Mechanistic Studies of Group Transfer Polymerization. Silyl Group Exchange Studies

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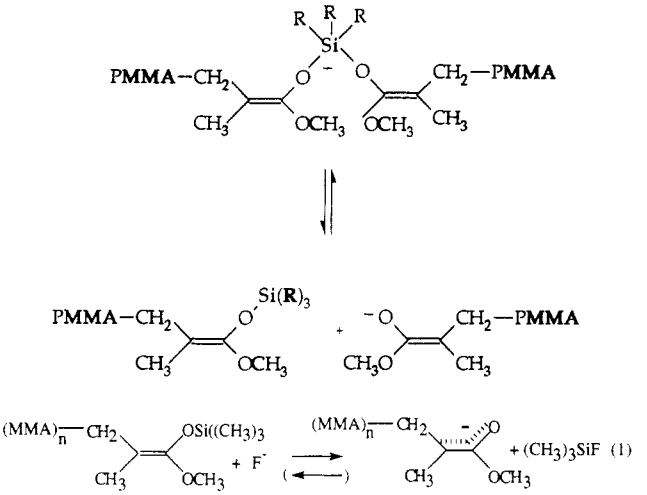
ABSTRACT: The role of trialkylsilyl group exchange during group-transfer polymerization has been investigated. Living trimethylsilyl-ended poly(methyl methacrylate) (M_n = 1.3 × 10⁴) was mixed with phenyldimethylsilyl-ended poly(methyl methacrylate) (M_n = 3.1 × 10³) using tris(dimethylamino)sulfonium bifluoride as nucleophilic catalyst for periods ranging from 0.33–2 h. After separation by fractionation, the polymers were analyzed by ^{1}H NMR spectroscopy. Evidence for silyl group exchange (40–76%) was obtained for both polymers; exchange (28%) also was observed when the labels were reversed. Exchange (80%) also occurred between the trimethylsilyl-labeled PMMA oligomer and phenyldimethylsilyl ketene acetal initiator. Control experiments established that no exchange occurred during fractionation. In contrast to previous reports, silyl group exchange was also detected during GTP polymerization. An equimolar mixture of living phenyldimethylsilyl-ended PMMA (M_n = 2.9 × 10³) and living trimethylsilyl-ended PMMA (M_n = 1.4 × 10⁴) was used to initiate GTP of methyl methacrylate in the presence of the bifluoride ion; silyl group exchange (38–44%) was observed in both polymers after fractionation. This evidence is consistent with the intermediacy of ester enolate anions as propagating species in GTP. These data are not consistent with the associative mechanism, i.e. "group-transfer polymerization", in which 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, and thus silyl group exchange is excluded.

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] GTP was a significant new development since it combined the important advantages of living polymerization with the ability to carry out polymerizations at room temperature and above. Thus, narrow molecular weight distribution polymers are formed in quantitative yields and the degree of polymerization is controlled by the ratio of monomer to initiator. This process was mechanistically described as "group transfer polymerization" on the basis of 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 a rather unusual eight-membered ring transition state.[5,6] In the intervening years, little modification or criticism of this mechanism has been proposed, other than to acknowledge the possible nonconcerted nature of the oxygen–oxygen silyl group transfer and the carbon–carbon bond formation.[5-11]

A new dissociative mechanism involving ester enolate anion intermediates as propagating species was recently proposed for the process currently categorized as nucleophile-catalyzed group transfer polymerization (GTP).[12] The key step in this proposed mechanism is a rapid, reversible complexation of the propagating enolate anion intermediates with a silyl ketene acetal chain-end functionality (Scheme I). This equilibrium provides a rationale for the living nature of these polymerizations and the role of 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 ester enolate anions[13,14] (eq 1). This proposed mechanism does not involve silyl group transfer in the chain-growth step;

Scheme I



however, group transfer does occur between propagating chain ends via ester enolate anion intermediates (Scheme I).

The following experimental observations are consistent with the hypothesis that the propagation reaction in group-transfer polymerization (GTP) of alkyl methacrylates is anionic in nature with enolate anions as propagating species, although alternative explanations in terms of the associative mechanism for GTP have generally been invoked in the cited references.

1. The primary termination reaction in methyl methacrylate GTP[15] involves a chain-end cyclization reaction to form a cyclohexanone-type chain end which is analogous to the termination product of ester enolate anions in corresponding anionic polymerizations.[16]

2. Chain transfer is observed to carbon acids which have pK_a values in the range 18–25 for methyl methacrylate GTP.[17] Estimates of the pK_a of the conjugate acids of ester enolate anions range from 24.5[18] to 27–28[19] in aqueous solution to 30–31 in dimethyl sulfoxide.[19] This chain-transfer process is analogous to the tetrabutylammonium

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fluoride catalyzed silylation of aldehydes and ketones with ethyl (trimethylsilyl)acetate for which an ester enolate anion intermediate has been postulated.[20]

3. The stereochemistry of GTP for methyl methacrylate is essentially the same as that observed for anionic polymerization when the counterions compared are the same[12] or similar.[11]

4. Enolate anions can function as the "nucleophilic catalysts" for anionic GTP.[12] The mechanistic significance of this fact has been discussed in our previous publication.[12]

5. The monomer reactivity ratios for GTP copolymerization are similar to the monomer reactivity ratios observed for anionic polymerization.[11]

6. The energies of activation and frequency factors for GTP polymerization of methyl methacrylate are very similar to the corresponding parameters for anionic polymerization;[11] it is significant to note, however, that no kinetic comparisons are available for the same counterions.

7. An unusual negative reaction order (−0.27) kinetic dependence on silyl ketene acetal end-group concentration (initiator) has been reported for GTP polymerization of both methyl methacrylate[9] and *tert*-butyl methacrylate.[21] This was ascribed to inhibition of the reaction by the initiator[9,21] and is in accord with the mechanism shown in Scheme I and eq 1.[12]

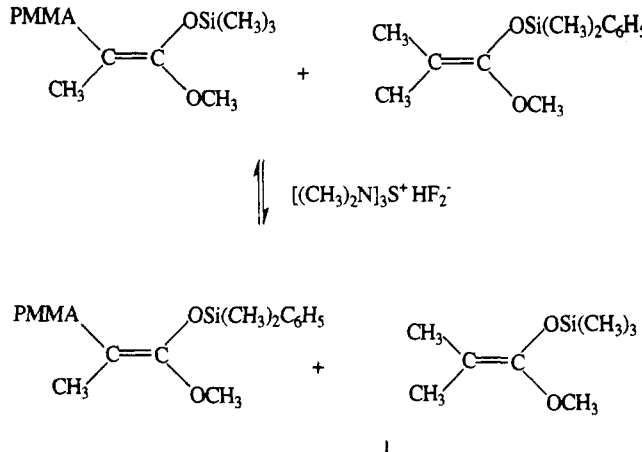
Given the weight of this evidence, it is doubtful that a new propagation mechanism, different from an enolate anion propagating species, would be proposed at this time. The logical question is what experimental evidence can be used to support the originally proposed and generally accepted new type of mechanism for GTP involving intramolecular transfer of a silyl group with each monomer addition step? The evidence to support the cyclic GTP mechanism consists of (A) the ability to carry out the living polymerization of methyl methacrylate at ambient temperature and above, which certainly stands in sharp contrast to conditions required for living anionic polymerization of alkyl methacrylates (other than *tert*-butyl methacrylate), e.g. −78 °C,[22,23] and (B) no exchange reported between silyl groups on growing polymer chains as would be required by the dissociative anionic mechanisms.[5,6] This lack of silyl group exchange is perhaps the most significant experimental evidence to support the basic GTP mechanism which explicitly states that every monomer addition is accompanied by a silyl group transfer 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. It is also these pivotal results which force researchers to invoke rather convoluted mechanistic alternatives such as nonconcerted intramolecular silyl transfers rather than postulate ester enolate anion intermediates which are consistent with the majority of experimental evidence as cited previously in terms 1–7. In spite of the importance of these exchange experiments, they have not been described in detail with experimental evidence in a refereed journal nor have they been reproduced by another laboratory.

