

# Mechanism of the Anionic Polymerization of Methyl Methacrylate Initiated by Tetramethylammonium–Triphenylmethide in Tetrahydrofuran

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**ABSTRACT:** A tetramethylammonium (TMA)–triphenylmethide (TPM) initiator generated *in situ* by the reaction of trimethyltriphenylmethylsilane with tetramethylammonium fluoride in tetrahydrofuran was found to have greater stability than the corresponding tetrabutylammonium or tetrahexylammonium derivatives. The predominant mode of degradation of TMA–TPM was found to be the TMA-mediated methylation of TPM anions. The initiation of methyl methacrylate by TMA–TPM in tetrahydrofuran at  $-78\text{ }^{\circ}\text{C}$  was demonstrated to produce quantitative yields of poly(methyl methacrylate) with polydispersities of less than 1.1. Although the initiator efficiencies were low (9–40%) because of relatively slow initiation on the polymerization timescale, the initiation appeared to be rapid enough to give relatively narrow molecular weight distributions. © 2003 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 42: 237–244, 2004  
**Keywords:** anionic polymerization; methyl methacrylate; triphenylmethide; anions; tetramethylammonium; living polymerization; polymerization mechanism

## INTRODUCTION

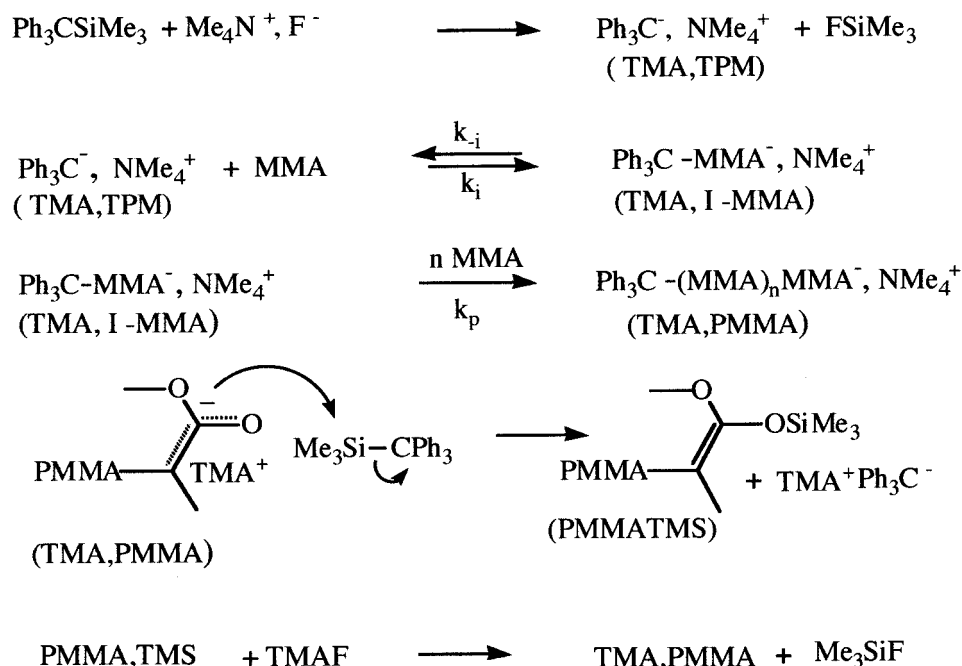
The anionic polymerization of (meth)acrylates in metal-free systems has been a subject of much recent activity and interest.<sup>1–14</sup> For so-called group-transfer polymerization,<sup>2</sup> the proposal has been made that this polymerization is dissociative; that is, the chain growth is anionic and proceeds in the presence of suitable large organic cations.<sup>3,4</sup> Thus, a number of large organic cations, such as tetrabutylammonium (TBA),<sup>3–7</sup> tetrahexylammonium (THA),<sup>10</sup> tetraphenylphosphonium,<sup>8,9</sup> and tetraoctylphosphonium,<sup>10</sup> and the protonated form of the P-4-phosphazene base and

similar systems<sup>11–14</sup> have been used to mediate such polymerizations. In the case of methyl methacrylate (MMA), several of these systems have indicated potential for the control of the molecular weight and narrow molecular weight distributions (MWDs).

