Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Webster, O. W.(1994) 'Does Anion-Catalyzed Group-Transfer Polymerization Proceed Via an Enolate Intermediate?', Journal of Macromolecular Science, Part A, 31: 8, 927 — 935

To link to this Article: DOI: 10.1080/10601329409349770

URL: http://dx.doi.org/10.1080/10601329409349770

J.M.S.—PURE APPL. CHEM., A31(8), pp. 927–935 (1994)

DOES ANION-CATALYZED GROUP-TRANSFER POLYMERIZATION PROCEED VIA AN ENOLATE INTERMEDIATE?*

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ABSTRACT

Group-transfer polymerization of methyl methacrylate was originally postulated to occur by an associate process wherein an activated trimethylsilyl group transferred to incoming monomer. The mechanism was based on double-labeling experiments. However, data published since this original work point to a dissociative process wherein the catalyst generates a small amount of enolate that is in rapid exchange with the main pool of silyl-ketene-acetal-ended chains. The monomer adds to this bare enolate.

INTRODUCTION

In group-transfer polymerization (GTP) a silyl ketene acetal activated by a small amount of nucleophilic anion initiates polymerization of acrylic monomers [1]. GTP is a living system that operates at ambient temperature and above. Equation (1) shows the process for MMA.

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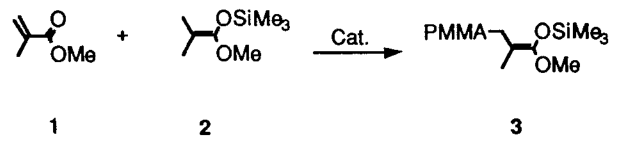
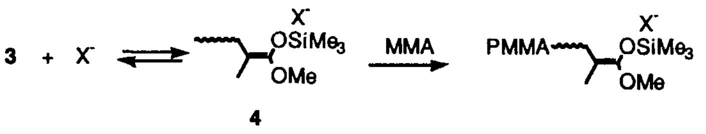
*Contribution No. 6739.



(1)

A controversy exists as to whether GTP operates by an associative mechanism (Eq. 2) wherein each silyl group remains with the same chain it started with (that is, monomer inserts in the chain ends) or by a dissociative mechanism (Eq. 3) wherein a small amount of the silyl groups is cleaved from the initiator by the catalyst X$^-$ and the resulting enolate end, **6**, adds monomer. Since low dispersity polymer is produced, the dissociative mechanism requires that chain ends equilibrate at a faster rate than that of polymerization. The associative mechanism requires that a catalyst equilibrate between chain ends at a faster rate than that of polymerization.



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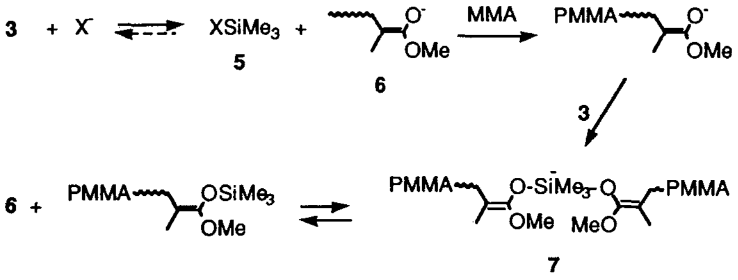

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On the basis of the similarity of poly(methyl methacrylate) produced by GTP and that produced by living anionic polymerization, the dissociative mechanism appears to be correct [2]. However, early work involving double-labeling experiments seemed to rule out the dissociative mechanism. These results, as well as new data relating to the GTP mechanism, will be discussed below.

LIVING ANIONIC POLYMERIZATION OF MMA

At the time GTP was discovered there were no reported examples of living polymerization of MMA above −20°C. Therefore, our best guess was that GTP could not be proceeding by the dissociative route since free enolate end would be involved well above room temperature. In the last few years, however, Reetz [3], Sivaram [4], and Seebach [5] have shown that living anionic polymerization of MMA proceeds at temperatures up to 60°C if a large nonmetallic gegenion is associated with the living chain ends.

