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Mechanistic role of enolate ions in "Group Transfer Polymerization"

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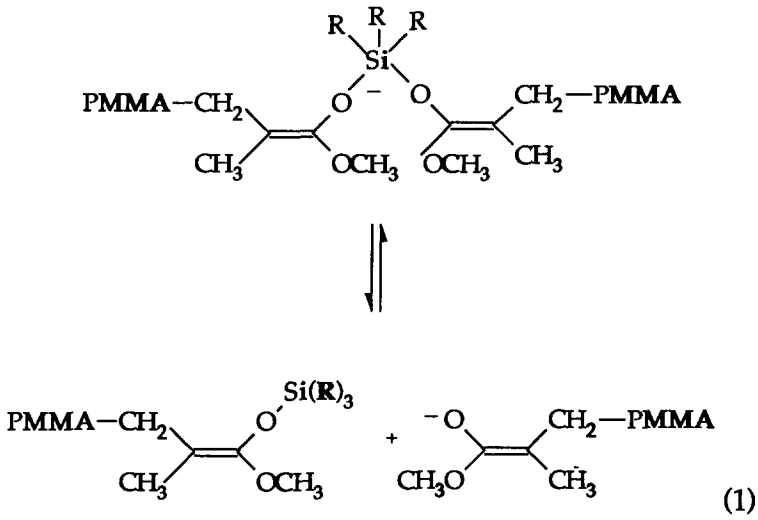
SUMMARY.

A new dissociative mechanism involving enolate anion intermediates is proposed for the process currently categorized as nucleophile-catalyzed "group transfer polymerization"(GTP). A rapid, reversible complexation of small concentrations of enolate anions with silyl ketene acetals (reversible termination) is proposed to explain the living nature of these polymerizations and the role of the silyl ketene acetals in "GTP". It is proposed that these polymerizations do not involve "group transfer" in the chain-propagating step. These mechanistic conclusions are based on studies of the tetrabutylammonium 9-methyl-fluorenide- and methyllithium-initiated polymerizations of methyl methacrylate at ambient temperatures in the presence and absence of silyl ketene acetal.

INTRODUCTION.

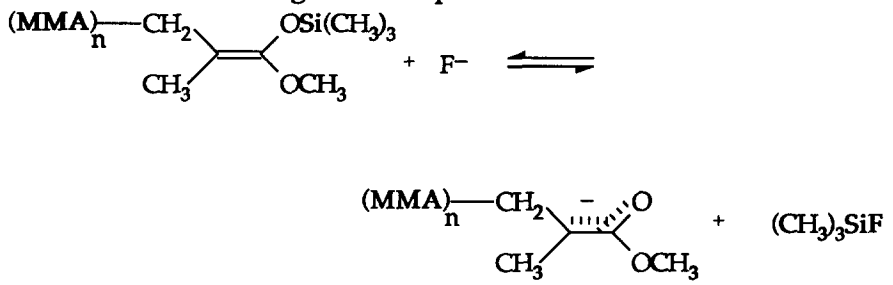
In 1983 workers at DuPont reported a new living polymerization method, called group transfer polymerization (GTP), for acrylate monomers initiated by silyl ketene acetals in the presence of nucleophilic or electrophilic catalysts[1-4]. This process was mechanistically described as "group transfer polymerization" based on the postulate that each chain-growth step for the nucleophile(Nu)-catalyzed polymerization explicitly involves transfer of a trialkylsilyl group from the silyl ketene acetal chain end of a growing polymer to the the carbonyl group of the incoming monomer to form a new silyl ketene acetal chain end via a hypervalent silicon intermediate and a rather unusual 8-membered ring transition state. In the intervening years, little modification or criticism of this mechanism has been proposed, other than to acknowledge the possible non-concerted nature of the oxygen-oxygen silyl group transfer and the carbon-carbon bond formation[5-9].

Herein we propose a new dissociative mechanism involving enolate anion intermediates for nucleophile-catalyzed group transfer polymerization. The key step in this proposed mechanism is a rapid, reversible complexation of the enolate anion intermediates with silyl ketene acetal chain-end functionality(eq 1). This equilibrium provides rationale for the living nature of these polymerizations and the role of



(1)

the silyl ketene acetals in controlling molecular weight. The role of the nucleophilic "catalyst" (e.g. fluoride ion) is to react with the silyl ketene acetal initiator or chain end to form a small concentration of enolate anions (eq 2). This proposed mechanism does not involve "group transfer" in the chain-growth step.



