

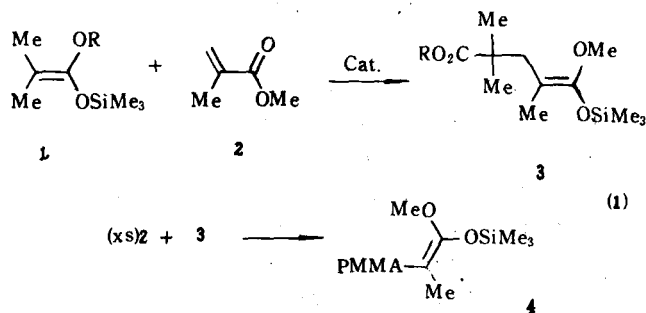
THE CONTROL OF POLYMETHACRYLATE MOLECULAR STRUCTURE BY GROUP TRANSFER POLYMERIZATION

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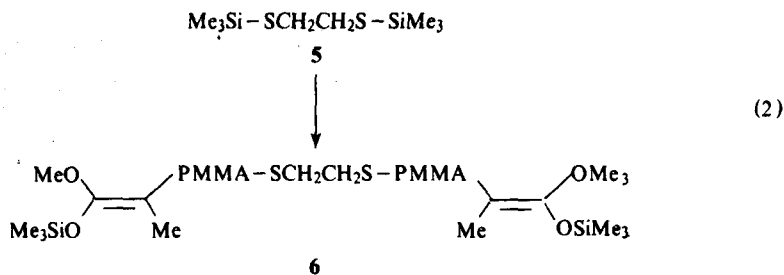
INTRODUCTION

Group transfer polymerization (GTP) is a method for controlling the structure of acrylic polymers in which reactive chain ends are covalently bound to a trimethylsilyl group^[1,2]. In the presence of a catalyst, monomer inserts into these chain ends between the silyl group and the last monomer unit. The process is illustrated by equation (1) for methyl methacrylate. GTP is a living polymerization, i. e., there is little or no chain termination and no chain transfer^[3]. A significant advantage of GTP is that it operates at room temperature and above. Most anionic polymerization of acrylic monomers, on the other hand, operate well only at low temperatures^[4].



INITIATORS

In any living polymerization, the initiator must react with monomer at a rate comparable to or faster than the rate of chain propagation if one is to obtain low polydispersity. This is most readily accomplished if the initiator structure is similar to that of the growing chain end. For GTP therefore silyl ketene acetals are ideal initiators. The most commonly used is 1, where $R = \text{Me}$. A number of silyl derivatives which add to acrylic double bonds to generate a silyl ketene acetal also function as initiators, for example, XSiMe_3 , where $X = -\text{CN}$, $-\text{SR}$, $-\text{CH}_2\text{CO}_2\text{R}$ or $-\text{OP}(\text{OEt})_2$ ^[2]. If X is multifunctional, for example, as in 5, polymer chains with more than one active growing end, as in 6, will result^[5] (Equation 2). RS-SiMe_3 is claimed to be better for acrylate initiation than is 1^[5]. This is unlikely since after initiation, the growing chain end would be the same in each case.

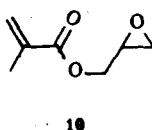
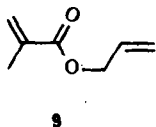
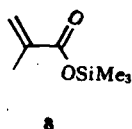
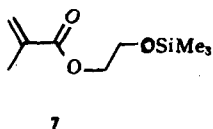


CATALYSTS

Catalysts for GTP include a large number of mildly nucleophilic salts^[6], as well as, mild Lewis acids^[7]. Soluble bifluorides are by far the most active catalysts. However pure bifluorides are difficult to prepare and keep, therefore tetraalkyl ammonium carboxylates are the catalysts of choice. Low levels of catalyst work best (about 0.1–1% based on initiator). Mercuric iodide^[8] is the best catalyst for acrylate polymerization by GTP. Surprisingly it does not catalyze GTP of methacrylates. Lewis acids in general are not preferred for GTP catalysts since amounts comparable to initiator must be used.