We have found that the size of the gegenion is more important than the fact that it is nonmetallic. Indeed, crown ether complexed potassium gegenion also works [6]. Potassium dimethyl methylmalonate (**8**)/18-crown-6 polymerizes MMA

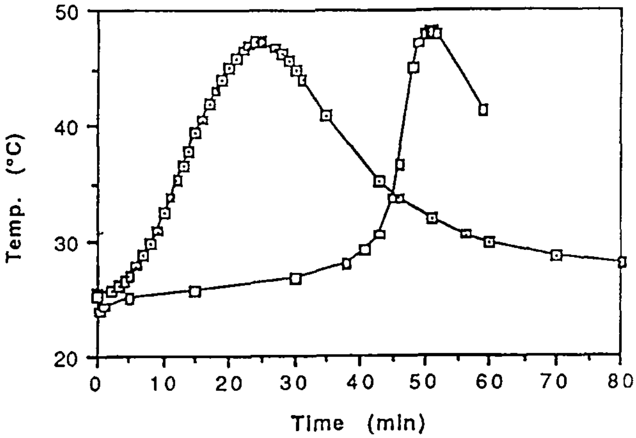


FIG. 1. Effect of 18-crown-6 on the rate of MMA polymerization: 94 mmol MMA, 2 mmol dimethyl methylmalonate, 1 mmol K^+ t-BuO^-, 30 mL THF. (□) No crown ether, (⊡) 1 mmol 18-crown-6.

at 25–60°C to give quantitative yields of PMMA, M_w/M_n = 1.5–1.9 (Eq. 4). Without the crown ether, induction periods up to 40 minutes were noted (Fig. 1). A plot of M_n vs conversion showed that the polymerization was living. M_n values were lower than theory by as much as 30% (Fig. 2), indicating chain transfer by the t-butanol produced during initiator formation. To check this possibility, polymerization of MMA with potassium dimethyl methylmalonate/18-crown-6 was conducted in the presence of excess dimethyl methylmalonate and also with excess alcohol. Much to our surprise, the excess malonate did not kill the polymerization but lowered the molecular weight in fair agreement with the well known DP =

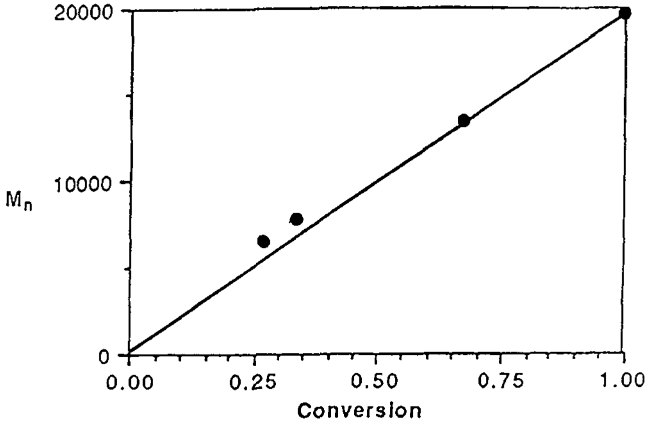


FIG. 2. Molecular weight vs conversion: 1 mmol diethyl ethylmalonate; 1 mmol K^+ t-BuO^-, 1 mmol polyethylene glycol 2000 dimethyl ether; 8, 10, 20, 30 mL MMA.

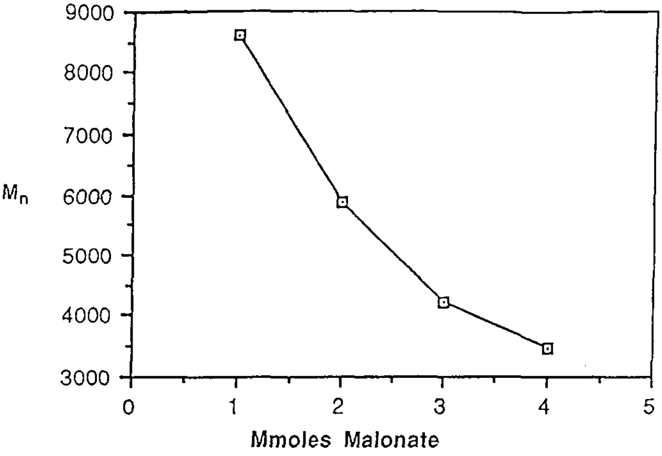
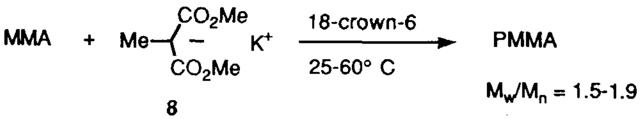


FIG. 3. Effect of excess malonate on MMA molecular weight: 94 mmol MMA, 1 mmol K^+ *t*-BuO$^-$, 1 mmol 18-crown-6, 30 mL THF, 1-4 mmol dimethyl methylmalonate.