(2)

This simple and more conventional mechanism is consistent with the proposed role of enolate anions as intermediates in the reaction of silyl enol ethers with nucleophiles such as tris(diethylamino)sulfonium difluorotrimethylsiliconate[10,11], the fact that carbon acids with pKa values in the range of 18-25 function as chain-transfer agents in methyl methacrylate GTP[12], and the recent report that the primary termination mode in methyl methacrylate GTP involves chain-end cyclization[13] analogous to terminations of enolate anions in corresponding anionic polymerizations[14]. These conclusions are based on a real test of the role of enolate anions in "GTP" as described herein.

EXPERIMENTAL.

Materials. Methyl methacrylate (Fisher Scientific) was purified by stirring over freshly crushed CaH_2(Alfa), passage through a column of activated alumina (Woelm) and distillation on a vacuum line. Tetrahydrofuran(Fisher, Reagent Grade)(THF) was freshly distilled from sodium benzophenone ketyl. 1-Methoxy-1-(trimethylsiloxy)-2-methyl-1-propene (Aldrich) was freshly distilled before use. Tetrabutylammonium tetraphenylborate (Aldrich) was dried by extended evacuation on a vacuum line. 9-Methylfluorene was prepared by alkylation of fluorene (Aldrich) with methyl iodide after metalation with methyllithium(Aldrich, 1.4M in Et_2O) in THF; mp 44.3-46.2^oC; Lit[15] mp 45.5-46.5^oC. Cesium metal(Alfa) was used as received.

9-Methylfluorenyl cesium was prepared by reaction of 9-methylfluorene with the cesium dianion of 1,1,4,4-tetraphenylbutane in tetrahydrofuran using the procedure of Ellingsen and Smid[16]. The tetrabutylammonium salt of 9-methylfluorene was prepared by reaction of the corresponding cesium salt with excess tetrabutylammonium tetraphenylborate in THF according to the procedure of Hogen-Esch and Smid[17]. The anion exhibited a a λ_{max} at 372nm in tetrahydrofuran which is comparable to λ_{max} of 368nm reported for tetrabutylammmonium fluorenide[18].

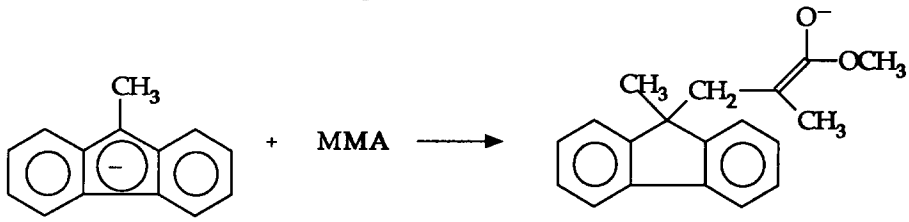
Polymerizations. All polymerizations of methyl methacrylate were carried out in a recirculating, purified argon atmosphere glovebox at ambient temperatures. Methyl methacrylate was added slowly to the tetrahydrofuran solutions of initiator or initiator/silyl ketene acetal mixtures. The polymerizations were exothermic with temperatures reaching 50-65^oC, depending on the rate of monomer addition.

Analyses. Size exclusion chromatographic analyses were performed using four Ultrastyragel columns (two 500, two 10^3, 10^4,10^5 A) in THF at 30^oC after calibration with methyl methacrylate standards obtained from Polymer Laboratories. ^1H NMR analyses in $CDCl_3$ were performed at 200MHz using a Varian Gemini spectrometer.

RESULTS AND DISCUSSION.

