiator is possible. However, since the chain end is generally capped by a halogen group, functionalization of chain end requires a separate post polymerization reaction.

5. High Mₙ with a high number average degree of functionalization (Fₙ) is possible in case of LAP. However, attempts to increase Mₙ generally leads to loss of Fₙ in the case of GTP and LRP.

6. Where as use of functional initiators is the preferred method of introducing functionality in ATRP and LAP, GTP is amenable to use of both functional initiators and termination by
electrophiles. Consequently, the range of functional groups that can be introduced is far more diverse for GTP.

1.4. Scope and objectives of present work

Hydroxyl, carboxylic acid-terminated PMMA\textsuperscript{87} and macromonomer\textsuperscript{97} by GTP obtained by employing properly designed initiators. The use of functional initiators ensures that each polymer chain contains one functional group, but initiators of this type are of limited availability and generally requires protection of the functional group. However, little attention has been paid to the study of GTP technique for the synthesis of end-functional poly(alkyl methacrylate)s by `electrophilic termination’ of the living ketene silyl acetal chain ends. Hydroxyl\textsuperscript{87}, bromine\textsuperscript{102,103}, amine\textsuperscript{104} end-functional and a styryl ended macromonomer\textsuperscript{97} of poly (methyl methacrylate) are reported by terminating the living GTP chain-ends of PMMA with benzaldehyde, bromine, methyl E-3- (2-dimethylaminophenyl)-2-phenylacrylate, and with 4-(bromomethyl) styrene respectively. Some other end-capping reactions of silyl ketene acetals with benzyl bromide\textsuperscript{109,110} benzoyl fluoride, benzoic anhydride and many other reagents\textsuperscript{108c} were reported in patents issued to DuPont. The disadvantage of this type of functionalization is that any polymer chains that are not living will not result in functionalization. All of the functionalization reactions reported in the literature have not been adequately optimized or characterized for general utility.

Sogah et al., reported\textsuperscript{87} PMMA with a terminal benzhydryl alcohol group by end capping reaction of silyl ketene acetal ended PMMA with benzaldehyde using TASHF\textsubscript{2}. However detailed information on functionalization efficiency was not provided.

Quirk et al., reported\textsuperscript{104} living functionalization of PMMA by GTP using sterically hindered, low ceiling temperature monomers like methyl-2-phenylpropenote (MPHA). Although oligomerization of MPHA is observed at −78°C, this is reversible and only monoaddition is observed at room temperature. Similarly, amino-functionalized PMMA was prepared quantitatively (proceeds via monoaddition) by end-capping reactions of silyl ketene acetal-ended PMMA with methyl E-3-(2-dimethylaminophenyl)-2-phenylacrylate using TASHF\textsubscript{2} as a catalyst. According to their methodology, various functional groups can be introduced via substituents on the aromatic ring of MPHA. Furthermore, they anticipated that these reactions maintain the living nature of the chain-end.
Asami\textsuperscript{9} reported poly (methyl methacrylate) macromonomer by reacting silyl ketene acetal ended PMMA with vinylbenzyl bromide or tosylate using one equivalent catalyst TASF\textsubscript{2}Si-Me\textsubscript{3} in THF with $M_n = 4000$ g/mol ($M_w/M_n = 1.1$) and with ~ 83\% functionality. Lower extent of functionalization can be ascribed to either a loss of living ends of the PMMA or to side reactions in the coupling reaction with vinylbenzyl derivatives.

All of the above end-functional PMMA's were prepared using moisture sensitive catalyst TASHF\textsubscript{2}/ TASF\textsubscript{2}Si-Me\textsubscript{3} in THF. Here we report use of non-hygroscopic catalyst TBABB for functionalization reactions along with model reactions as each functionalization/end-capping reaction is unique and optimized the reaction conditions to obtain high functionalization efficiency. Also we herein report our efforts to prepare lactone-end capped PMMA (macromonomer) and anhydride terminated PMMA for the first time via GTP and characterized by state-of-the-art MALDI-ToF mass spectrometry which is a powerful technique for the fast and accurate determination of a number of polymer characteristics.

1.4.1. Objectives of the present work:

1) To examine electrophilic termination of silyl ketene acetal ended poly (methyl methacrylate)s in group transfer polymerization. A model reaction between 1-Methoxy-1-(trimethylsiloxy)-2-methylprop-1-ene (MTS) and benzaldehyde will be studied to establish the most suitable condition for reactions. Hydroxyl terminated PMMA will be synthesized via GTP by terminating silylketeneacetal ended PMMA with benzaldehyde using TBABB catalyst.

2) To explore the synthesis of lactone end-capped poly (methyl methacrylate) by group-transfer polymerization. Bayer-Villiger rearrangement of cyclohexanone end-capped PMMA will be carried out to prepare lactone end-capped PMMA. The conjugate addition of silyl ketene acetal with cyclic $\alpha, \beta$-unsaturated esters will be carried out. Functionalization of living GTP chain-end with cyclic $\alpha, \beta$-unsaturated esters to obtain directly lactone-end capped PMMA is attempted.
3) To prepare amine-terminated poly (methyl methacrylate) by group-transfer polymerization. The functionalization reaction of the living ketene silyl acetal ended PMMA with N-trimethylsilyl benzaldehyde will be studied to accomplish this goal.

4) To synthesize anhydride-terminated poly (methyl methacrylate) by group-transfer polymerization. For this, model reactions between MTS and various unsaturated anhydrides namely, itaconic anhydride, citraconic anhydride, maleic anhydride, 2,3-dimethylmaleic anhydride will be carried out to establish the feasibility of preparing anhydride-terminated poly (methyl methacrylate).

1.5 References


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