[MMA]/[malonate] equation for living conditions (Fig. 3). GC analysis showed that the malonate was consumed in the early stages of the polymerization. Excess methanol also controlled the molecular weight in a similar manner. Excess malonate retarded the rate of polymerization (Fig. 4); excess methanol had no effect on the rate (Fig. 5).



$$\text{MMA} + \text{Me}\!-\!\overset{\text{CO}_2\text{Me}}{\underset{\text{CO}_2\text{Me}}{\text{C}^-}}\;\text{K}^+ \xrightarrow[25\text{-}60°\ \text{C}]{18\text{-crown-6}} \text{PMMA} \qquad M_w/M_n = 1.5\text{-}1.9 \tag{4}$$

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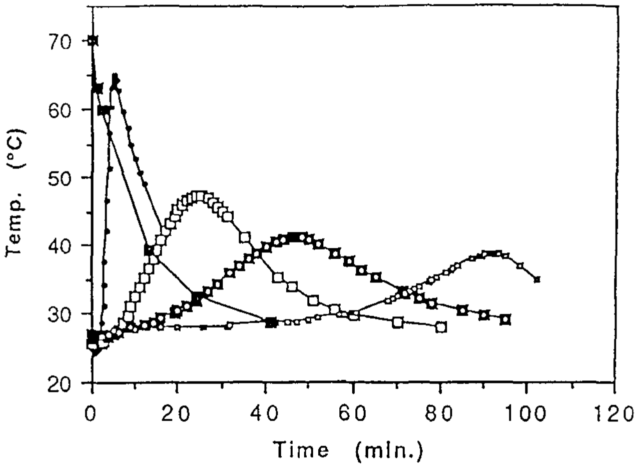


FIG. 4. Effect of excess malonate on MMA polymerization rate: 94 mmol MMA, 1 mmol K^+ *t*-BuO$^-$, 1 mmol 18-crown-6, 30 mL THF. (■) No dimethyl methylmalonate, (●) 1 mmol, (□) 2 mmol, (■) 3 mmol, (□) 4 mmol.

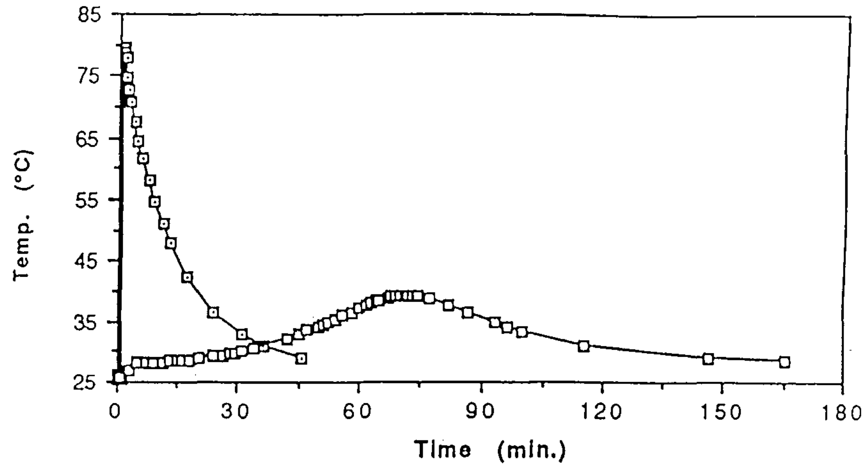
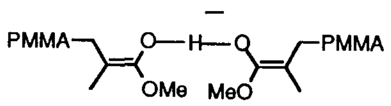


FIG. 5. Effect of methanol vs dimethyl methylmalonate: 30 mL dry toluene, 94 mmol MMA, 1 mmol K^+ *t*-BuO^-, 1 mmol 18-crown-6. (⊡) 5 mmol methanol, (□) 5 mmol dimethyl methylmalonate.