Against this background, we undertook a detailed examination of the question of whether silyl group exchange occurs between propagating chain ends during nucleophile-assisted group-transfer polymerization and the results are reported herein.

Experimental Section

Chemicals and Solvents. Methyl methacrylate (MMA), tetrahydrofuran (THF), hexane, and 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene were purified as described previously.[12] Acetonitrile (99%, Aldrich) was stirred over CaH_2 overnight and vacuum-distilled before use. Phenyldimethylchlorosilane (98%, Petrarch Systems Silanes & Silicones) was stirred over CaH_2 for 4 h and fractionally distilled (bp 63 °C/2 mmHg). Petroleum ether (Aldrich, ACS reagent, bp 35–60 °C) was stirred over concentrated H_2SO_4 (Fischer, ACS reagent) for 3–5 days, decanted onto sodium hydroxide (Fisher certified ACS), stirred for at least 1 day, and then decanted onto and stored over molecular sieves (Aldrich 4 Å). Silver nitrate (99+%, Aldrich), diisopropylamine (99%, Aldrich), and methyl isobutyrate (99%, Aldrich) were used as received.

Scheme II



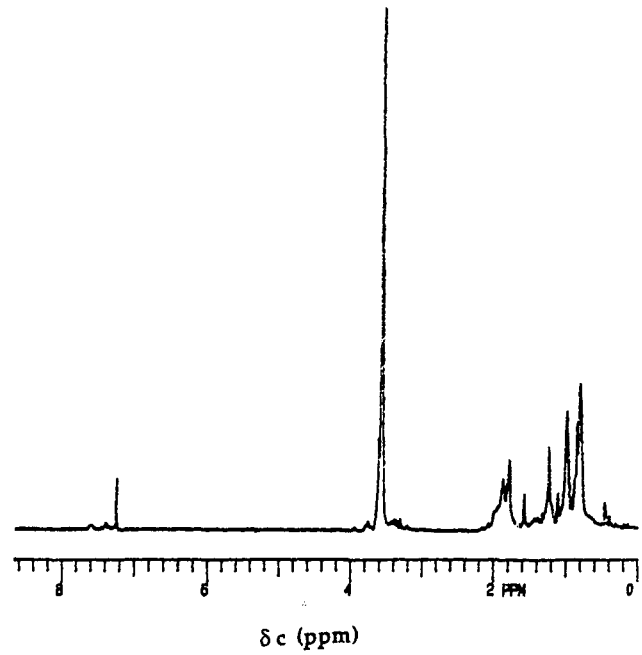


Figure 1. ^1H NMR spectrum of the precipitated PMMA after mixing phenyldimethylsilyl ketene acetal with trimethylsilyl-ended PMMA in the presence of catalyst for 1 h.

Tris(dimethylamino)sulfonium bifluoride ($TASHF_2$) was prepared by the reaction of water with tris(dimethylamino)sulfur trimethylsilyl difluoride (TASF) (Aldrich, 95%) in acetonitrile and recrystallized from THF/acetonitrile;[8] mp 152.5–153.5 °C (Lit.[8] mp 153.0–153.5 °C). 1-Methoxy-1-(phenyldimethylsiloxy)-2-methyl-1-propene was prepared by adding methyl isobutyrate at −78 °C to freshly prepared lithium diisopropylamide in THF,[8,24,25] followed by the slow addition of phenyldimethylchlorosilane.[26] The product was obtained by vaccum distillation twice (bp 135 °C/10 mmHg) in 88% yield. ^1H NMR ($CDCl_3$): δ 7.35–7.48 and 7.65–7.72 (m, C_6H_5), 3.55 (s, OCH_3), 1.54, 1.60 (s, CH_3), and 0.52 ppm (s, CH_3Si); intensity ratio 5:3:6:6. ^{13}C NMR ($CDCl_3$): δ 150.0 (C—O), 128.1, 130.1, 134.0, 137.9 (C_6H_5), 91.8 (C—CH_3), and 18.1, 18.8 ppm (CH_3). IR (KBr): 1700 cm^{-1} (C=C). The characteristic ester absorption band at 1740–1750 cm^{-1} was absent in the IR spectrum of the silyl ketene acetal, which is consistent with the absence of ester impurities.

Polymerizations. All polymerizations of methyl methacrylate were carried out in a recirculating, purified argon atmosphere

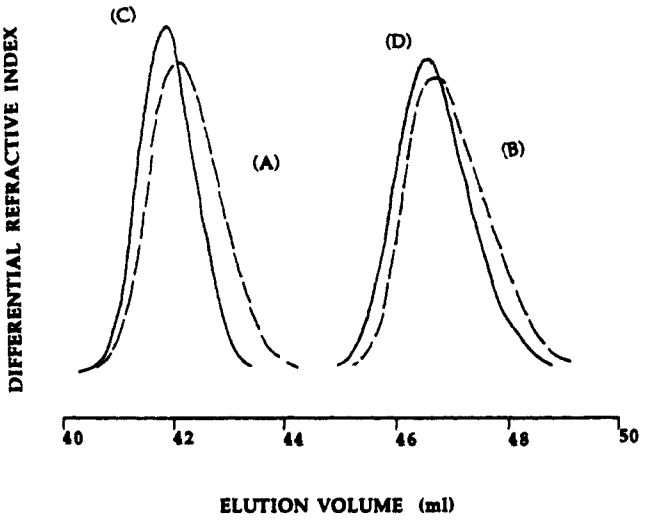


Figure 2. SEC chromatograms of PMMA(*H*) (A), PMMA(*L*) (B), and the high (*F*)PMMA(*H*) (C) and low (*F*)PMMA(*L*) (D) molecular weight filtrate.