Here we report the tetramethylammonium (TMA)–triphenylmethide (TPM)-initiated anionic polymerization of MMA in the presence of TMA ions. The initiating TMA–TPM ion pair is generated *in situ* by the reaction of trimethyltriphenylmethylsilane (TPMTMS) with tetramethylammonium fluoride (TMAF) in tetrahydrofuran (THF; Scheme 1). We present evidence indicating that the TMA–TPM ion pair is far more stable under ambient conditions than other TPM tetraalkylammonium salts. Our results also indicate that this system is capable of producing poly(methyl methacrylate) (PMMA) with narrow MWDs.

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**Scheme 1.** TMA-TPM-initiated polymerization of MMA in THF and related reactions.

## EXPERIMENTAL

TMAF (Aldrich; 97%) was used as received and dried under a high vacuum ( $10^{-5}$  Torr) overnight before use. Nevertheless, not all of the water of hydration may have been removed under these conditions.<sup>15</sup> THF was stored over a sodium/potassium alloy and was distilled from  $\text{Ph}_3\text{CK}$  before use. TPMTMS was synthesized by the reaction of triphenylmethylithium ( $\text{Ph}_3\text{CLi}$ ) and chlorotrimethylsilane. Thus, the addition via syringe of 11 mL (22 mmol) of *n*-butyllithium (Aldrich; 2.0 M in pentane) into a three-necked flask containing a stirred solution of 4.90 g (20 mmol) of triphenylmethane (Aldrich; 99%) in 100 mL of dry THF under argon at  $-78^\circ\text{C}$  produced  $\text{Ph}_3\text{CLi}$ . Subsequently, 3.05 mL (24 mmol) of  $\text{ClSiMe}_3$  (Aldrich; 99%) was syringed into the flask at  $-78^\circ\text{C}$  until the red color of the TPM anion disappeared. After 1 h of stirring, the cooling bath was removed, and the reaction mixture was stirred overnight. The solvent was removed under reduced pressure (1 Torr), and the resulting solid was purified by column chromatography [silica (75–200  $\mu\text{m}$ ) and hexane]; this yielded 5.70 g of TPMTMS (85% isolated yield).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm,  $\delta$ ): 0.15 (s, 9H), 7.05 (d,  $J = 6.8$  Hz, 6H), 7.17 (t,  $J = 7.3$  Hz, 3 H), 7.25 (t,

$J = 7.4$  Hz, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm,  $\delta$ ): 1.68, 53.60, 125.35, 127.86, 130.06, 146.70. MS ( $m/e$ ): 316 ( $\text{M}^+$ ), 301, 243, 197, 165, 139, 115.

Diphenylmethyltrimethylsilane (DPMTMS) was synthesized from diphenylmethane ( $\text{Ph}_2\text{CH}_2$ ) and was purified with a method similar to that used for TPMTMS (82% isolated yield).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm,  $\delta$ ): 0.03 (s, 9H), 3.51 (s, 1H), 7.12–7.24 (m, 10H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm,  $\delta$ ):  $-1.70$ , 46.10, 125.04, 128.26, 128.71, 142.88. MS ( $m/e$ ): 240 ( $\text{M}^+$ ), 225, 197, 165, 152, 121, 105, 89, 73.

MMA (Aldrich; 99%) was purified by distillation, first over  $\text{CaH}_2$  and then over 2 mL (1 mmol) of trioctylaluminum (Aldrich; 25 wt % in hexanes). This was followed by dilution with 90 mL of purified THF distilled from triphenylmethylpotassium.