After finding that excess malonate acted to control MW, the fact that methanol would do so also was not surprising since Haggard and Lewis had shown that the molecular weight of PMMA produced by alkoxide initiation of MMA was controlled by the addition of excess alcohol [7]. They also noted that tetraalkylammonium alkoxides were particularly good initiators.

The fact that the molecular weight of the polymer produced by initiation with excess malonate or methanol is determined by the monomer/malonate or monomer/methanol ratio requires a rapid exchange between protonated chain ends and enolate ends. An intriguing possibility is that the active chain ends are stabilized by hydrogen bonding to the neutral chain ends, bienolate stabilization (**9**).



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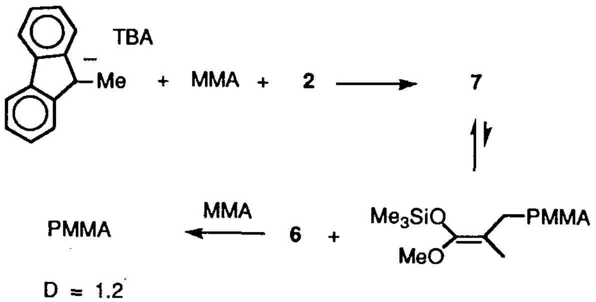
GTP MECHANISM

The fact that under the right conditions one can conduct room temperature living polymerization of MMA removes one of the major objections for a dissociative mechanism for GTP. With this knowledge in hand, Quirk attacked the associative/dissociative controversy head on by adding a known ionic initiator for MMA (which would, of course, react with MMA to generate the proposed intermediate in the dissociative process) to excess GTP initiator and MMA [2]. Low polydispersity polymer was obtained, and the molecular weight was controlled by the amount of

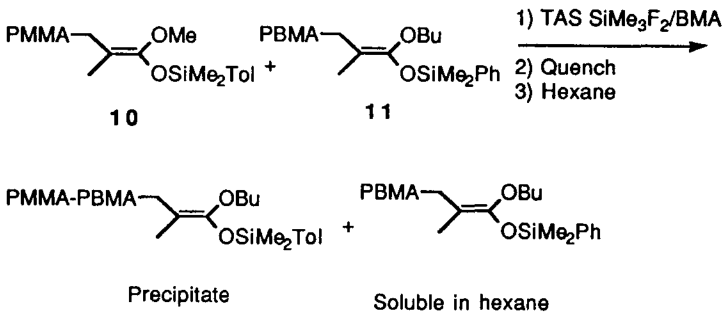
GTP initiator (Eq. 5). Without the added GTP initiator only a 14% yield of PMMA was obtained. These results dramatically demonstrate the stabilizing effect of trimethylsilyl ketene acetal, and since low dispersity polymer was obtained, the enolate end groups must be in rapid equilibrium with neutral chain ends and thus be available for addition of monomer. Under these conditions then, the dissociative mechanism appears operative. One other possibility remains for the associative mechanism. Could the intermediate 7 be so stable that no equilibrium with bare enolate exists and it, itself, adds monomer by the associative process? This route would require that 7 equilibrate with neutral end groups.



(5)

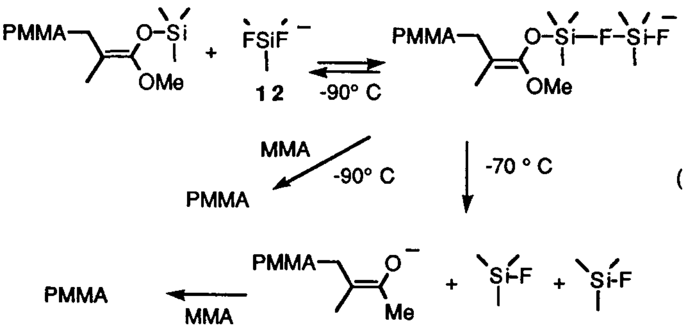
The dissociative mechanism would also satisfy the curious fact that it is essential to maintain low levels of catalyst to get good GTP results. In the associative process, more catalyst should merely increase the rate of polymerization and not affect livingness. In the dissociative process, the catalyst reacts with initiator to generate a small amount of enolate which by itself would be unstable at room temperature but which is stabilized by complexation with the much larger amounts of silyl-ketene-acetal-ended polymer in the system. If too much enolate is generated, this stabilization mechanism is thwarted. The reaction of bifluoride catalyst with GTP initiator on a molar basis has been shown to give products one would associate with enolate production [8].