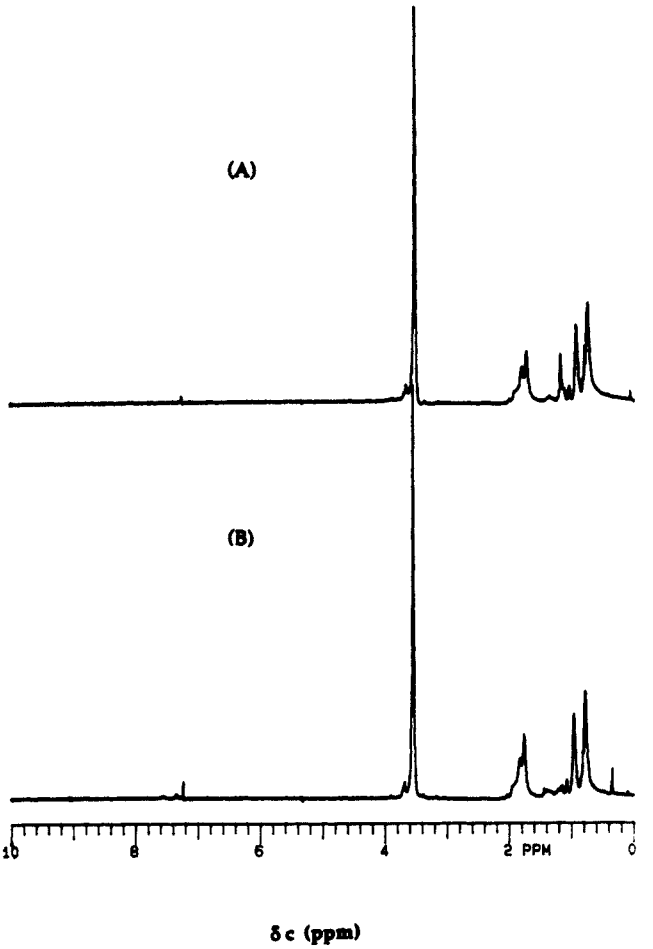


Figure 3. ^{1}H NMR spectra of the trimethylsilyl-ended PMMA-(*H*) (A) and high molecular weight filtrate (*F*)PMMA(*H*) (B).

glovebox at ambient temperatures. Methyl methacrylate was added slowly to the tetrahydrofuran solutions of initiator. $TASHF_2$ catalyst was introduced via CH_3CN solutions (0.4 mg/mL). The polymerizations were exothermic with temperatures reaching 40–65 °C, depending on the rate of monomer addition and the type of initiator.

Fractionations. THF was used as the solvent and petroleum ether as the nonsolvent. A sample (2.0 g) of a PMMA mixture was dissolved in 250 mL of dry THF. Dry petroleum ether was gradually added with vigorous stirring until turbidity was observed (ca. 800 mL of petroleum ether), and then the solution was allowed to stand overnight. The resulting clear solution was

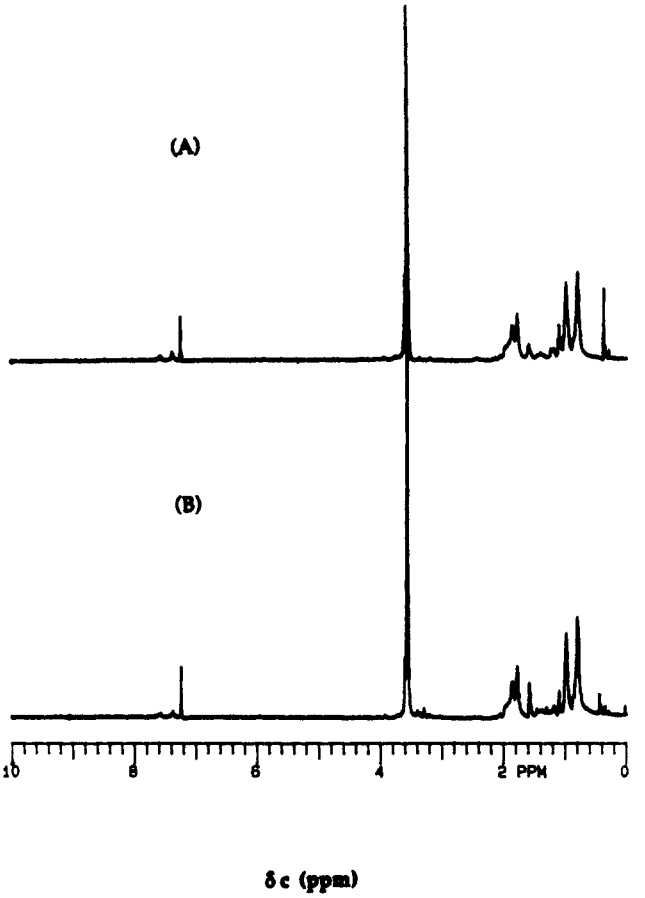


Figure 4. ^{1}H NMR spectra of the phenyldimethylsilyl-ended PMMA(*L*) (A) and low molecular weight fitrate (*F*)PMMA(*L*) (B).

mixed gradually with an additional amount of petroleum ether (ca. 150 mL) until turbidity was observed. The solution was then warmed until clear and cooled gradually with slow stirring. After 3 days, the concentrated phase was precipitated out, separated, and dried (0.7 g). To avoid any overlap between fractions, this procedure was repeated twice. Lower molecular weight fractions were obtained in a similar manner except the diluted phase was collected instead of the concentrated phase.

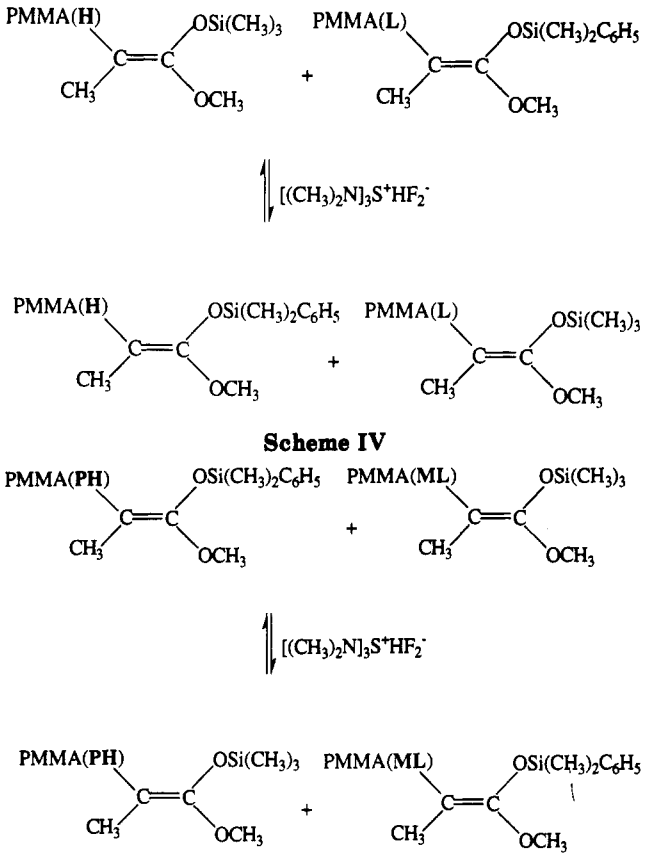
Characterization. Size exclusion chromatographic analyses were performed using six Ultrastyragel columns (two 500, two 10^3, 10^4, 10^5 Å) in THF at 30 °C after calibration with poly(methyl methacrylate) standards obtained from Polymer Laboratories. ^{1}H NMR and ^{13}C NMR analyses in $CDCl_3$ (99.8 at % D, Aldrich; stored over 4-Å molecular sieves) were performed at 200 MHz using a Varian Gemini spectrometer. The amount of silyl group exchange was determined by integrating the peak corresponding to a given silyl group relative to the methoxy methyl protons of the repeating unit in conjunction with the SEC-determined value of M_n. FT-IR were recorded using a Beckman FT2100.