## Polymerizations

The polymerizations were carried out with high-vacuum ( $10^{-5}$  Torr) techniques.<sup>16</sup> The TMA-TPM initiator was prepared by the addition from a break-seal of 18 mg of carefully dried solid TMAF (2 equiv) to a solution of 5–50 mg of TPMTMS ( $1.4 \times 10^{-4}$  to  $1.4 \times 10^{-5}$  mol) dissolved in 20 mL of THF and cooled to  $-78^\circ\text{C}$ . The mixture was stirred for 5 min with no appearance of color.

After this solution was warmed to  $-20\text{ }^{\circ}\text{C}$ , a faint reddish color of the triphenylmethyl anion appeared after about 1 min and intensified over the next 30 min. The reaction mixture was then cooled to  $-78\text{ }^{\circ}\text{C}$ , and MMA (0.30–1.00 g), dissolved in 10 mL of purified THF and cooled to about  $-20\text{ }^{\circ}\text{C}$ , was added dropwise, typically over a periods of 20 s to 10 min; the polymerization was then terminated after 1–2 min. The distillation of degassed methanol (MeOH) into the flask led to the disappearance of the initiator color. Polymers were isolated by the pouring of 35-mL terminated polymer solutions into 300 mL of MeOH, followed by filtration. The yields were quantitative.

Initiator degradation experiments were carried out by the preparation of the TMA–TPM [or TMA–diphenylmethyl (DPM)] initiator in the same amounts as in the polymerizations, followed by heating to the ambient temperature. Stirring was allowed to continue until all the color had disappeared, typically within 2–4 h. The solvent and other volatile components of the reaction mixture were then vacuum-distilled into a 50-mL, round-bottom flask kept at  $-78\text{ }^{\circ}\text{C}$  and attached to the apparatus via a ground glass joint; this left a solid residue in the reaction flask. The round-bottom flask was then frozen with liquid nitrogen, capped with a septum under argon, and allowed to warm. About 0.5 mL of this solution was removed via syringe and added to 10 mL of *N*-methylpyrrolidinone for gas chromatography/mass spectrometry (GC–MS) analysis.

The isolation of the amine products generated by the degradation of the TMA cation was carried out through the injection of 10 mL of HCl vapor obtained by syringe from a concentrated HCl reagent bottle (EM Science; 36.5–38.0%) into the septum-capped round-bottom flask at  $-10\text{ }^{\circ}\text{C}$ ; the mixture was then swirled by hand until the appearance of white crystals. The addition of gaseous HCl was repeated typically three or four times until no further precipitation was observed. The contents of the flask were then evacuated and allowed to warm to the ambient temperature; this left a white, crystalline residue. The crystals were dissolved in dry  $\text{CDCl}_3$  for  $^1\text{H}$  NMR analysis. The solid contents in the reaction flask were isolated by extraction in THF.

### Characterization

Size exclusion chromatography (SEC) was carried out in THF at a flow rate of 1.0 mL/min with an

LC system consisting of a Waters 510 HPLC pump, a Waters 410 refractive-index detector, and a U6K injector. Two Waters Ultrastaygel columns (500- and  $10^4\text{-}\text{\AA}$  pores and  $10\text{-}\mu\text{m}$  particles) calibrated with PMMA standards (Polysciences, Inc.) had a linear separation range of 800–350,000 Da. SEC analysis was carried out on the crude product (not the precipitated polymer), which may have contained low-molecular-weight oligomers (Table 1).

$^1\text{H}$  NMR spectra were recorded on a Bruker AC-250 MHz spectrometer in  $\text{CDCl}_3$  (Cambridge Isotopes Laboratories, Inc.; 99.8%). GC–MS analysis was carried out on a Hewlett–Packard 5890 gas chromatograph equipped with a Hewlett–Packard 5971 mass selective detector at 70 eV with *N*-methylpyrrolidinone (Aldrich; >99%) as a solvent.