MONOMERS

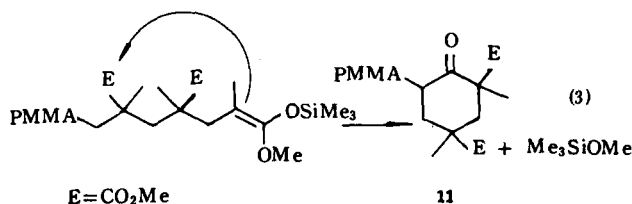
Acrylic monomers in general undergo GTP^[2]. The order of reactivity is: acrylonitrile > methacrylonitrile > acrylates > dieneoates > methacrylates. A reactivity ratio, $r_{\text{mm}} = 0.44$ and $r_{\text{bm}} = 0.26$, was determined for MMA and BMA^[9]. Since GTP must be conducted under aprotic conditions, monomers which contain hydroxy and amino functions must be protected during polymerization. A trimethylsilyl group is adequate for this purpose. For example to obtain poly(hydroxyethyl methacrylate) one can polymerize **7**^[2] and to obtain poly(methacrylic acid) one can polymerize **8**^[10]. Monomers which contain free radical sensitive functionality, for example **9**, and acid and base sensitive functionality, such as **10**, are readily polymerized by GTP^[2].



MOLECULAR WEIGHT CONTROL

Acrylates, dieneoates^[11], and methacrylates, polymerize to give molecular weights which are regulated by the monomer/initiator ratio. The molecular weight dispersity is

typically in the 1.3 range and under ideal conditions approaches 1.0. Chain termination occurs by a cyclization process in which the silyl ketene acetal end group reacts with the second ester group from the end to produce a cyclohexanone ring on the end of the polymer ring^[12] (Equation 3). This termination process occurs at about 1/100 the rate of chain propagation and is the major cause for the deviation of molecular



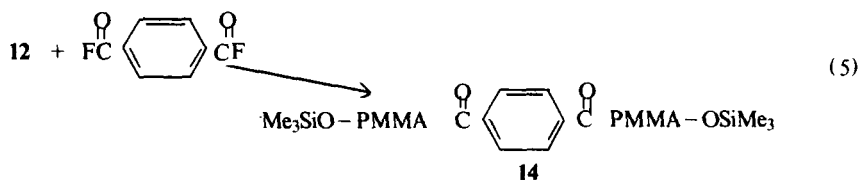
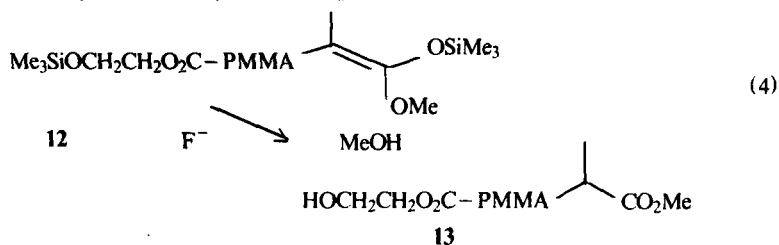
weight dispersity from ideality. Dead chain ends also result from protic impurities. Acrylonitrile and methacrylonitrile polymerize extremely rapidly under GTP conditions to give high molecular weight polymer. There appears to be little or no correspondence of molecular weight to initiator concentration^[2].

CHAIN STEREOCHEMISTRY

The principal parameters influencing tacticity of GTP PMMA are catalyst and temperature. the isotactic component remains small under all conditions, while the syndiotactic component increases from 50 to 80% as the temperature is lowered to -90°C . The tacticity of PMMA produced by GTP is similar to that of free radical produced polymer and is not sensitive to solvent parameters as is PMMA produced by anionic polymerization. Lewis acid catalyzed GTP produces polymer with a higher syndiotactic content than anionic catalysis does^[2].

