

MECHANISTIC ASPECTS OF SILICON-MEDIATED POLYMERIZATION (GROUP TRANSFER POLYMERIZATION) OF METHYL METHACRYLATE WITH ESTER ENOLATE ANIONS AS NUCLEOPHILIC CATALYSTS

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The role of ester enolate anions in silicon-mediated polymerization (group transfer polymerization) of methyl methacrylate (MMA) was investigated using cesium, tetrabutylammonium and lithium salts of 9-methylfluorene as the nucleophilic catalysts. The results of normal anionic polymerization of MMA using these carbanion salts were compared directly with those of analogous GTP procedures with these carbanions in the presence of the silyl ketene acetal initiator 1-methoxy-1-(trimethylsiloxy)-2-methylprop-1-ene (MTS). In the absence of MTS these reactions are characterized by low conversions (14–52%), no control of M_n and broad molecular weight distributions. In the presence of MTS, controlled MMA polymerization is observed with molecular weights calculated based on the moles of MTS and not fluorene anion. The MMA stereochemistry was also determined for both anionic polymerization and GTP for the same counter ions (tetrabutylammonium, cesium, lithium); within experimental error, the triad tacticities are the same for anionic polymerization and GTP. It is concluded that these results are consistent with the ester enolate anions as propagating intermediates in nucleophile-catalyzed GTP. These results are consistent with an associative GTP mechanism only if it is postulated that the chemistry and stereochemistry of a pentacovalent siliconate anion are the same as those of an ester enolate anion intermediate.

INTRODUCTION

A number of recent studies have described methods for the controlled polymerization of acrylate and methacrylate esters to produce polymers with well defined structures.^{1–10} In general, polymerizations which have the characteristics of a living polymerization, i.e. no chain transfer and no chain termination, can provide the methodologies for the preparation of polymers with control over the major variables affecting polymer properties, such as molecular weight, molecular weight distribution, copolymer composition (e.g. random or block), chain-end functional groups and molecular architecture (linear, branched or cyclic).^{11,12} Although the controlled anionic polymerization of methacrylates, and in some cases acrylates, can be effected using appropriate initiators, solvents and additives (lithium salts and crown ethers), the use of low temperatures is generally required, e.g. -78°C .^{9,10,13–15} Hence the report of the silicon-mediated, living polymerization of acrylates and methacrylates initiated by silyl ketene acetals in the presence of nucleophilic (e.g. trisdimethylamino-sulfonium bifluoride, TASHF₂) or electrophilic (e.g. Lewis acids) catalysts at room temperature or above, called group

transfer polymerization (GTP), was an exciting discovery.^{16,17} The use of this polymerization methodology to prepare poly(alkyl methacrylates) [especially poly(methyl methacrylate), PMMA] and poly(alkyl acrylates) has been extensively investigated and reviewed.^{18–21}

In spite of all of the interesting and important synthetic applications of GTP, the mechanism of this polymerization is a subject of current controversy and ambiguity.^{22–28} This process was mechanistically described as group transfer polymerization by the inventors of GTP based on the postulate that each chain-growth step for the nucleophile-catalyzed polymerization explicitly involves transfer of a trialkylsilyl group from the silyl ketene acetal chain end of a growing polymer to the carbonyl group of the incoming monomer to form a new silyl ketene acetal chain end via a hypervalent silicon intermediate and an unusual eight-membered ring transition state.¹⁶ Later modifications of this mechanism incorporated the possible non-concerted nature of the oxygen–oxygen silyl group transfer and the carbon–carbon bond formation.²⁹ The principal experimental data to support this associative mechanism were provided in preliminary

communications in 1985 and 1986 which reported the absence of silyl group exchange for mixtures of living PMMA with a dimethyltolylsilyl ketene acetal end group and poly(*n*-butyl methacrylate) (PBMA) with a dimethylphenylsilyl ketene acetal end group when treated with a fluoride ion source [$\text{TAS}^+(\text{CH}_3)_3\text{SiF}_2^-$] and butyl methacrylate monomer at -95°C ; a similar experiment at room temperature with bifluoride catalyst was also reported to result in no silyl group exchange.^{30,31}

In contrast to these double labeling results which indicated the absence of exchange, a careful and thoroughly described set of exchange experiments between trimethylsilyl-ended PMMA and phenyldimethylsilyl-ended PMMA of different molecular weights with added methyl methacrylate and TASHF_2 catalyst provided clear and unambiguous evidence for silyl group exchange (38–44%) after fractionation.²³ Although these exchange results have been criticized because of 'incomplete exchange', i.e. less than 100%,² it should be noted that complete exchange would correspond to 50% of each label on a given polymer and not '100% exchange'.