## RESULTS AND DISCUSSION

The metathesis reaction giving the TMA–TPM initiator did not take place at  $-78\text{ }^{\circ}\text{C}$ , but over a period of about 30 min at  $-20\text{ }^{\circ}\text{C}$ , the deep red color of the TPM anion developed (Scheme 1). After the initiator solution cooled to  $-78\text{ }^{\circ}\text{C}$ , polymerizations were carried out through the dropwise addition of MMA dissolved in THF over periods varying from 20 s to 10 min. In all cases, except runs 1 and 7, SEC analysis showed high-molecular-weight PMMA with narrow MWDs [polydispersity index (PDI) as low as 1.04] and quantitative monomer conversions (Table 1). The relatively wide MWD in run 1 correlates with a brief inadvertent exposure of highly hygroscopic TMAF to the atmosphere. Significantly, when MMA was added dropwise over a much longer period (10 min rather than 20 s), PMMA with a narrow polydispersity was obtained (Table 1, run 6).

### Initiation

The initiator stability in the absence of a monomer was excellent, as shown by the indefinite persistence of the deep red color of TMA–TPM at  $-78\text{ }^{\circ}\text{C}$ . Even at  $25\text{ }^{\circ}\text{C}$  in THF in the absence of MMA, the red color from the TMA–TPM ion pair persisted for 2–4 h. This is remarkable as the TBA or THA triphenylmethyl initiators undergo termination on the timescale of several seconds to minutes under ambient conditions.<sup>10,17</sup> In those cases, rapid decomposition is consistent with a

**Table 1.**  $\text{Ph}_3\text{C}^-\text{NMe}_4^+$ -Mediated Polymerizations of MMA in THF at  $-78\text{ }^\circ\text{C}^{\text{a}}$ 

Run	Yield (%) <sup>b</sup>	$M_n$			PDI	$f^e$
		Calcd. <sup>c</sup>	SEC	NMR <sup>d</sup>		
1 <sup>f,g</sup>	85	12,100	92,900	—	1.30	0.13
2 <sup>f</sup>	>95	4,100	35,700	—	1.09	0.11
3	>95	8,600	96,000	—	1.04	0.09
4	>95	13,200	57,300	—	1.07	0.23
5	>95	4,700	11,900	12,000	1.09	0.40
6 <sup>h</sup>	>95	3,200	16,100	16,300	1.07	0.20
7 <sup>i</sup>	>95	4,200	7,100	7,400	4.07	0.56
8 <sup>j</sup>	>95	7,300	75,000	—	1.26	0.10

<sup>a</sup> Amount of MMA = 0.3–1.0 g; amount of TPMTMS = 10–50 mg; amount of THF = 30 mL; metathesis time = 30 min; metathesis temperature =  $-20\text{ }^\circ\text{C}$ .

<sup>b</sup> Determined gravimetrically.

<sup>c</sup> Number-average degree of polymerization (calcd.) =  $[\text{MMA}]/[\text{TPMTMS}]$ .

<sup>d</sup> Determined from the ratio of the aromatic signals of the TPM initiator to the methyl ester signals.

<sup>e</sup> Initiator efficiency  $[M_n(\text{Calcd.})/M_n(\text{SEC})]$ .

<sup>f</sup> Metathesis temperature =  $25\text{ }^\circ\text{C}$ .

<sup>g</sup>  $\text{NMe}_4\text{F}$  was momentarily exposed to air.

<sup>h</sup> The MMA solution was added dropwise over 10 min.