Results and Discussion

As discussed in the Introduction, the most important question with regard to the mechanism of group-transfer polymerization is whether silyl group exchange is competitive with chain propagation. In the postulated associative mechanism, silyl exchange among growing chains is excluded: the identity of the silicon atom of the initiator molecule remains invariant throughout the growth of a given polymer chain.[5,6]

The nature of silyl group exchange reactions was first investigated by examining the rate of silyl group exchange between living oligomer and silyl ketene acetal initiator. Thus, phenyldimethylsilyl ketene acetal initiator (1×10^{-3}mol) was reacted with a living trimethylsilyl-ended

Scheme III



Scheme IV

PMMA (1×10^{-3}mol, $M_n = 2.3 \times 10^3$, $M_w/M_n = 1.06$) in the presence of the tris(dimethylamino)sulfonium bifluoride ($TASHF_2$) catalyst (2×10^{-5}mol) in 20 mL of THF for 1 h at room temperature (see Scheme II). The ^1H NMR spectrum of PMMA (Figure 1) isolated after reprecipitation in dry hexane showed signals at δ 0.38, 7.32–7.44, and 7.55–7.64 ppm, indicating that the phenyldimethylsilyl group is readily incorporated (80%) into the living polymer chains. To ensure that the observed phenyldimethylsilyl end group was not due to the presence of free phenyldimethylsilyl ketene acetal, the above experiment was repeated without bifluoride catalyst. The ^1H NMR of PMMA obtained after reprecipitation in dry hexane reproduced the original ^1H NMR spectrum of trimethylsilyl-ended PMMA (only CH_3–Si resonance at δ 0.05 ppm) with no evidence for phenyldimethylsilyl group incorporation. This experiment shows that free silyl ketene acetal initiator would not be present as a contaminant in the final product after normal workup and that silyl group exchange does not occur in the absence of catalyst. It is important to note that analogous results were also reported by Farnham and Sogah,[5,6] i.e., silyl exchange was reported to occur between initiator and living GTP oligomer. They concluded that "Hence, resilylation of the ester enolate by other silyl ketene acetals (monomeric or oligomeric), may be facile and pronounced at the early stages of the reaction".[5] However, they concluded that they could not rule out "intervention of the irreversible dissociative mechanism for very short chain lengths",[6] but they believed that it was reasonable "to assume, however, that the mechanism for GTP propagation is independent of chain length".[6] Thus, with this rationalization, the mechanistic significance of these exchange experiments was dismissed.

In contrast to the conclusions of Farnham and Sogah,[5,6] it is prudent to conclude that *at room temperature and during time intervals which correspond to the time required for monomer addition in typical group-transfer polymerizations (20 min), silyl group exchange occurs between living oligomers possessing trimethylsilyl ketene acetal end groups with the phenyldimethylsilyl groups of a silyl ketene acetal initiator.*

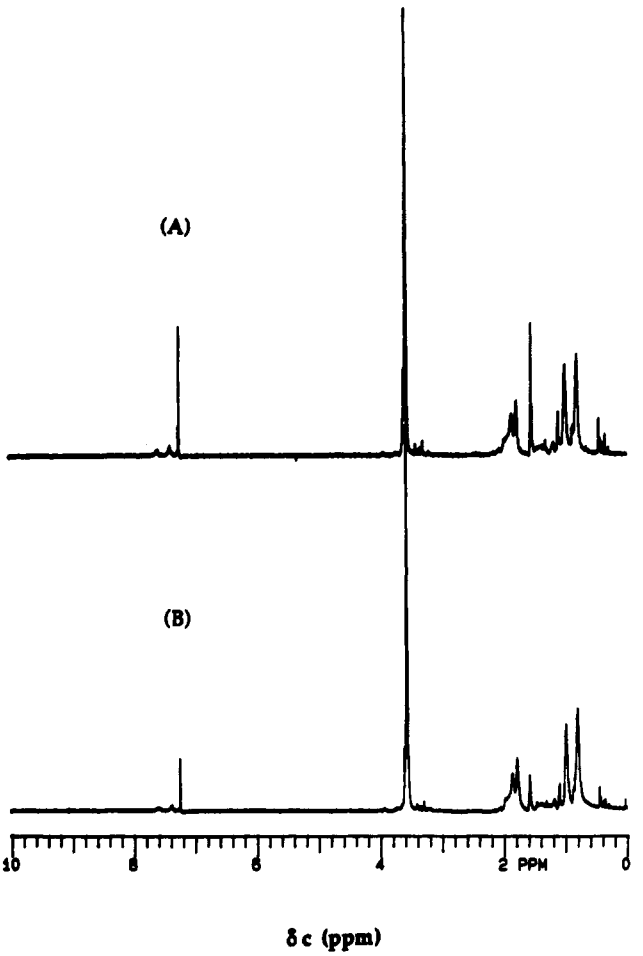


Figure 5. ^1H NMR spectra of the phenyldimethylsilyl-ended PMMA(*PH*) (A) and high molecular weight fitrate (*F*)PMMA-(*PH*) (B).

Since GTP requires only minute amounts of the nucleophilic catalyst (≪1 mol % relative to chain ends), the concentration of silyl ketene acetal chain ends far exceeds that of the propagating species. Thus, only a small fraction of the polymer chains is active at any given time; i.e. the propagating chain ends are diluted by "dormant" ones. Nucleophilic catalyst entities (whether they are ester enolate anions or bifluoride anions) are exchanged between polymer chain ends through catalyst exchange equilibria, which may or may not be the same as the silyl group exchange process. This catalyst exchange is rapid relative to monomer propagation; otherwise the relatively narrow molecular weight distributions of poly(alkyl) methacrylates would not be obtained by group-transfer polymerization.[11] Therefore, the rate of silyl group exchange among living oligomers is as important as the relative rate of nucleophilic catalyst exchange between growing polymer chains during propagation.

It has been reported that oligomeric silyl ketene acetals do not exchange silyl groups intermolecularly.[5,6] *We have reexamined this conclusion using the simple technique of mixing living polymers of different molecular weights and with different silyl end groups in the presence of the TAS bifluoride nucleophilic catalyst, followed by separation by fractionation* (see Scheme III). Living trimethylsilyl-ended PMMA(*H*) (1×10^{-3} mol, $M_n = 1.3 \times$