We report here recent investigations of the role of ester enolate anions as nucleophilic catalysts for GTP and comparisons of the stereochemistry of PMMA obtained by GTP and anionic polymerizations using the same counter ions and reaction conditions. This work is an extension of previous preliminary studies.²⁴

EXPERIMENTAL SECTION

Materials. Tetrahydrofuran (THF) (Fisher) and toluene (Fisher) were dried over CaH_2 for several days and distilled under vacuum into a reservoir containing sodium benzophenone and poly(styryl)lithium, respectively. Methyl methacrylate (MMA) (Aldrich) was first passed through a column of neutral alumina (Aldrich, activated, Brockmann I) and was then dried over CaH_2 for 24 h. Before polymerization it was distilled under vacuum and then treated with triethylaluminum (Aldrich, 1.0 M solution in hexane) until a yellowish green color was observed.³² 1-Methoxy-1-(trimethylsiloxy)-2-methylprop-1-ene (MTS) (Aldrich) was freshly distilled under vacuum prior to polymerization. Tetrabutylammonium tetraphenylborate (Aldrich) and LiCl (99.99+%, Aldrich) were dried overnight at 150°C under vacuum. Cesium metal (Alfa) was used as received. *sec*-Butyllithium (FMC) (1.5 M in cyclohexane) was used as received. 9-Methylfluorene was prepared by alkylation of fluorene (Aldrich) with methyl iodide after metalation with methylithium (Aldrich) (1.4 M solution in Et_2O) in THF; m.p. 45–46°C; lit.³³ m.p. 45.5–46.5°C.

9-Methylfluorenyllithium (LiMF) was prepared by adding *sec*-butyllithium to a THF solution of 9-

methylfluorene. The corresponding cesium salt (CsMF) was prepared by first reacting 1,1-diphenylethylene with cesium metal in THF at room temperature; this procedure instantaneously produced the deep-red dianion of 1,1,4,4-tetraphenylbutane.³⁴ A small excess of 9-methylfluorene was added to this solution to produce the cherry-colored cesium 9-methylfluorenyl. The tetrabutylammonium salt of 9-methylfluorene (TBAMF) was prepared by the reaction of the corresponding cesium salt with excess tetrabutylammonium tetraphenylborate (0.2 molar excess).³⁵ The λ_{max} values measured for these anions were 386 nm (LiMF), 378 nm (CsMF) and 382 nm (TBAMF) at room temperature in THF. A molar absorptivity $\epsilon = 11,800$ was used to calculate concentrations for all salts.^{34,36}

Group transfer polymerizations using 9-methylfluorenyl alkali salts in THF. Polymerizations were carried out in a recirculating, purified argon atmosphere glove-box at room temperature. To a 100 ml, three-necked, round-bottomed flask equipped with a magnetic stirring bar, addition funnel, thermometer and condenser were added *ca* 50 ml of THF as solvent and 0.4 ml (2.0×10^{-3} mol) of silyl ketene acetal. A 5 ml aliquot of a THF solution of 9-methylfluorenyl alkali metal salt (5.6×10^{-3} M for LiMF, 1.4×10^{-2} M for CsMF and 1.2×10^{-2} M for TBAMF) was introduced via a syringe. The color of the carbanion salts remained until addition of monomer. MMA (e.g. 4.68 g, 0.0468 mol) was added slowly (10–20 min) through the addition funnel. The temperature rose to approximately 50°C , although this depended on the rate of monomer addition and the quantity of solvent. After stirring for 2–3 h the polymerization solution was removed from the dry-box and quenched with 3 ml of degassed methanol. After stirring for 0.5 h, the reaction mixture was poured into 300 ml of either hexane or cyclohexane. The polymer was filtered and dried overnight in a vacuum oven at 50°C .