END GROUP CONTROL

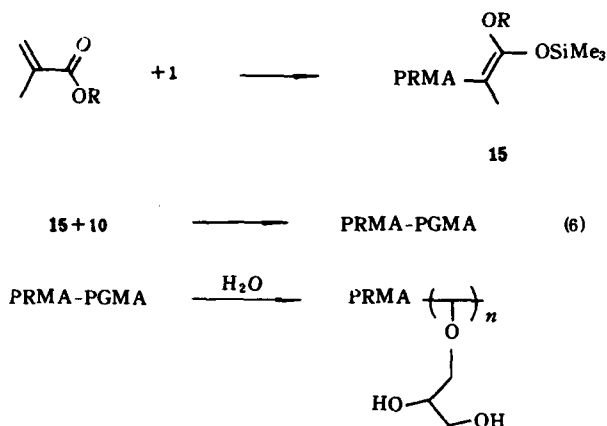
The ability to obtain linear polymer chains with reactive functionality on one or both ends is highly useful for later synthesis of block and graft copolymers. One can readily do this with GTP by using an initiator bearing the functional group (in a masked form if reactive to GTP conditions). For example, to get hydroxy ended polymer, 13, one initiates MMA with 1 where $R = -\text{CH}_2\text{CH}_2\text{OSiMe}_3$ and removes the silyl group by fluoride catalyzed solvolysis^[13] (Equation 4).



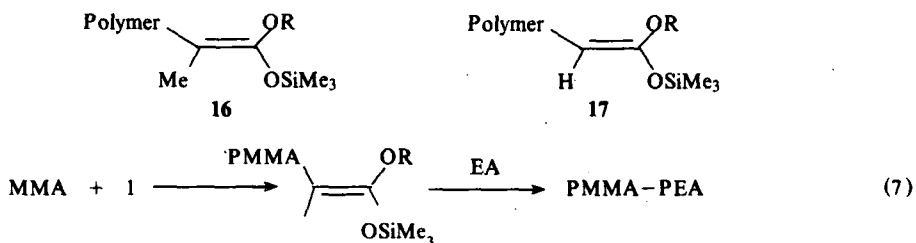
A telechelic polymer, **14**, can be made by coupling a chelic polymer, for example **12** (Equation 5). Although earlier work^[14] used dibromo-*p*-xylylene as the coupling agent, better results have recently been obtained with terephthaloyl fluoride^[13].

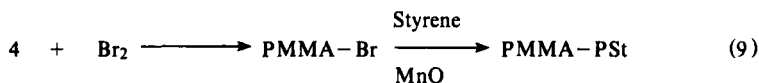
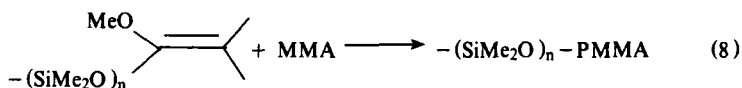
BLOCK COPOLYMERS

Block copolymer formation in the methacrylate series can be accomplished with ease. One simply adds a new monomer when the first one is depleted. Highly efficient pigment dispersants can be made by placing a block of glycidyl methacrylate on the end of a methacrylate chain which is similar in composition to the resin in which the pigment is to be dispersed. The glycidyl groups are then ring opened to form a polar end block which adsorbs on the pigment particles^[15] (Equation 6).



Block polymer formation from two dissimilar monomers presents some problems. In general one can proceed from a block of the least reactive monomer to a block of the more reactive monomer. This is so because the reactive ends, e. g. **16**, from the less reactive monomer are more reactive as initiators than the ends from the reactive monomer, e. g. **17**. Under these conditions, initiation of the second block is faster than propagation and all the chain ends grow at the same rate. If the reverse order is used, during the second block formation the first formed chains would grow faster than new chains would be initiated, resulting in nonuniform blocks. The synthesis of PMMA/PEA block polymer illustrates this principle^[1] (Equation 7). A combination of two types of polymerization can be used to make dissimilar block polymers. Thus polysilane/bPMMA was made by a combination of GTP with anionic polymerization^[16] (Equation 8). A combination of GTP with free radical polymerization was used to make PMMA/styrene block polymer^[17] (Equation 9)



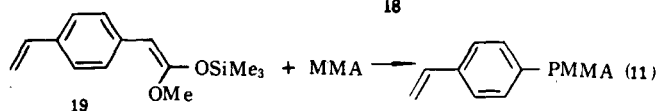
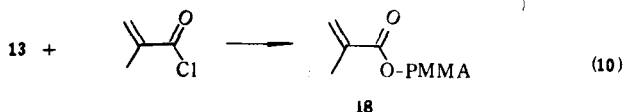