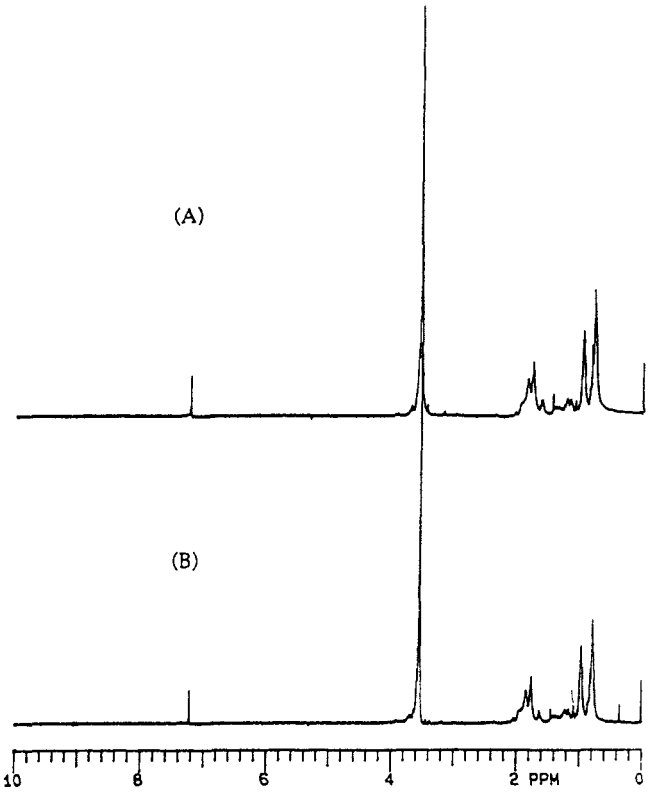


Figure 6. ^{1}H NMR spectra of the trimethylsilyl-ended PMMA(*ML*) (A) and low molecular weight fitrate (*F*)PMMA(*ML*) (B).

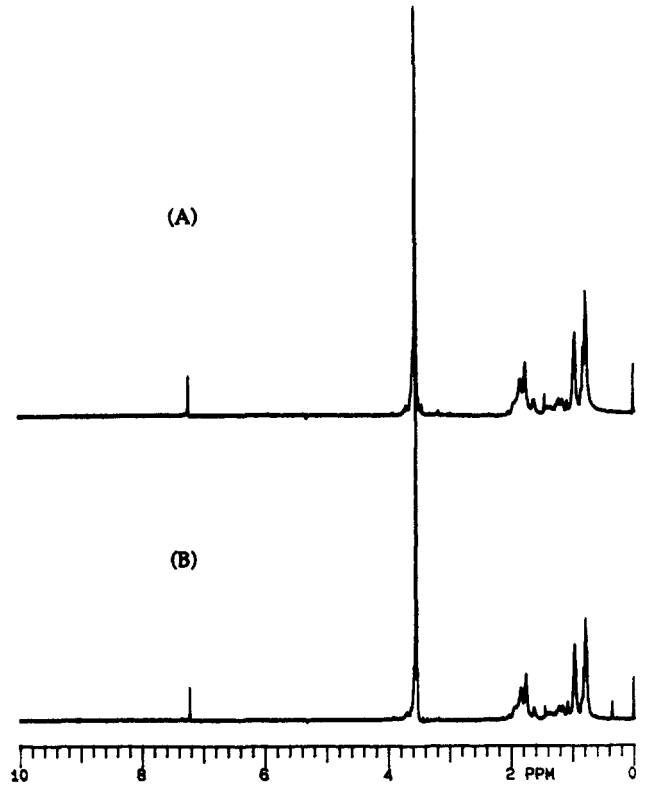


Figure 7. ^{1}H NMR spectra of the trimethylsilyl-ended PMMA(*H*) (A) and high molecular weight fitrate (*F*)PMMA(*H*) (B) after mixing for 2 h.

10^4, M_w/M_n = 1.06) [see (A), Figure 2], was mixed with phenyldimethylsilyl-ended PMMA(*L*) (1×10^{-3}mol, $M_n = 3.1 \times 10^3$, M_w/M_n = 1.07) [see (B), Figure 2] in the presence of bifluoride catalyst (2×10^{-5} mol) in 20 mL of THF for 20 min. PMMA20 was obtained by precipitating the living polymer into dry hexane after 20 min. Fractionation of this polymer provided (*F*)PMMA(*H*) ($M_n = 1.4 \times 10^4$, M_w/M_n = 1.03) [see (C), Figure 2] from the less soluble fraction and (*F*)PMMA(*L*) ($M_n = 3.21 \times 10^3$, M_w/M_n = 1.04) [see (D), Figure 2] from the soluble fraction. The ^{1}H NMR spectrum of (*F*)PMMA(*H*) [see (B), Figure 3] showed signals at δ 0.38, 7.32–7.44, and 7.55–7.64 ppm, *providing clear evidence for the incorporation of phenyldimethylsilyl groups (72%) into the higher molecular weight chains.*[27] The ^{1}H NMR of (*F*)PMMA(*L*) [see (B), Figure 4] showed minor signals at δ 0.05 ppm, *indicating incorporation of 40% of the trimethylsilyl groups into the lower molecular weight chains* (see Scheme III).

Analogous exchange experiments were also carried out with the initial labels reversed, as shown in Scheme IV. Thus, exchange experiments for 20 min were carried out for phenyldimethylsilyl-ended PMMA(PH) (1×10^{-3} mol, $M_n = 1.2 \times 10^4$, M_w/M_n = 1.05) with trimethylsilyl-ended PMMA(ML) (1×10^3 mol, $M_n = 2.1 \times 10^3$, M_w/M_n = 1.06) in the presence of bifluoride catalyst (2×10^{-5} mol) in 20 mL of THF for 20 min. After fractionation, silyl group exchange was detected by ^{1}H NMR for both the higher (28% exchange) and lower (27% exchange) molecular weight chains (see Figures 5 and 6, respectively).

The silyl group exchange experiment was also carried out for trimethylsilyl-ended PMMAMH (1×10^{-3} mol, $M_n = 1.3 \times 10^4$, M_w/M_n = 1.06) and phenyldimethylsilyl-ended PMMAPL (1×10^{-3} mol, $M_n = 3.1 \times 10^3$, M_w/M_n = 1.07) in the presence of bifluoride catalyst (2×10^{-5} mol) in 20 mL of THF for a longer time period, 2 h (see Scheme III). The ^{1}H NMR spectral results are given in Figures 7 and 8 for the high and low molecular weight fractions, respectively. The percentage of silyl group exchange was 51% for the higher molecular weight fraction and 40% for the lower molecular weight fraction.

It should be noted that the estimates of the percentage of exchange are only semiquantitative, because the integration ratio of silyl-ended protons with respect to methoxyl protons is complicated by cyclotermination[15,28] and catalyst deactivation.[8] However, it was observed that more than 90% of the chains retained their active silyl ketene acetal functionality throughout the exchange and fractionation processes; one exception was in the oligomer-exchange experiment which was carried out for 2 h in the presence of nucleophilic catalyst, in which 28% of the chains were calculated to be inactive after the fractionation process.

