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New Synthetic Methods

New Synthetic Methods

With contributions by

Y. Chujo · R. Faust · Y. Kwon · K. Naka

J.J. Robin · T. Uemura · O.W. Webster



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Group Transfer Polymerization: Mechanism and Comparison with Other Methods for Controlled Polymerization of Acrylic Monomers

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Abstract Group transfer polymerization (GTP) was announced 20 years ago by DuPont as a method for synthesis of acrylic block polymers. It operates at high enough temperatures to allow reactor cooling by water-cooled reflux condensers, rather than more costly refrigeration units. GTP uses 1-methoxy-1-(trimethylsiloxy)-2-methylprop-1-ene (MTS) as initiator and a carboxylic acid salt as catalyst. The number of growing polymer chains corresponds to the amount of MTS used. Chain growth stops when the monomer is depleted. Addition of a new monomer at this point starts chain growth again to produce a block polymer. DuPont sells pigmented inks containing GTP block polymer dispersing agents.

Initial mechanism studies pointed to a trimethylsilyl transfer process that now appears to be incorrect. Strong evidence is presented for a dissociative anionic process. Reactivation of silylated chain ends by the alkoxide eliminated during end group cyclization is proposed as the reason GTP works at 80 °C.

A comparison of GTP with other methods for block polymer synthesis is presented.

Keywords Group transfer polymerization · Polymethacrylates · Polyacrylates · Living polymerization · GTP mechanism · Living anionic polymerization of MMA

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List of Abbreviations

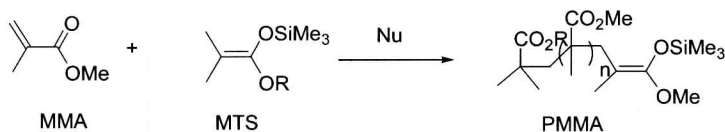
Ac	Acetate
ATRP	Atom transfer polymerization
BMA	Butyl methacrylate
Bz	Benzoate
CCT	Catalytic chain transfer
DP	Degree of polymerization
GTP	Group transfer polymerization
MA	Methyl acrylate

MMA	Methyl methacrylate
MTS	1-Methoxy-1-(trimethylsiloxy)-2-methylprop-1-ene
Mn	Number average molecular weight
Mw	Weight average molecular weight
MWD	Molecular weight dispersity, Mw/Mn
MW	Molecular weight
P	Polymer
P5	Tetrakis[tris(dimethylamino)phosphoranylidene-amino]phosphonium
PBMA	Poly(butyl methacrylate)
PMA	Poly(methyl acrylate)
PMMA	Poly(methyl methacrylate)
RAFT	Reversible addition fragmentation transfer
S	Styrene
SFRP	Stable free radical polymerization
TAS	Trisdimethylaminosulfonium
TBA	Tetrabutylammonium
tol	Tolyl
TEMPO	2,2,6,6-Tetramethyl-1-piperidinyloxy
TMS	Trimethylsilyl

1

Introduction

Twenty years have passed since DuPont announced a startling new process for polymerization of methacrylate monomers [1]. The method uses a trimethylsilyl ketene acetal initiator catalyzed by nucleophilic anions. It operates at 80 °C and gives unprecedented control over polymer chain architecture (Scheme 1).



Scheme 1

Based on evidence available at the time, the DuPont workers proposed that the trimethylsilyl group was transferring to monomer as it was adding to the polymer chain ends and thus named the new procedure Group Transfer Polymerization (GTP). Based on all the evidence *now* available this mechanism is almost certainly wrong but the name should remain since it is firmly imbedded in the chemical literature.

There are already several excellent detailed reviews on GTP [2–5]. In this chapter I will critically analyze the existing data that strongly support a dissociative (anionic) mechanism originally proposed by R. Quirk of Akron University [6]. I will also explain how GTP can operate at 80 °C when it is well known that the classical anionic polymerization of methacrylates does not proceed above ambient temperatures. In addition, GTP will be compared to other controlled polymerization methods.