Group transfer polymerization using *sec*-butyllithium in toluene. Toluene (50 ml) was distilled under vacuum into a 100 ml, flame-dried, round-bottomed flask equipped with a septum-covered side arm and a stirring bar. Silyl ketene acetal (1.0 ml, 5.0×10^{-3} mol) and *sec*-butyllithium (0.27 ml, 4.0×10^{-4} mol) were added via a syringe through a rubber septum under a positive pressure of argon. MMA (9.36 g, 0.0936 mol) was added slowly (5 min) to the toluene solution through the septum via a cannula. After 1 h the polymerization was terminated by addition of 4–5 ml of degassed methanol. Precipitation, filtering and drying were performed as described for the fluorenyl anion GTP systems.

Anionic polymerizations. Anionic polymerizations of MMA initiated with 9-methylfluorenyl salts (cesium or tetrabutylammonium) were carried out in

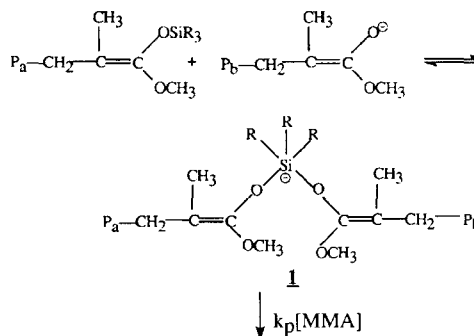
all-glass, sealed reactors using standard high vacuum techniques and break-seals.³⁷ After distillation of THF into a 100 ml, flame-dried, round-bottomed flask, the initiator solution and neat MMA were added successively via break-seals. When *sec*-butyllithium or 9-methylfluorenyllithium was used as the initiator, the solvent and monomer were distilled under vacuum successively into the flask. Then the system was filled with argon gas and the corresponding initiator solutions were introduced through a rubber septum in a side-arm by a syringe. After stirring for 30 min at room temperature, methanol (2–3 ml) was added. Precipitation, filtering and drying were performed as described for GTP polymerizations.

Characterization. The molecular weight and molecular weight distribution were determined by size exclusion chromatography (SEC) using six Ultrastaygel columns (2×500 , 2×10^3 , 1×10^4 , 1×10^5 Å) in THF as eluent at 30 °C after calibration with PMMA standards obtained from Polymer Laboratories. ¹H NMR analyses in CDCl₃ were carried out on Varian Gemini spectrometer (200 MHz). The triad tacticity of the chain was measured from integration of α -methyl protons (*mm*, $\delta = 1.18$ ppm; *mr*, $\delta = 0.98$ ppm; *rr*, $\delta = 0.80$ ppm).³⁸

RESULTS AND DISCUSSION

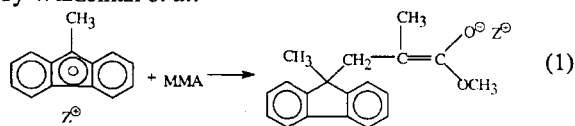
An important and interesting characteristic of GTP is the fact that narrow molecular weight distribution PMMAs can often be obtained, even for relatively low molecular weight polymers. This result indicates not only that the rate of initiation is competitive or faster than the rate of propagation, but also that the exchange process which activates the generally dormant silyl ketene acetal chain ends also occurs with rates which are competitive with propagation.^{12,39} This last condition assures that all growing chains have equal access to the growth reaction by addition of monomer. It was envisioned that ester enolate anions could serve as nucleophilic catalysts for GTP (see Scheme 1) and that investigation of the effect of ester enolate anions on GTP could provide insight into their possible role as reactive, propagating intermediates in these polymerizations.²⁴ Thus, in terms of the associative GTP mechanism, the nucleophile adds to the silicon group in the silyl ketene acetal to form the pentavalent silicate anion (e.g. 1) which reacts with monomer in the chain propagation step.