RANDOM COPOLYMERS

The formation of random copolymers by GTP is readily accomplished if one chooses monomers from a given family, for example methyl methacrylate and butyl methacrylate. Generating random copolymers from dissimilar monomers, for example acrylates and methacrylates is difficult. The acrylates polymerize about 100 times faster than methacrylates and the initial polymer produced is mainly polyacrylate followed by methacrylate rich polymer. When one adds an acrylate slowly to a pool of polymerizing methacrylate it will be introduced in a more or less random manner until near the end of the run, then, as the concentration of methacrylate decreases, blocks of acrylate will form^[2].

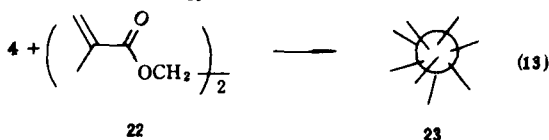
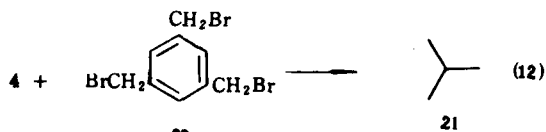
GRAFT OR COMB POLYMERS

The most convenient route to graft polymers is through polymerization of macromonomers. Macromonomers can be made by attachment of a vinyl monomer to a reactive ended polymer made by GTP. Thus hydroxy ended PMMA, **13**, was converted to macromonomer **18** by reaction with methacryl chloride **15** (equation 10). Another route to macromonomers is through use of a GTP initiator containing a vinyl group inert to GTP conditions, like the one present in **19**^[18] (Equation 11). Macromonomers are polymerized by free radical initiation usually in the presence of a comonomer to give graft polymers.



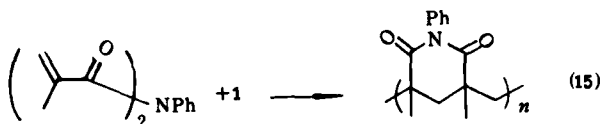
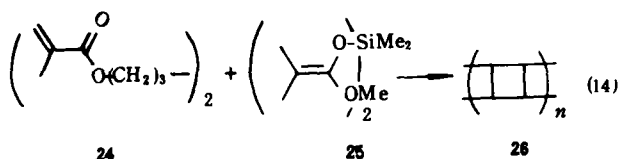
STAR POLYMERS

Star polymers result when living GTP polymer is coupled with a polyfunctional alkylating agent. For example, treatment of **4** with **20** gives the three armed star **21**^[2] (Equation 12). When a difunctional methacrylate, **22**, is added to living GTP polymer a star with a dispersity of arms, **23**, is produced^[15] (Equation 13). Star polymers with hydroxy ends blended with enamels improve the hardness / flexibility ratio of the the enamel.