2

Desirable Attributes for Commercial Controlled Polymerization of (Meth)acrylates

During the mid-1970s DuPont investigated the living polymerization of methacrylate monomers by anionic initiation at –80 °C [7]. Di and tri block polymers were made that had potential for use as pigment dispersing agents and for rheology control. The project was abandoned when calculations showed that the refrigeration necessary to keep the reactors at –80 °C was too costly. To be commercially viable the following characteristics for controlled polymerization were deemed necessary:

- Operating temperatures in the 50–80 °C range so that reflux condensers can be used to remove the heat of polymerization
- The ability to make block polymers containing no more than 10% homopolymer (minimal chain termination)
- Nearly colorless product
- Low sensitivity to impurities
- Overall cost of resin under \$5/lb
- Ability to produce resin with molecular weights in the 20,000 range and molecular weight distributions (MWDs) under 1.3
- Minimal metallic or halide impurities in the final product
- Nontoxic ingredients
- Product free from unpleasant odors

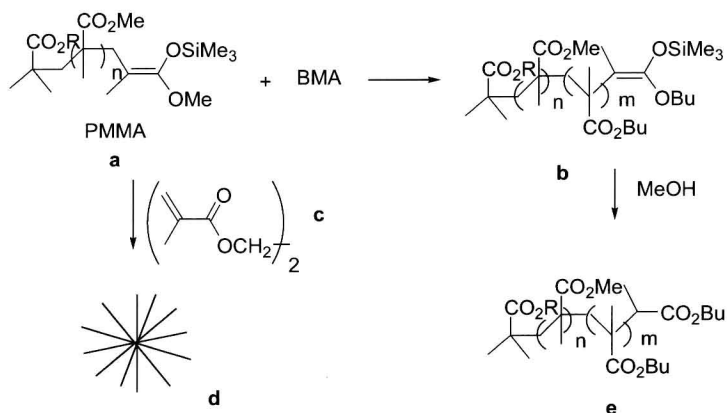
Group transfer polymerization meets most of these criteria. However, it is sensitive to protic impurities and the present cost of the initiator is too high. Other living processes for polymerization of (meth)acrylates will be evaluated with respect to these criteria.

3

The GTP Process

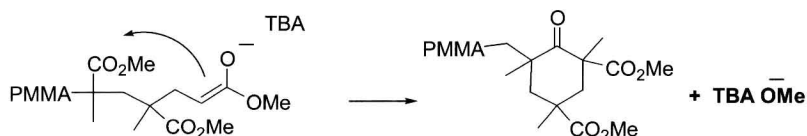
As shown in Scheme 1, GTP converts methacrylate monomer to a polymer with one end group corresponding to the R on the initiator and the other end a trimethylsilyl ketene acetal. If the initiator contains a vinyl group not reactive to GTP, a macromonomer results [8]. The silyl ketene acetal end can be used to initiate another monomer, for example butyl methacrylate, to give

a block polymer (Scheme 2b) [1] or with other reagents to add additional functionality. Thus benzaldehyde generates a phenylhydroxymethyl end [9]. Reaction of silyl ended polymer with a difunctional methacrylate (Scheme 2c) generates a multi-armed star polymer (Scheme 2d) [10]. GTP can be quenched by addition of methanol (Scheme 2e) [1]. Thus one can safely abort a polymerization run that is proceeding too fast.



Scheme 2

GTP operates at temperatures up to 100 °C when catalyzed by weak nucleophiles such as tetrabutylammonium benzoate [11]. Molecular weights in the 20,000 range are easily obtained but generation of polymer in the 60,000 range is difficult. As in other living systems the molecular weight is controlled by the monomer/initiator ratio and the MWDs are narrow. During the polymerization especially at higher temperatures the resulting polymer will contain up to 30% dead ends, the result of backbiting of enolate chain ends (Scheme 3) and/or reaction with protic impurities [10]. Brittain [12] has studied chain termination and found that at the trimer stage (3 DP) the rate of backbiting is ten times that occurring at higher DPs. Thus one should start GTP with more than three equivalents of monomer to by-pass the trimer stage quickly.