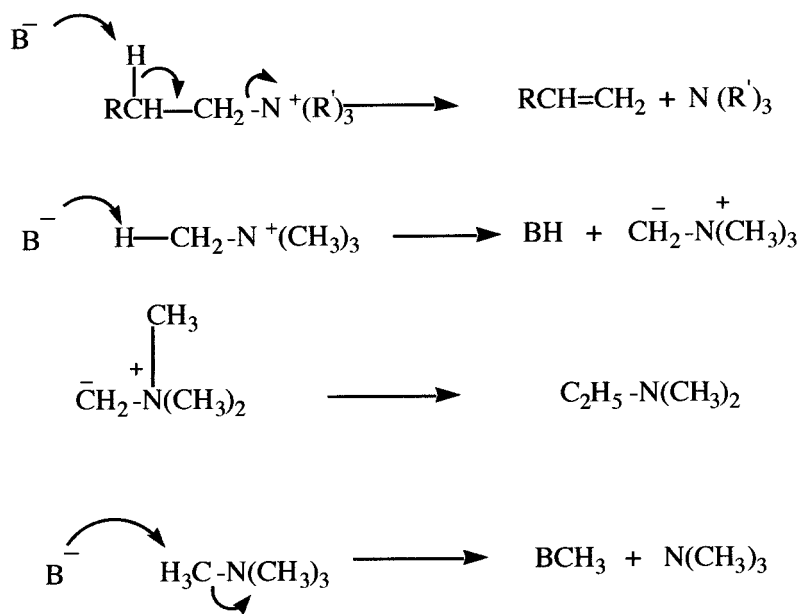
<sup>i</sup> Metathesis time = 10 min.

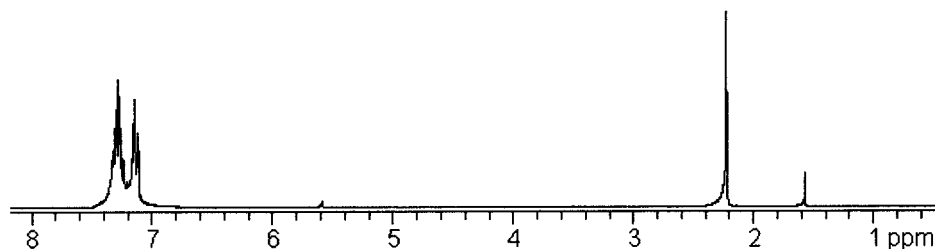
<sup>j</sup> Amount of DPMTMS = 40 mg; amount of MMA = 1.1 g.

Hoffman-type elimination (Scheme 2, eq 6), which is not possible for the TMA cation for which the  $\beta$ -hydrogens are absent.

$^1\text{H}$  NMR (Fig. 1) and GC–MS (data not shown) analysis of the TMA–TPM initiator decomposition reaction products revealed the presence of

10% triphenylmethane and 90% 1,1,1-triphenylethane as well as the presence of trimethylamine. Triphenylmethane is most likely the result of a small amount of residual water in TMAF, the complete dehydration of which is difficult.<sup>15</sup> Protonation of the TPM anion by the TMA cation,

**Scheme 2.** Decomposition of TBA–TPM, TMA–TPM, and TMA–DPM.



**Figure 1.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) spectrum of  $\text{Ph}_3\text{CCH}_3$  containing  $\text{Ph}_3\text{CH}$  (10 mol %) produced from the reaction of  $\text{Ph}_3\text{CSiMe}_3$  with  $\text{NMe}_4\text{F}$  in THF at  $25^\circ\text{C}$ .

forming a nitrogen ylide and its Stevens rearrangement<sup>18</sup> (Scheme 2, eqs 7 and 8), is expected to generate dimethylethylamine, which was not detected. Also, the nitrogen ylide that could have initiated MMA is an unlikely intermediate because  $^1\text{H}$  NMR integration of the aromatic TPM and PMMA methyl resonances gave number-average molecular weights ( $M_n$ 's) that were in good agreement with those determined by SEC (Table 1). Furthermore, the narrow PMMA polydispersities indicated that, at least on the polymerization timescale (20 s to 10 min), termination by protonation or methylation of the PMMA anion did not appear to be a factor. The narrow distribution (Table 1, run 6) indicates that the polymerization is living over a period of at least 10 min of monomer addition (discussed later).