In general, the trialkylsilyl groups in silyl ketene acetals are readily cleaved by moisture in the atmosphere; however, it was observed that the silyl groups in silyl ketene acetal-ended polymers are relatively stable. In order to cleave all of the silyl groups in living PMMA chains, it was necessary to react the THF solution of the polymer with methanol and stir at reflux for 0.5–1 h. The relative stability of the trialkylsilyl groups in the polymers made it possible to perform fractionations outside of an inert atmosphere drybox.[8]

An important question is whether trialkylsilyl group exchange can occur during the fractionation process. It is known that the minute amounts of anionic catalysts (0.1% with respect to initiator concentration) required for GTP are easily deactivated by the catalytic amounts of protonic impurities in the atmosphere; in experiments reported by

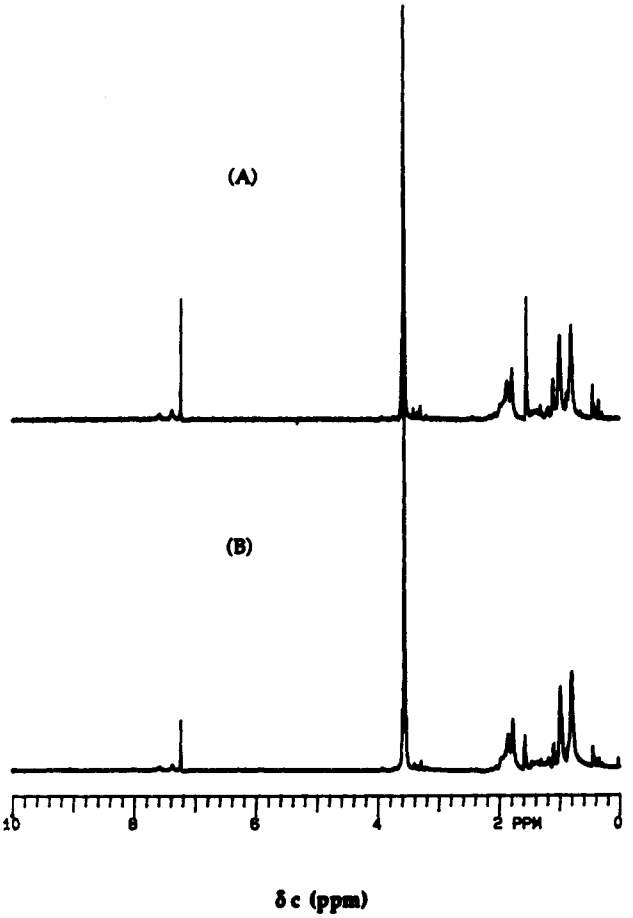


Figure 8. ^{1}H NMR spectra of the phenyldimethylsilyl-ended PMMA(*L*) (A) and low molecular weight fitrate (*F*)PMMA(*L*) (B) after mixing for 2 h.

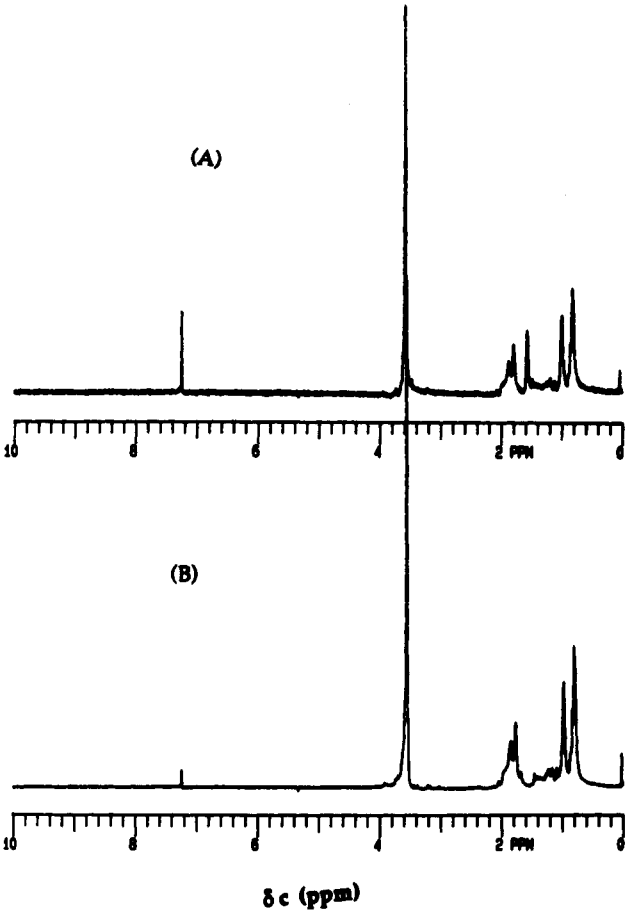


Figure 9. ^{1}H NMR spectra of the trimethylsilyl-ended PMMA-(*H*) (A) and high molecular weight fitrate (*F*)PMMA(*H*) (B) in the control experiment for fractionation.

DuPont scientists,[8] additional catalyst was often required to make block copolymers or to complete the polymerization. Thus, it was deduced that the anionic catalyst might be deactivated and not available to catalyze the trialkylsilyl group exchange during the fractionation process. To test this hypothesis and determine if exchange was occurring during the fractionation process, fractionation was carried out directly on mixtures of two living polymers. Living trimethylsilyl-ended PMMA (M_n = 7.6 × 10^3, M_w/M_n = 1.06) and phenyldimethylsilyl-ended PMMA (M_n = 2.1 × 10^3, M_w/M_n = 1.06) were each isolated by precipitatation into low-boiling petroleum ether and dried in an inert-atmosphere drybox. Equal numbers of moles (1 × 10^{-3} mol) of these trimethylsilyl-ended PMMA and phenyldimethylsilyl-ended PMMA were dissolved in 20 mL of THF, and then the standard fractionation procedure was immediately carried out for the mixture. The ^{1}H NMR results of the high (Me_3Si–) and low ($PhMe_2Si$–) molecular weight fractions are shown in Figures 9 and 10, respectively; no evidence for silyl group exchange is apparent in these spectra; i.e., compare these results with those from the exchange experiments (Figures 3,4; 5,6; and 7,8). These results show that exchange did not occur during the fractionation process and that the chains retain their silyl ketene acetal functionality. These results also demonstrate that even if some of the nucleophilic catalyst was coprecipitated with the polymer, it does not catalyze exchange during fractionation. It is concluded that the minute amounts of catalyst present are easily deactived. Thus, there is no apparent need to add silver nitrate to trap the catalyst in silyl-ended oligomer-exchange experiments.[5,6]

Since silyl groups readily exchange among living oligomers as predicted by the proposed mechanism based on previous studies of ester enolate anion-catalyzed GTP[12] (see Scheme I), it seems reasonable to conclude that analogous nucleophile-promoted dissociation of the silyl-ended PMMA chains to form ester enolate anions (see eq 1) occurs during propagation also.[12] In order to address this question directly, two living polymers labeled with different silyl groups and with different molecular weights were used to initiate further propagation (see Scheme V); silver nitrate was added in order to try to reproduce some of the reported details of the exchange experiments of Sogah and Farnham[5,6] for which no exchange was reported. $TASHF_2$ was reported to react with $AgNO_3$ to form $AgHF_2$ which was not a GTP catalyst.[5,6] Trimethylsilyl-ended PMMA(H) (1 × 10^{-3} mol, M_n = 1.4 × 10^4, M_w/M_n = 1.05) was mixed with phenyldimethylsilyl-ended PMMA(L) (1 × 10^{-3} mol, M_n = 2.9 × 10^3, M_w/M_n = 1.05) in the presence of $TASHF_2$ catalyst (2 × 10^{-5} mol) in 20 mL of THF; then 9.6 g (80% of total monomer added) of methyl methacrylate (MMA) was added dropwise over a 20-min period (see Scheme V). At this point, silver nitrate (2.5 × 10^{-3} mol) was added,[5,6] while the remainder (2.4 g, 20%) of the MMA monomer was continually added. The mixture was then precipitated into petroleum ether. The SEC curves of the original oligomers and of the polymers obtained after extensive fractionation are shown in Figure 11. The high molecular weight fraction [FPMMA(H_p)] exhibited M_n = 2.0 × 10^4 and M_w/M_n = 1.03. The low molecular weight fraction [FPMMA(L_p)] exhibited M_n = 6.0 × 10^3 and M_w/M_n = 1.04. The ^{1}H NMR spectra of the fractionated polymers [FPMMA(H_p) and FPMMA(L_p)] and