Scheme 3

The tetrabutylammonium (TBA) catalysts are slowly consumed during the progress of the polymerization and in longer runs additional amounts




$$\text{Bu}_3\text{N}^+-\text{CH}_2-\text{CH}_2\text{Et} + \text{RCO}_2^- \longrightarrow \text{Bu}_3\text{N} + \text{H}_2\text{C}=\underset{\text{H}}{\text{C}}-\text{Et} + \text{RCO}_2\text{H}$$

$$\downarrow$$

$$\text{Bu}_3\text{N} + \text{RCO}_2\text{Bu}$$

It would be of interest to see if the more stable cesium carboxylates would be better catalysts for GTP than TBA carboxylates since Quirk showed that cesium 9-methylfluorenone works as well as TBA 9-methylfluorenone as a catalyst in his mechanism studies [6].

GTP Monomers

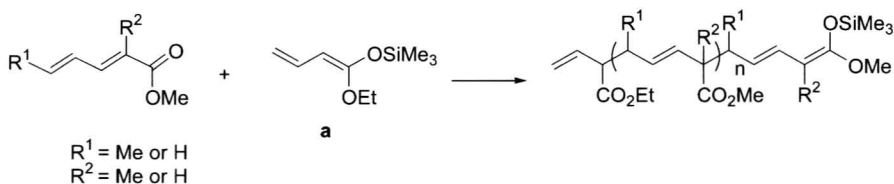

 $R =$


, OSiMe₃ , Me , Bu , t-Bu

Acrylates polymerize two orders of magnitude faster than methacrylates by anion catalyzed GTP; however, the polymerization dies at about 10,000 MW. During the anion catalyzed 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 [9].

The living polymerization of acrylates by GTP does proceed under Lewis acid catalysis [14]. ZnCl_2 or ZnBr_2 are effective but require concentrations of catalyst at a level of 10% based on monomer. R_2AlCl works at lower levels. However, HgCl_2 activated by TMS iodide is the best Lewis acid system and

gives living acrylate polymers at low catalyst levels [15]. For industrial use the toxicity of mercury compounds is a problem.

Under GTP conditions conjugated dienoates as well as trienoates polymerize faster than methacrylates with anionic catalysis. The dienesilyl acetal **6a** is a better initiator than MTS [16] (Scheme 6).



Scheme 6

Acrylonitrile and methacrylonitrile (MAN) polymerize extremely rapidly by GTP [9]. Molecular weight control is difficult since the polymers form before uniform mixing occurs. Although **7a** can be used to initiate MAN, MTS is better. The silyl imine end **7b** is the likely chain carrier (Scheme 7).

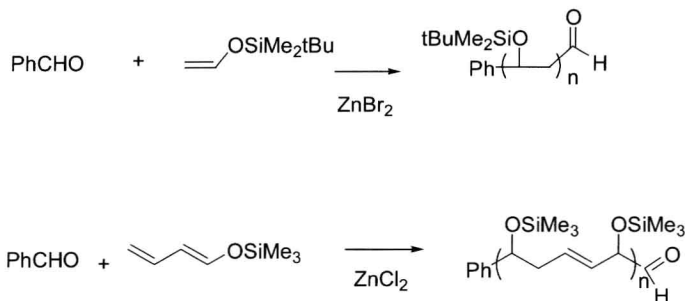


Scheme 7

3.2

Aldol GTP

In a process related to GTP, aldehydes initiate the polymerization of silyl vinyl ethers and silyl diene ethers. Here the silyl group is present in the monomer and transfers to the aldehyde ended chains regenerating aldehyde ends [17] (Scheme 8). A Lewis acid catalyst is required. *tert*-Butyldimethylsilyl works best as a transfer group for vinyl ether while trimethylsilyl is suitable for diene ethers [18]. Even though aldol GTP provides a route to polyvinyl alcohol segments in the subsequent block polymer synthesis, the projected cost of the monomers discouraged further research aimed at commercialization.