The formation of 1,1,1-triphenylethane indicates methylation of the TPM anion by the TMA cation as the predominant initiator decomposition reaction (Scheme 2, eq 9). However, as this reaction was slow (as discussed previously), this would seem to preclude it from occurring during the very short time of the polymerization consistent with the narrow MWDs (discussed later). Such initiator methylation was also observed by Bandermann and coworkers.<sup>19,20</sup>

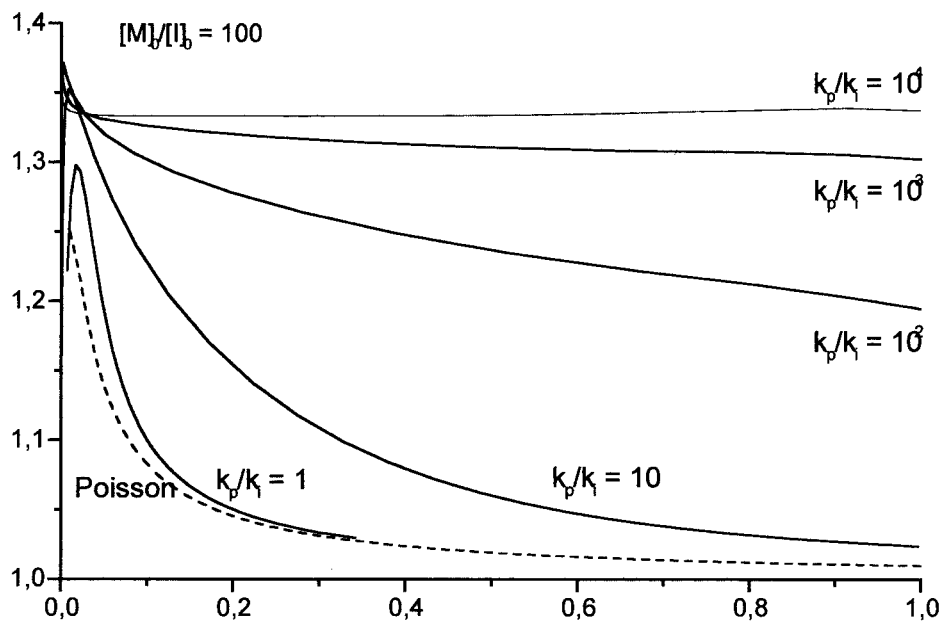
$^1\text{H}$  NMR analysis of the degradation products of the DPM-TMA ion pair indicated the presence of trimethylamine and 1,1-diphenylethane but not the protonated initiator ( $\text{Ph}_2\text{CH}_2$ ), although the presence of a few percent of  $\text{Ph}_2\text{CH}_2$  cannot be excluded. Here also, the TMA-mediated methylation of the anion initiator appears to be the major side reaction. The DPM-anion-initiated polymerization of MMA in the presence of TMA cation gave PMMA with a wider MWD (PDI = 1.26) but with a similar low initiator efficiency (10%; Table 1, run 8). The trifluoromethyl anion/TMA system ( $\text{CF}_3\text{-TMS}$ )<sup>21</sup> in only one instance was observed to initiate MMA with the formation of less than 5% of a high-molecular-weight broad-distribution

PMMA. From the  $^{19}\text{F}$  NMR spectra of the reaction products, the  $\text{CF}_3$  anion appeared to have reacted with the ester group of MMA. Acylation of the  $\text{CF}_3$  anion by the reaction of methyl esters to produce trifluoromethyl ketones is known.<sup>21</sup>

Under the polymerization conditions, initiation is incomplete and/or slow, as shown qualitatively by the characteristic deep red initiator color that persisted during and after MMA addition. This is consistent with the low initiator efficiencies, which ranged from 9 to 40% (Table 1). Slow initiation and initiator efficiencies (with respect to polymerizations initiated by Li or K TPM salts<sup>22,23</sup>) were also observed for TPM-TBA<sup>3,5-7,17</sup> and TPM-THA<sup>10</sup> initiated MMA polymerizations (<1.0–1.5%). This was very likely due, at least in part, to Hoffman elimination that could not occur for the TPM-TMA initiator.