LADDER POLYMERS

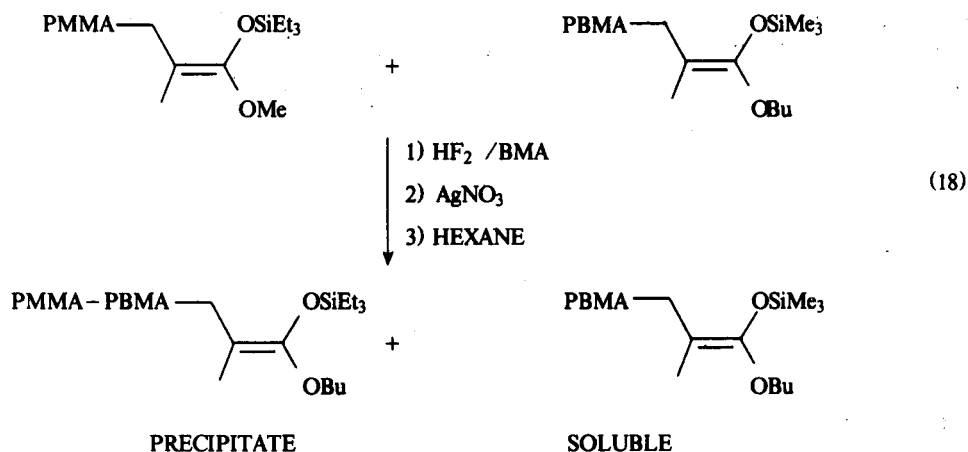
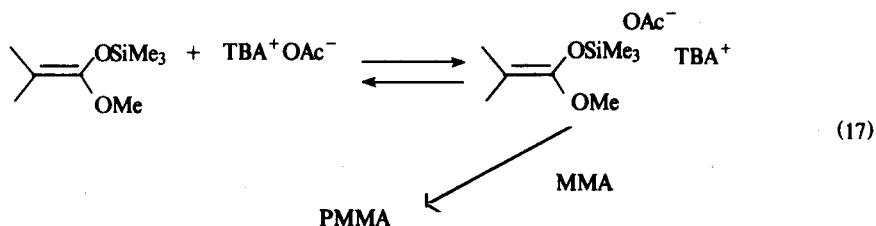
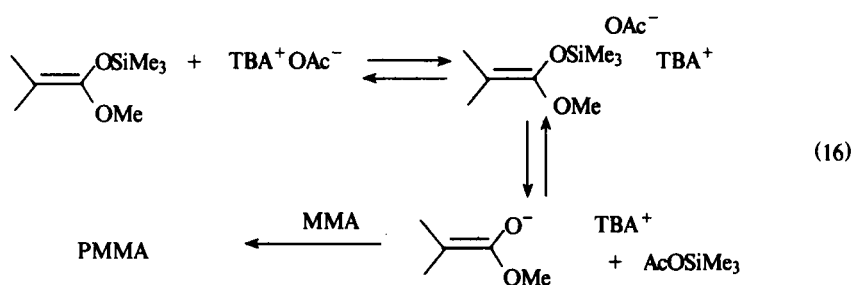
Ladder polymers, **26**, result when a dilute solution of difunctional monomer with a suitable spacer between the monomer units, **24**, is treated with a difunctional initiator, **25**,^[19] (Equation 14). When the difunctional monomer has the correct spatial configuration cyclopolymerization occurs^[20] (Equation 15).



MECHANISM

The main mechanistic question for GTP is whether monomer addition takes place through steady state generation of minute quantities of ester enolate (dissociative group transfer) (Equation 16) or by insertion of monomer into activated covalent chain ends (associative group transfer). (Equation 17). A double labelling experiment shows that during chain growth each trialkylsilyl group stays with the chain it started with^[21]. Thus a PMMA chain with $-\text{SiEt}_3$ on its reactive ends retains the $-\text{SiEt}_3$ group when mixed with living PBMA with a $-\text{SiMe}_3$ on its reactive end during polymerization of BMA (equation 18). This experiment plus the low temperature requirement for traditional living anionic polymerization of methacrylates with lithium gegenions seemed to rule out the dissociative mechanism. However, some recent work^[22] with tetrabutylammonium gegenions indicates that living anionic polymerization can be conducted at room temperature. This result brings up the possibility that addition could be taking place through an ion pair where the trialkylsilyl group stays in the solvent cage and returns to the chain end from whence it came.

GTP kinetics have been studied^[23,24,25]. The rate of initiation with **1** is faster than propagation. The reaction is first order with respect to carboxylate catalysis but second order with respect to catalyst when bifluoride is used^[23]. This result indicates that two



equivalents of bifluoride generate F^- and H_2F_3^- and that F^- is the true catalyst. GTP appears to proceed at rates comparable to anionic polymerization when one corrects for the equilibrium concentration of active ends produced by the catalyst.

Although no mechanistic studies have been conducted, Lewis acid catalyzed GTP is almost certainly associative and operating by monomer activation. (Polymerization of an electron deficient monomer by a cationic process would be highly unlikely).

SOME PROCESSES RELATED TO GTP

In aldol GTP^[26] a silyl vinyl ether monomer (27) adds in two fragments to an aldehyde initiator. In the process a new aldehyde group is generated for addition of more monomer. A silylated poly (vinyl ether), 28, is produced. Removal of the silyl groups by hydrolysis gives poly (vinyl alcohol) (Equation 19).

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