In order to investigate the possible role of ester enolate anions in GTP, a typical initiating species for anionic polymerization of MMA has been used to form ester enolate anions. For this purpose, we have prepared various salts of 9-methylfluorenyl and these were reacted with methyl methacrylate to form the corresponding ester enolate anion [equation (1)] as described



Scheme 1

by Warzelhan *et al.*⁴⁰



In order to delineate the effects of these ester enolate anions on GTP, the GTP results were compared with those of analogous anionic polymerizations using 9-methylfluorenyl anions as initiators under GTP conditions except in the absence of silyl ketene acetal initiator. Since the nucleophilic catalysts for GTP are generally used at low concentrations, e.g. $[F^-]/[\text{silyl ketene acetal}] = 10^{-3}$, low concentrations (*ca* 10^{-3} M) of 9-methylfluorenyl were used for both the anionic polymerizations and GTP.

The results of the anionic polymerizations are shown in Table 1 in runs 1, 4, 6 and 8. Earlier preliminary results obtained by Quirk and Biding²⁴ are also included in Table 1. It is obvious from these data that the anionic polymerization of MMA at room temperature is not a controlled, living polymerization with either lithium, cesium or tetrabutylammonium counter ions. These reactions are characterized by low conversions (14–52%); the highest conversion was obtained for cesium counter ion, which is consistent with kinetic studies which have shown that the rate of termination decreases with increasing counter ion size.⁴¹ In addition, the molecular weights were not related to the number-average molecular weights calculated based on the weight (grams) of monomer polymerized and moles of initiator as shown in equation (2). Furthermore, the molecular weight distributions were also broad.

$$\bar{M}_n = \frac{\text{grams of MMA polymerized}}{\text{moles of initiator}} \quad (2)$$

The dramatic effect of added silyl ketene acetal [1-methoxy-1-(trimethylsilyloxy)-2-methylprop-1-ene] is illustrated by experiments 3, 5, 7 and 9 and an earlier experiment by Quirk and Biding.²⁴ Under the same experimental conditions which produced uncontrolled

Table 1. Comparison of GTP and anionic polymerization of MMA in THF^a at an initial temperature of 25 °C using ester enolate anions generated from 9-methylfluorene salts (MF) as catalysts or initiators, respectively

Run no.	Wt of MMA (g)	[MF] salt (mol)	[MTS] ^b (mol)	Conversion (%)	M_n (calc.) (g mol ⁻¹) ^{c,d}	M_n (obs.) (g mol ⁻¹) ^e	M_w/M_n (SEC)
1	4.68	LiMF 2.8×10^{-5}	—	16	26700	63200	2.38
2	4.68	LiMF 2.8×10^{-5}	2.0×10^{-3}	43	1000	8100	1.93
3	4.68	LiMF 2.8×10^{-5}	2.0×10^{-3} ^f	81	1000	3100	1.78
4	9.36	CsMF 7.2×10^{-5}	—	52	67200	104000	1.22
5	9.36	CsMF 7.2×10^{-5}	2.0×10^{-3}	98	4490	4600	1.12
6	9.36	TBAMF 6.0×10^{-5}	—	24	37400	72000	2.16
Ref. 24	9.0	TBAMF 2.0×10^{-6}	—	14	6.3×10^6	1.29×10^5	2.0
7	9.36	TBAMF 6.0×10^{-5}	2.0×10^{-3}	98	4490	4600	1.19
Ref. 24	20.0	TBAMF 2.0×10^{-6}	4.7×10^{-3}	100	4300	5000	1.2
8	9.36	<i>sec</i> -BuLi 4.0×10^{-4}	—	19	4400	18600	3.28
9	9.36	<i>sec</i> -BuLi 4.0×10^{-4}	5.0×10^{-3}	35	660	1300	2.54

^a Except where noted otherwise.

^b 1-Methoxy-1-(trimethylsiloxy)-2-methylprop-1-ene.

^c Calculated based on equation (2).

^d Based on [MTS] for GTP polymerizations.

^e SEC using PMMA standards.

^f LiCl added (6.0×10^{-3} mol).