A fair test of the role of enolate anions in "GTP" requires the generation and study of such intermediates under typical GTP conditions and reagents. For this purpose, we have prepared the tetabutylammonium salt of 9-methylfluorenide (**TBAMF**) and reacted

this anion ($2x10^{-6}$ mol) with methyl methacrylate (9 g) in tetrahydrofuran (20 mL) at room temperature. It is assumed that 9-methylfluorenide reacts with methyl methacrylate to form the ccorresponding enolate anion (eq 3) as described by Hocker and coworkers[19]. Polymer was produced in 14%



(3)

yield with an estimated number average molecular weight (SEC) of $1.29x10^5$g/mol and M_w/M_n=2.0 (see Figure 1). Thus, on the average more than 1,000 monomer units are added to the growing enolate chain end at room temperature prior to termination. This indicates that at low concentrations these enolate anions have relatively long lifetimes and that propagation is much faster than termination. A similar polymerization of 20g of methyl methacrylate (55 min addition time) with **TBAMF** in the presence of a silyl ketene acetal [1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene, 0.814 g, $4.7x10^{-3}$mol] quantitatively produced poly(methyl methacrylate) with M_n(GPC)=$5x10^3$g/mol and M_w/M_n=1.2 (see Figure 1). The theoretical number average molecular weights were 10^7g/mol and $4.5x10^3$g/mol based on the number of moles of initiator and silyl ketene acetal, respectively. This suggests that the molecular weight is being controlled not by the initial concentration of fluorenide salt, but by the concentration of silyl ketene acetal analogous to other nucleophilic GTP systems. It is important to note that the ratio of acetal to enolate in this polymerization is $2.3x10^3$.

The living nature of these polymerizations was examined by sequential monomer additions. An initial monomer charge corresponded to a theoretical molecular weight of $2.2x10^3$g/mol(obs M_n =$3.4x10^3$g/mol, M_w/M_n=1.2). After 3.75 h a second portion of methyl methacrylate was added to give a polymer with M_n=$12.0x10^3$g/mol and M_w/M_n=1.1. The results are shown in Figure 2 and indicate that the majority of the polymer chains retain their ability to add additional

Figure 1. SEC chromatograms for **TBAMF**-initiated polymerizations in the absence (A) and presence (B) of silyl ketene acetal.

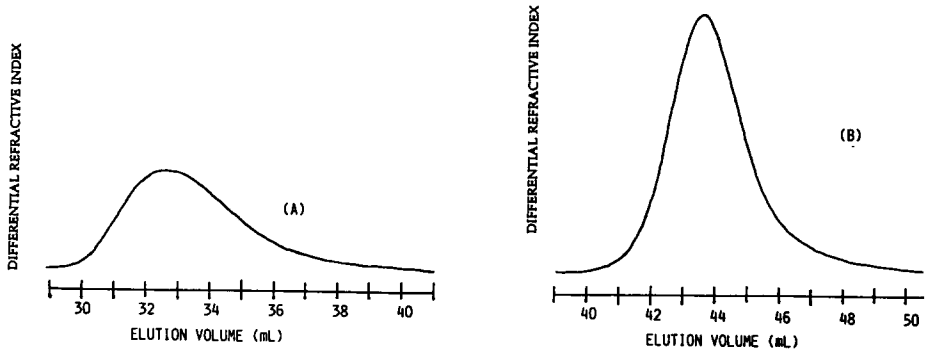
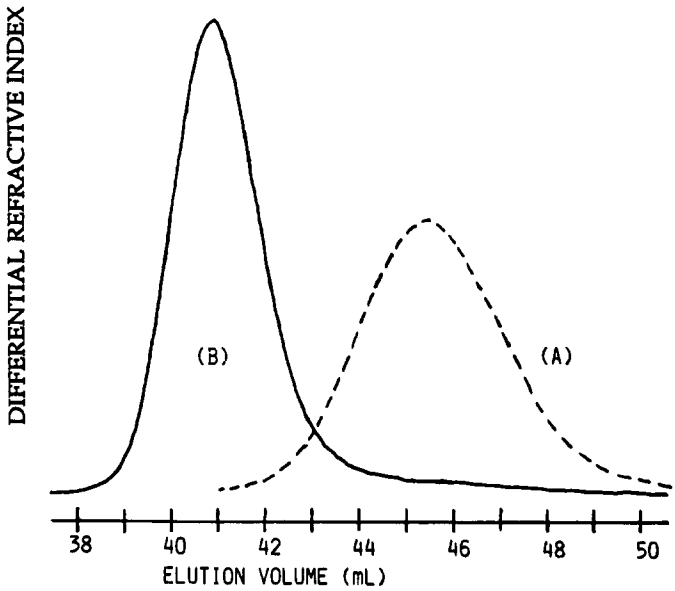
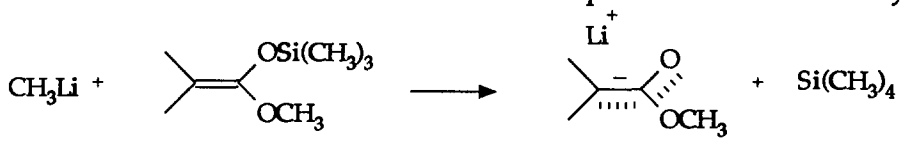