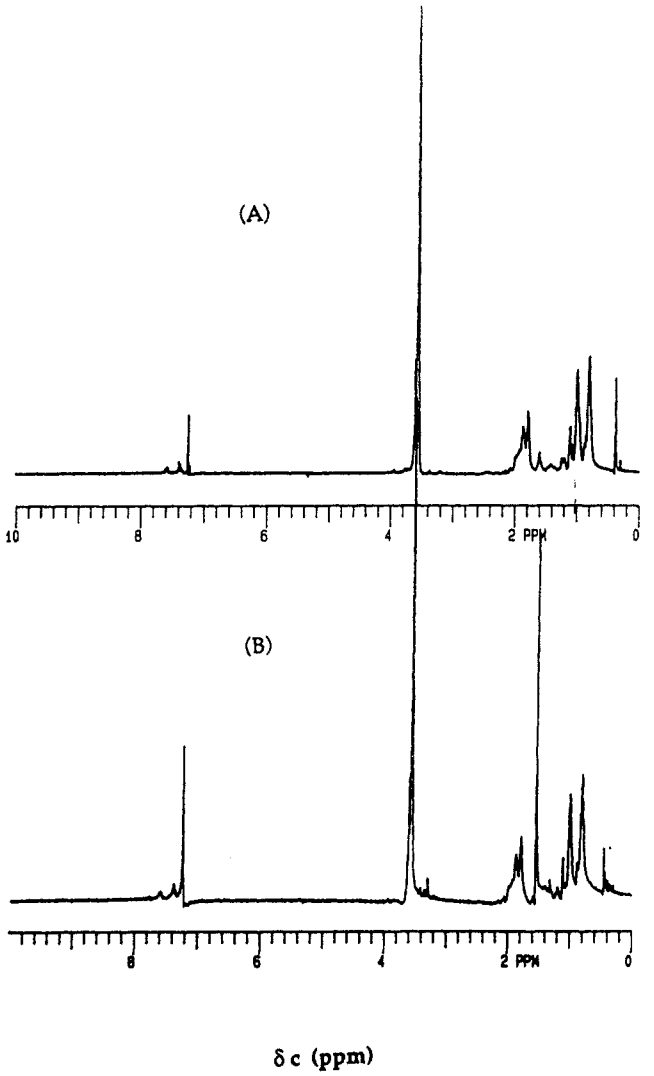
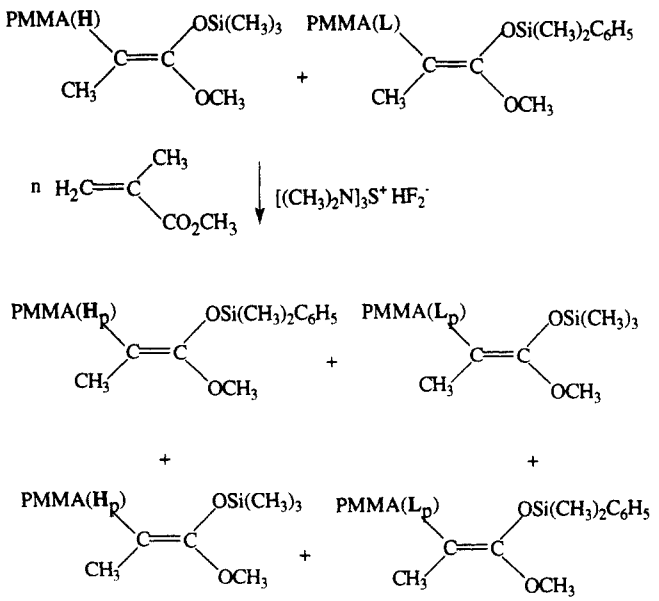


Figure 10. ^{1}H NMR spectra of the phenyldimethylsilyl-ended PMMA(*L*) (A) and low molecular weight fitrate (*F*)PMMA(*L*) (B) in the control experiment for fractionation.

Scheme V



the corresponding base polymers [PMMA(H) and PMMA(L)] for the high and low molecular weight fractions are shown in Figures 12 and 13, respectively. Silyl group exchange was again clearly detected in both the high molecular weight fraction (44% exchange) [Figure 12B,

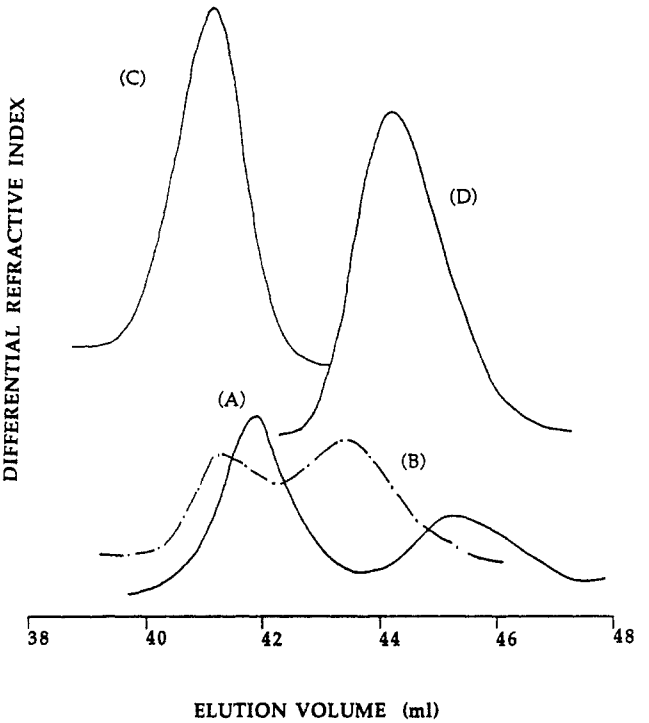


Figure 11. SEC chromatograms of the PMMA(H) and PMMA(L) mixture (A), continued propagation product (B), high molecular weight fractionation product, PMMA(H_p) (C), and low molecular weight fractionation product, PMMA(L_P) (D).