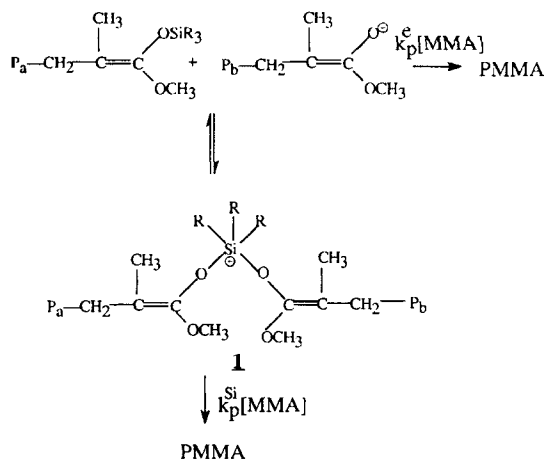
anionic polymerization, the presence of added silyl ketene acetal provided a quantitative yield of PMMA with number-average molecular weights which agree well with values calculated based on the grams of MMA polymerized and the number of moles of trimethylsilyl ketene acetal initiator [equation (2)], especially for Cs⁺ and TBA⁺ counter ions, and not on the concentration of fluorene salt. In addition, the molecular weight distributions were 'relatively narrow' (1.12–1.2 for Cs⁺ and TBA⁺).¹² In the preliminary report of Quirk and Bidinger,²⁴ it was also shown that polymerizations of MMA initiated with catalytic amounts of tetrabutylammonium 9-methylfluorene and trimethylsilyl ketene acetal initiator are living polymerizations using the criterion of sequential monomer addition.¹² No evidence for chain termination was obtained when additional MMA monomer was added after 3.75 h.

The data in Table 1 also indicate that the ability to obtain controlled polymerization of MMA at room temperature and above using nucleophile-catalyzed, silicon-mediated polymerization is critically dependent on the nature of the counter ion and the solvent. The best results are obtained for the larger counter ions, cesium and tetrabutylammonium.⁴¹ The poorest and least repro-

ducible results were obtained with lithium as counter ion in toluene. However, even with lithium as counter ion, the silicon-mediated polymerizations proceeded in higher yield to give molecular weights which were closer to the stoichiometric values and with narrower molecular weight distributions compared with the corresponding polymerizations in the absence of silyl ketene acetal. It is also interesting that the best results with lithium as counter ion (run 3) were obtained in the presence of added lithium chloride. This is consistent with the effect of lithium chloride in enhancing the controlled anionic polymerization of MMA in THF at lower temperatures with lithium as counter ion.^{9,10}

Perhaps the most important conclusion from the data in Table 1 is that ester enolate anions can function as nucleophilic catalysts in the silicon-mediated polymerization (GTP) of MMA. In considering the implications of this conclusion, it is important to re-examine the reaction sequence described in Scheme 1. For the associative GTP mechanism, the pentavalent silicate anion (**1**) coordinates with monomer and then transfers the silyl group to the carbonyl oxygen of the monomer while forming the carbon-carbon bond. In the traditional GTP mechanism, one of the ester enolate groups would be

replaced by a nucleophilic catalyst such as fluoride or benzoate. From the experiments described in Table 1, the direct addition of monomer to the silicate intermediate, **1**, cannot be excluded. However, the fact that relatively narrow molecular weight distributions are obtained indicates that the rate of the nucleophile exchange process among active chain ends must be competitive with the rate of propagation. This, in turn, means that the nucleophile, in this case an ester enolate anion, must exchange among active chain ends. As concluded in the preliminary work of Quirk and Bidinger,²⁴ the requisite presence of ester enolate anion intermediates for this exchange process (Scheme 1) means that these same ester enolate intermediates are available for direct addition of monomer in a polymer growth forming sequence. This conclusion dictates that Scheme 1 should be modified as shown in Scheme 2 to reflect the possibility that propagation could occur by monomer addition to both the ester enolate anion intermediate (k_p^e) via a 'dissociative mechanism' and the pentacoordinate silicate anion (**1**, k_p^{Si}) via an 'associative mechanism'. The data in Table 1 cannot rule out propagation via the associative mechanism, but they do support the premise that ester enolate anion intermediates can be involved as propagating species in nucleophile-catalyzed, silicon-mediated MMA polymerizations.²⁴ Furthermore, the effectiveness of such low amounts of carbanion (10^{-5} – 10^{-6} mol) relative to silyl ketene acetal (10^{-3} mol) suggests that this process is very efficient for the generation of the required ester enolate ion intermediates. With respect to the requirements for controlled anionic polymerization of MMA at room temperature, these results also suggest that it may be essential to maintain a very low concentration of ester