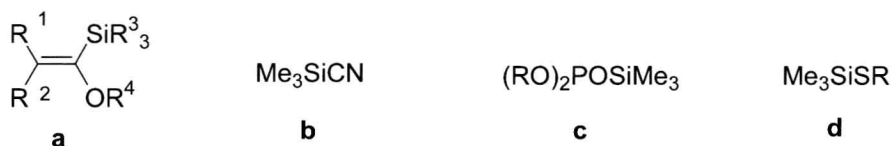


Scheme 8

3.3

Initiators for GTP

To obtain polymer with low MWDs in a living polymerization the rate of initiation must be faster or similar to the rate of propagation. This can suitably be accomplished if the structure of the initiator is the same as that of the growing chain end. For GTP this is a silyl ketene acetal (Scheme 9). The



If $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{R}^4 = \text{Me}$ then "a" is MTS

Scheme 9

pre-ferred initiator for GTP is MTS where R^1 , R^2 , R^3 , and R^4 are all methyl groups [1]. MTS is made by addition of trimethylsilane to MMA and, although it is commercially available, it is relatively expensive. A low cost initiator would greatly increase the use of GTP for commercial products. If R^1 is large and R^2 methyl, initiation is not retarded but if both R^1 and R^2 are large the ketene acetal will not work as an initiator [9]. Trimethylsilyl is ideal for the silyl function. Phenyldimethylsilyl seems to have about the same activity as MTS but *tert*-butyldimethyl [9] and triethylsilyl [19] groups are much less reactive. Large groups on the ether function R^4 do not appear to affect the rate of initiation [9]. Silyl ketone enolates initiate GTP but the rate of initiation is slower than the rate of propagation [20]. A number of silicon compounds initiate GTP by first adding to the methacrylate monomer to generate silyl ketene acetals (Scheme 9b,c,d).

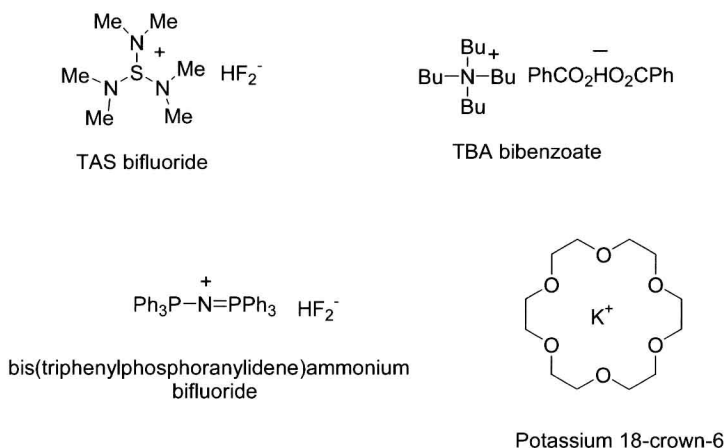
3.4

Catalysts for GTP

3.4.1

Nucleophilic Anions

The preferred catalysts for GTP are nucleophilic anions. The most active catalysts are fluorides and bifluorides [1]. At above ambient temperatures, however, carboxylates and bicarboxlates are preferred [11]. A large counter ion is required for maximum efficiency. In the early work trisdimethylaminosulfonium (TAS) was used, but later the more readily available tetrabutylammonium (TBA) salts have gained favor. Since TBA slowly decomposes under the basic conditions used for GTP, other positive ions may work better. Quirk used cesium ion for his mechanistic studies and found it to be equivalent to TBA [6]. Bywater worked with the very stable $\text{Ph}_3\text{PNPPh}_3^+$ bifluoride in his mechanistic probes [19] and Jenkins [21] showed that potassium complexed with 18-crown-6 was a possible alternative to TBA (Scheme 10).



Scheme 10

The catalysts are used at about 1–0.1% vs initiator concentration; in fact if too much catalyst is used the polymerization ceases [1].

3.4.2

Lewis Acids

Lewis acid catalysts were discussed in the acrylic monomer section. They are used at about 10% concentration vs monomer. Although no significant research has been done with them, other than looking for new ones, they most likely work by activating the monomers. Type Y zeolites catalyze GTP at about 25% concentration vs initiator. Conversions are quantitative and