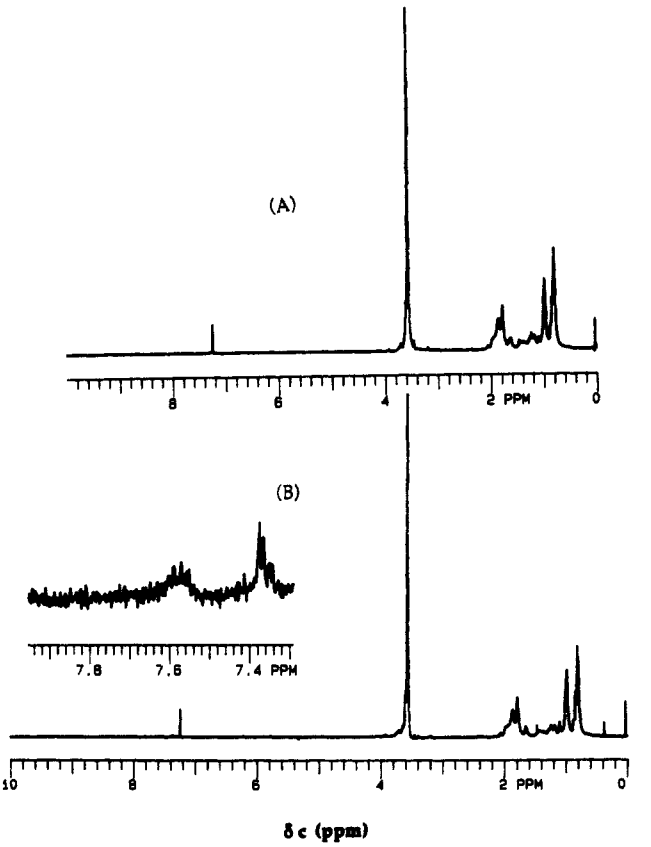


Figure 12. ^{1}H NMR spectra of the trimethylsilyl-ended PMMA(H) base polymer (A) and the high molecular weight fraction, (F)PMMA(H_p), from continued propagation (B).

δ = 0.38 ppm for Ph(CH_3)$_2$–Si] and the low molecular weight fraction (38% exchange) [Figure 13B, δ = 0.05 ppm for (CH_3)$_3$–Si]. Thus, *significant amounts (38–44%) of silyl group exchange occur readily between living polymer chains under GTP polymerization conditions in the*

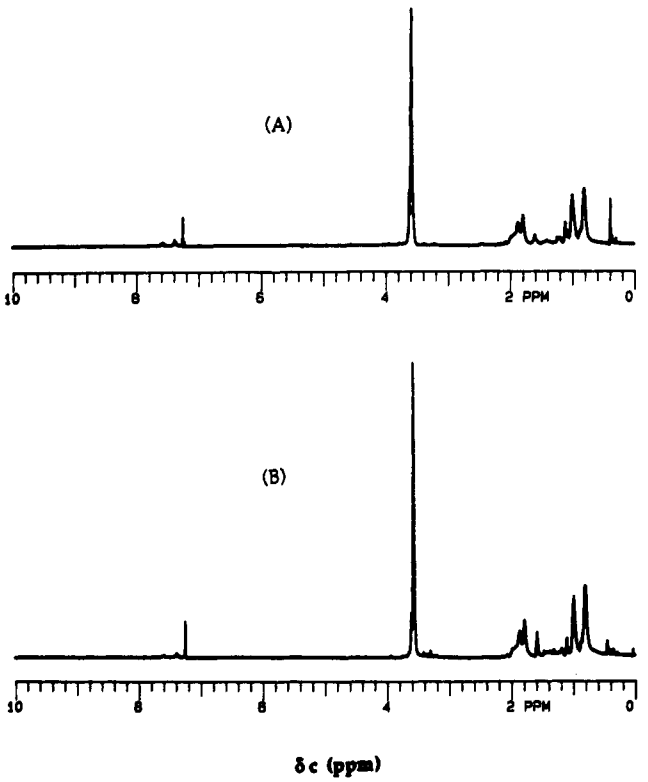


Figure 13. ^{1}H NMR spectra of the phenyldimethylsilyl-ended PMMA(L) base polymer (A) and the low molecular weight fraction, (F)PMMA(L_p), from continued propagation (B).

presence of polymerizing monomer in contrast to previous preliminary reports and conclusions.[5,6]

Previous silyl group exchange experiments of Sogah and Farnham[5,6] were carried out between tolyldimethylsilyl-ended PMMA and phenyldimethylsilyl-ended poly(butyl methacrylate) (PBMA) in the presence of excess butyl methacrylate by adding all of the monomer at once and quenching at 70% conversion; it was reported that under these conditions, no detectable silyl group exchange was observed. Since the polymers were separated on the basis of the solubility differences between PMMA and PBMA, the incompatibility of these different polymers may have favored silyl exchange between like polymer chains with the same silyl groups; thus, silyl group exchange would not be detected.[30]

Conclusions. The mechanism for the process described as group-transfer polymerization is 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 a rather unusual eight-membered ring transition state.[5,6] As clearly and unambiguously stated by Sogah and Farnham,[5,6] "in this associative mechanism, silyl exchange among growing chains is excluded: the identity of the silicon atom of the initiator molecule remains invariant throughout the growth of the polymer chains". In the experiments reported herein, significant amounts of both trimethylsilyl and phenyldimethylsilyl group exchange (27–76%) were observed for both the high and low molecular weight chains in the presence of the nucleophilic catalyst, $TASHF_2$, during the time interval for continuous addition of monomer (e.g., 20 min); exchange was observed in the presence and absence of polymerizing monomer. Using the GTP criterion set forth by Sogah and Farnham,[5,6] the observance of such significant amounts of silyl group exchange is not consistent with the generally accepted associative mechanism, but it is consistent with a mechanism involving ester enolate anion intermediates, reversibly complexed with silyl ketene acetal chain ends, as propagating species.[12] However, these results cannot exclude exchange occurring as a side reaction which is chemically distinct from propagation.[31] Although this is certainly a possible explanation for the exchange results reported herein, the exchange results (38–44% silyl group exchange in the presence of polymerizing monomer) suggest that the mechanistic evidence to support the non-enolate, associative mechanism for GTP is tenuous.

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(27) As pointed out by a referee, since 50% exchange would be predicted at equilibrium, this result is difficult to explain. It may reflect either a molecular weight dependence for the exchange process or for side reactions.
(28) Preliminary evidence for competing cyclotermination was obtained by ^{13}C NMR analysis of living trimethylsilyl ketene acetal-end PMMA (precipitated into hexane) which showed an

absorbance at δ = 206 ppm, which corresponds closely to the peak position expected for a cyclohexanone carbonyl carbon (δ = 208.8 ppm[29]); this signal exhibited a high intensity, suggesting that this carbon had a different relaxation time compared to those of the other peaks in the spectrum.

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(31) This possible explanation for the observation of silyl group exchange is included at the suggestion of one of the referees. This referee also stated that the exchange results reported herein are not mechanistically relevant because they were carried out under monomer-starved conditions (dropwise addition of MMA monomer) in contrast to the exchange experiments of Sogah and Farnham[5,6] which were carried out in the presence of excess polymerizing monomer (butyl methacrylate).

Registry No. $TASHF_2$, 85248-37-9; TASF, 59218-87-0; MMA, 80-62-6; PMMA, 9011-14-7; 1-methoxy-1-(phenyldimethylsiloxy)-2-methyl-1-propene, 119401-57-9; methyl isobutyrate, 547-63-7; phenyldimethylchlorosilane, 768-33-2.