Scheme 2

enolate anions ($<10^{-4}$ – 10^{-6} M) in equilibrium with a dormant species (e.g. **1**).

In order to evaluate the role, if any, of the pentacoordinate silicate intermediate, **1**, in MMA propagation using ester enolate-catalyzed, silicon-mediated polymerization, the polymer stereochemistry was investigated for both the anionic polymerization and the silicon-mediated polymerization and the results are shown in Table 2. The run numbers in Table 2 correspond to the experiments described in Table 1. The results were compared with representative data from the literature as indicated. The data in Table 2 indicate that

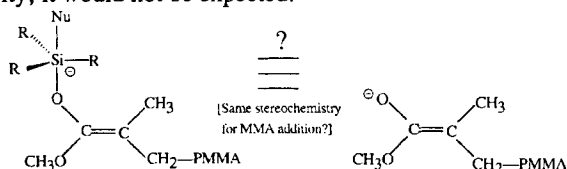
Table 2. Stereochemistry of anionic and silicon-mediated polymerizations of MMA using the same counter ions and initiated at 25°C

Run no.	Counter ion	Polymerization	Polymer microstructure (triads, %)		
			Isotactic (<i>mm</i>)	Heterotactic (<i>mr + rm</i>)	Syndiotactic (<i>rr</i>)
1	Li ⁺	Anionic	3	29	68
2		GTP	4	33	63
3		GTP	4	30	66
4	Cs ⁺	Anionic	8	52	40
Ref. 42		Anionic ^a	5	53	42
5		GTP	9	52	39
6	Bu ₄ N ⁺	Anionic	6	37	57
Ref. 24		Anionic	5	39	56
7		GTP	6	40	54
Ref. 24		GTP	5	42	53
8	Li ⁺	Anionic	71	20	9
Ref. 43		Anionic ^b	71	21	8
9	Li ⁺	GTP	77	16	7

^a Cumylcesium-initiated polymerization in THF at -66°C.

^b α -Lithioethyl isobutyrate as initiator in toluene at 20°C.

the stereochemistry of ester enolate-catalyzed silicon-mediated polymerization of MMA is essentially the same, within experimental error, as the stereochemistry of corresponding anionic polymerizations when the same counter ions are compared for each process. These are compelling results with respect to the nature of the propagation reactions for these two polymerizations. The most direct conclusion would be that the same propagating species are involved in ester enolate catalyzed GTP and for anionic polymerization. This conclusion would be consistent with a dissociative mechanism for GTP (see Scheme 2), without the need to invoke propagation via the pentacoordinate silicate intermediates, **1**; thus, k_p^{Si} [MMA] would not contribute to the propagation rate. It is important to consider carefully this possibility with respect to the data presented in Tables 1 and 2. The role of ester enolate anion intermediates as propagating species is consistent with the data in both Tables 1 and 2. With respect to the role of pentacoordinate silicate intermediates as propagating species, the data in Table 2 cannot exclude their contribution. However, as discussed previously,²² it is necessary to rationalize that the chemistry, especially the stereochemistry of monomer addition, of the pentavalent silicate intermediate is essentially identical with that of an ester enolate anion intermediate (see the structures shown). Although this is a possibility, it would not be expected.



Further, as pointed out several times, the mechanistic evidence to support the intervention of pentavalent silicate intermediates as propagating species is minimal. As described here, the demonstrated ability of ester enolate intermediates to serve as nucleophilic catalysts for silicon-mediated polymerizations (GTP) and the observations of the same polymer microstructures for anionic polymerization and GTP support the proposed intermediacy of ester enolate anions as propagating species in nucleophile-catalyzed GTP.

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