Figure 2. SEC chromatograms for two-step addition of monomer to **TBAMF**/silyl ketene acetal. (A) First addition; (B) second addition(3.75h).



monomer and produce relatively narrow molecular weight distribution polymers.

We have also examined the use of methyllithium and 9-methylfluorenyl cesium as initiators for methyl methacrylate polymerizations in the presence and absence of silyl ketene acetal. The enolate anion of methyl isobutyrate was generated from excess silyl ketene acetal at 25°C in THF as shown in eq 4[20]. Addition of methyl



(4)

methacrylate at room temperature to the lithium enolate/silyl ketene acetal mixture quantitatively produced the polymer with M_n=9.2x10^{3}g/mol and M_w/M_n=2.2. The theoretical molecular weights were 6.5x10^{3}g/mol and 2.4x10^{5}g/mol based on the number of moles of silyl ketene acetal and methyllithium, respectively. Similar results were obtained for the cesium carbanion.

This evidence convincingly indicates that enolate anions generated by a variety of methods in the presence of excess silyl ketene acetal react with methyl methacrylate to produce a living polymer system in which the molecular weight is controlled by the moles of silyl ketene acetal and not by the initial concentration of enolate anions. The simplest mechanistic interpretation of these results is that propagating enolate anions are rapidly and reversibly complexed with excess dormant silyl ketene acetal end groups (eq 1). The narrow molecular weight distribution obtained with the tetrabutylammonium cation when the initial ratio of enolate anion to silyl ketene acetal is low (e.g. 4.3x10^{-4}) requires that the reaction of enolate anions with the silyl ketene acetal end groups is rapid and reversible to explain the molecular weight control. The broad molecular weight distributions obtained with the lithium and cesium counterions suggest that association effects complicate the equilibration processes in these systems. The effectiveness of such low concentrations of carbanion also suggests that this process is very efficient for the generation of the required enolate ion intermediates compared to previously used nucleophiles such as fluoride sources.

We have utilized ^{1}H NMR spectroscopy to examine the tacticity of the poly(methyl methacrylates) produced with tetrabutylammonium 9-methylfluorenide in THF at room temperature and these results were compared with the tacticities obtained with this carbanion in the

presence of the silyl ketene acetal. The methyl resonances in the range of δ1.2-0.6ppm and the peak assignments of Bovey[21] were used for tacticity determinations. The triad distributions for both polymers are very similar, i.e. 5% isotactic, 39% heterotactic and 56% syndiotactic for the carbanion and 5% isotactic, 42% heterotactic and 53% syndiotactic for the carbanion/silyl ketene acetal. These results represent a direct comparison of tacticities for anionic and group transfer polymerizations with the same counterions under the same experimental conditions and they suggest that similar species, i.e. enolate anions, are involved in these two types of polymerizations. This result stand in sharp contrast to the conclusion that the tacticity in GTP is inconsistent with the tacticities obtained in analogous anionic polymerizations[2,5].

CONCLUSIONS.

All of the evidence presented herein is consistent with the intermediacy of enolate anions as propagating species in what has previously been called group transfer polymerization. The unique role of silyl ketene acetal groups is to reversibly complex with the enolate anions to insure that their concentration is kept low. The majority of growing chains would be in the dormant silyl ketene acetal form until complexation with enolate generates a new enolate ion propagating species.

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