The main evidence for the associative mechanism consists of double-labeling experiments conducted by Farnham and Sogah [9]. At −90°C in THF, a mixture of PMMA with a dimethyltolylsilyl ketene acetal end group (**10**) and PBMA with a dimethylphenylsilyl ketene acetal end group (**11**) was treated with a small amount of BMA and TASF catalyst (Eq. 6). After 5 minutes the polymerization was quenched and the two polymers separated by solubility. NMR showed a small amount of BMA in the PMMA/PBMA block from **10**, yet little exchange of end groups had occurred. Since the dissociative mechanism requires end-group exchange to occur faster than polymerization, this result would appear to demand the associative mechanism. In the experiments at −70°C, end-group scrambling occurred. Supposedly the difluorotrimethylsiliconate (**12**), a strong fluoride ion donator, reacts with the trimethylsilyl ketene acetal end group to give two molecules of fluorotrimethylsilane and TAS enolate (Eq. 7). The small amount of TAS enolate then catalyzes GTP by the dissociative mechanism. The data indicate that at −90°C the difluorosiliconate initiator complex dissociates by breaking the SiF bond to give difluorosiliconate back and not the weaker SiO bond to give TAS enolate. One wonders if there is not some other explanation for the lack of chain scrambling at −90°C.



(6)

Similar results were obtained with PBMA and PMMA with triethylsilyl and trimethylsilyl ketene acetal end groups catalyzed by TAS bifluoride. However, triethylsilyl-ended polymer polymerizes much more slowly than trimethylsilyl-ended polymer, and there is a danger that significant polymerization of the triethyl-capped chains did not occur in the 5 minutes before quenching [9]. Thus there would be no exchange [8].

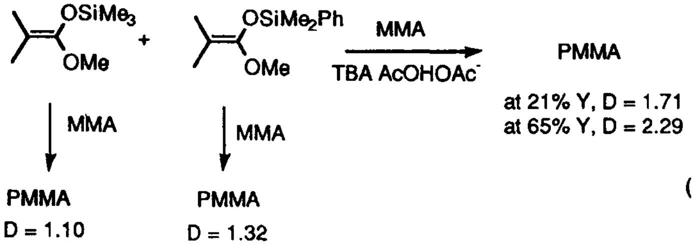


(7)

In double-labeling experiments using PMMA of two different molecular weights designed for separation by solubility differences in the two samples, Quirk obtained partial exchange [10]. In these experiments reaction times up to 2 hours and insufficient catalyst were used to keep the polymerization going. Since by either mechanism significant exchange would occur in 2 hours and the dissociative mechanism requires 100% exchange, a definitive answer was not obtained.

Repeating the room temperature double-labeling experiments of Farnham and Sogah with the labels they used in their low temperature studies would be worthwhile. Repeating them with a carboxylate catalyst would be even more worthwhile, since Muller [11] has calculated that there is a mechanism shift from dissociative to associative when one changes the catalyst from bifluoride to TBA benzoate.

We find evidence for the associative mechanism in dual initiator studies [12]. Under an associative mechanism with dual initiators, each set of chains would grow at slightly different rates. Therefore the molecular weight distribution would be broader than when only one initiator is operating. This is the case when dimethylphenylsilyl ketene acetal and trimethylsilyl ketene acetal were used to polymerize MMA with tetrabutylammonium biacetate as catalyst (Eq. 8).



(8)

Similar studies are underway with bifluoride and fluoride catalysts.

CONCLUSIONS

Although all of the data don't quite fit, the evidence weighs heavily on the side of a dissociative process for anion-catalyzed GTP, especially for the strongly nucleophilic systems. For carboxylate-catalyzed GTP, the jury is still out.

GLOSSARY

BMA	butyl methacrylate
GTP	group transfer polymerization
MMA	methyl methacrylate
OAc^-	acetate
PBA	poly(butyl acrylate)
PBMA	poly(butyl methacrylate)
PMMA	poly(methyl methacrylate)
TAS	tris(dimethylamino)sulfonium
TASF	tris(dimethylamino)sulfonium difluorotrimethylsiliconate

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