The low initiator efficiencies are consistent with well-known rapid anionic MMA polymerizations in THF and other polar media, especially in the presence of large organic cations such as cryptated Na cations, which deplete the monomer and truncate initiation. Studies by Johann and Müller<sup>24</sup> have shown that the rate constant of propagation for the PMMA anion in the presence of a cryptated Na ion pair is extremely fast (ca.  $10^3$  L/mol s at  $-75^\circ\text{C}$ ).<sup>24</sup> If the TMA ion pairs have a similar reactivity, this would correspond to polymerization half-lives of about 1 s under our conditions. Given that in the presence of larger cations ( $\text{Cs}$ ,  $\text{NR}_4$ ) the initiation of MMA by carbanions is slow with respect to propagation, incomplete initiation is not surprising.<sup>3,5-7,17</sup>

The PMMA anions are not readily terminated on the timescale of several minutes because an MMA addition over a period of 10 min also gives narrow MWDs (Table 1, run 6). The lack of rapid termination of the PMMA anion under the reaction conditions (e.g., by methylation) is consistent with the lower reactivity of the TMA cation, as shown by its greater thermal stability (as dis-



**Figure 2.** Effects of the  $k_p/k_t$  ratios on the MWDs at a monomer/initiator ratio of 100:1.

cussed previously). It seems clear, therefore, that the PMMA anions may be considered living on a polymerization timescale of at least 10 min.

The relatively narrow MWDs may appear to be inconsistent with slow initiation,<sup>25</sup> but this is misleading because the rate of initiation may still be rapid enough to lead to narrow MWDs. This is illustrated in simulations based on calculations by Gold<sup>26</sup> that show the effect of the ratio  $k_p/k_t$  of the rate constants of polymerization and initiation on the MWD-conversion profiles at a monomer/initiator ratio of 100:1 (Fig. 2).<sup>27</sup> The behavior of our system would appear to be consistent with a  $k_p/k_t$  ratio of about 10–100:1. However, under these conditions, the initiator efficiency is close to 100% and thus inconsistent with our observations and the data in Table 1. However, Gold's calculations are based on an irreversible initiation. This is not necessarily correct, given our conditions and observations.

Although true equilibrium conditions do not prevail here, there is the possibility of retroaddition of the TPM–MMA anion adduct into the MMA and TPM anion, particularly at high monomer conversions (Scheme 1, eq 2). The retroaddition of living PMMA oligomers has been demonstrated<sup>27</sup> and is consistent with the high basicity of the MMA ester enolate anion and the considerable steric hindrance of the TPM moiety. This may account for the low initiator efficiencies. Pre-

liminary results from simulations, including a reversible initiation step, have indeed shown narrow MWDs along with lower initiator efficiencies.<sup>27</sup> Thus, at high monomer concentrations, the forward reaction of equilibrium of eq 2 proceeds, and this gives rise to rapid polymerization. This leads to monomer depletion, which serves to effectively stop the initiation process as a result of the reverse reaction (eq 2) kicking in, thus truncating initiation.

#### Termination/Chain Transfer

The MWD for a polymerization in which TPMTMS was only partially converted into the TPM anion (Table 1, run 7; PDI = 4.07) was much wider than with complete conversion into the TPM anion (Table 1, run 5; PDI = 1.07). The apparent initiator efficiency for run 7 is also larger (0.56) than the values of runs 2 and 5 and is consistent with rapid chain termination/transfer to the initiator by silylation of the PMMA anion and regeneration of the TMA–TPM initiator. This accounts for both the higher initiator efficiency and the wider MWD (Scheme 1, eq 4). The TMS-terminated PMMA chain end may also react with residual TMAF to regenerate the PMMA anion, thus further widening the MWD (Scheme 1, eq 5).

The DPM-initiated polymerization of MMA gave results similar to those of the TPM system, but the MWD tended to be somewhat wider (Table 1, run 8). The reason for this difference is not completely clear because the basicity of the DPM anion is higher than that of the TPM anion and is also less sterically hindered.

From this, the reactivity of the PMMA anion toward MMA in THF at  $-78\text{ }^{\circ}\text{C}$  would appear to be at least one order of magnitude greater than that of the TPM anion, at least on the basis of the observed persistence of the initiator and in agreement with Gold's model (Fig. 2). This correlates with the steric hindrance of the TPM anion and the presumably high basicity of the PMMA anion. Thus, in dimethyl sulfoxide, the  $\text{p}K_{\text{a}}$  values of ethyl acetate and triphenylmethane have been estimated to be 30–31 and 30.6, respectively.<sup>29</sup> The electron-releasing effect of the additional two methyl groups should increase the basicity of the PMMA anion further.

In addition, ion-pairing effects are important in affecting the relative nucleophilicities of PMMA and TPM anions. The initiation of MMA by the TPM anion and other carbanions tends to be slower in the presence of the large organic tetraalkylammonium ions than for the Li ion.<sup>3,5-7,17</sup> For instance, the initiation of MMA polymerizations at  $-78\text{ }^{\circ}\text{C}$  initiated by triphenylmethylithium (TPMLi) and similar species is quite rapid, and this is consistent with the formation of a relatively narrow distribution PMMA (as discussed previously).<sup>22,23</sup> This is not altogether surprising. The thermodynamic driving force for initiation is due, in part, to strong ion pairing of the lithium enolates,<sup>30</sup> which is far stronger (by roughly 5 orders of magnitude) than that of the corresponding delocalized anion initiators, for which the presence of solvent-separated ion pairs ensures weak ion pairing. This should contribute significantly to the thermodynamic driving force of the initiation. A thermodynamically more favorable Michael addition in the presence of Li ions, in comparison with Cs ions, for model compounds has been demonstrated.<sup>30</sup> These ion-pairing effects are expected to be even more reduced for the bulky tetraalkylammonium and tetraalkylphosphonium ion pairs, which are expected to behave like cryptated ion pairs and free PMMA anions.<sup>24</sup>

The relatively narrow MWDs of Table 1, compared to those obtained in TBA- and THA-mediated polymerizations, are difficult to fully assess because of the differences in the experimental conditions. As indicated previously, they may be

due to the lower polymerization temperatures or the occurrence of rapid  $\beta$ -elimination of the TBA or THA ions by the highly basic ester enolate anions.

All of these results seem to be consistent with both reversible initiation and rapid monomer-depleting polymerizations, both leading to low initiator efficiencies but narrow MWDs.

Although the degree of polymerization in this case is not simply given by the ratio of the monomer and initiator, a measure of control of the polymerization is possible. The formation of high-molecular-weight PMMA (Table 1, run 3) is readily achieved without very low initiator concentrations. As a result, the TMA-mediated polymerization of MMA may have some synthetic utility. For instance, in one of the runs in the TBA-mediated polymerization of PMMA, a very high molecular weight narrow-distribution PMMA was formed ( $M_{\text{n}} = 322,000$  and  $M_{\text{w}}/M_{\text{n}} = 1.20$ ).<sup>17</sup> No attempts were made to generate ultra-high-molecular-weight PMMA.

## CONCLUSIONS

The TMA ion, which mediates the TPM-anion-initiated anionic polymerizations of MMA in THF, appears to be significantly less susceptible to side reactions than tetraalkylammonium ions with  $\beta$ -hydrogens. Thus, the TPM and DPM anions are slowly methylated by the TMA ion under ambient conditions but not at  $-78\text{ }^{\circ}\text{C}$ . The PMMA anion does not appear to be methylated either. Thus, polymerizations of MMA in THF at  $-78\text{ }^{\circ}\text{C}$  in the presence of the TMA ion produce high yields of narrow-MWD PMMA with relatively low initiator efficiencies (9–40%). This is consistent with rapid living polymerizations, which deplete the monomer at a rate that is competitive with initiation and with retroaddition of the TPM–MMA adduct during polymerization.

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