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Chain Transfer in Group-Transfer Polymerization

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ABSTRACT: When group-transfer polymerization (GTP) is carried out in the presence of carbon acids with pK_a values (in DMSO) in the range of 18–25, chain transfer can occur with lowering of the number average molecular weight and, usually, with an increase in polydispersity. Among the most effective chain-transfer agents are methyl α-phenylpropionate, methyl α-phenylacetate, and α-phenylpropionitrile. Chain-transfer constants in the range 0.4–1 were obtained for these compounds. Among the GTP catalysts that catalyze the chain-transfer process are bifluoride, acetate, *m*-chlorobenzoate, and bibenzoate. By the use of hydroxyl-labeled silyl ketene acetal initiator and α-phenylpropionitrile, the amount of polymer formed by direct initiation and by chain transfer can be measured by using HPLC to separate the resulting PMMA-OH from PMMA formed by chain transfer. Similarly, a labeled chain-transfer agent, 2-(trimethylsiloxy)ethyl α-phenylacetate, was used to permit direct measurement of PMMA formed by chain transfer. Other chain-transfer agents for GTP are indene, fluorene, and γ-thiobutyrolactone. Consistent with chain transfer by indene, 1-(trimethylsilyl)indene was shown to be an initiator for GTP of MMA.

Introduction

Chain-transfer processes in free radical and in ionic polymerizations have been thoroughly documented.[1a-d] Chain-transfer agents are often added to polymerizations to reduce the molecular weight or to introduce terminal functional groups. On the other hand, unwanted chain transfer to monomer occurs in some systems (notably in cationic polymerizations) placing an upper limit on the molecular weight which can be obtained. We have found several classes of compounds that are effective chain-transfer agents[1e] in the recently reported group-transfer polymerization of acrylic monomers using organosilicon initiators[2,3] and suitable catalysts.[4] The more effective of these chain-transfer agents can be used to replace nearly all of the organosilicon initiator (e.g., 1 in Scheme I) required for a given $\bar{M}_n$. This paper details these studies.

Experimental Section

Materials and Methods. Phenylacetonitrile, α-phenylpropionitrile, methyl phenylacetate, indene, and methyl (4-methoxyphenyl)acetate were purchased from Aldrich Chemical Co. and distilled in a 12-in. spinning-band column prior to use. γ-Thiobutyrolactone and fluorene were used as purchased from Aldrich Chemical Co. 2-(β-naphthyl)propionitrile was provided by Dr. R. J. McKinney.[5] Methyl α-phenylpropionate was prepared by the reaction of α-phenylpropionic acid with thionyl chloride followed by treatment with methanol and triethylamine and distillation in a spinning-band column. Solvents, 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene, 1-(2-(trimethylsiloxy)ethoxy)-1-(trimethylsiloxy)-2-methyl-1-propene, and tris(dimethylamino)sulfonium bifluoride ($TASHF_2$), were prepared and purified as described earlier.[3] The general procedures for performing group-transfer polymerizations of MMA were the same as described earlier.[3] Tetrabutylammonium acetate was used as purchased from Fluka Chemical Corp. Tetrabutylammonium *m*-chlorobenzoate and tetrabutylammonium bibenzoate were prepared as described earlier.[4] Molecular weights and polydispersities ($D = \bar{M}_w/\bar{M}_n$) were determined by gel permeation chromatography (GPC) in tetrahydrofuran (THF) using a Waters Associates 590 pump with elution over four consecutive columns containing microstyrogel 10000, 1000, 500, and 100 Å with 401 refractive index detection. The standard was PMMA. Proton NMR spectra were recorded on an IBM NR80 NMR spectrometer. Proton NMR analysis of reaction mixtures for extent of conversion was performed with a Varian EM390 spectrometer at 90 MHz. High-performance liquid chromatographic analysis of mixtures of PMMA and PMMA with a terminal hydroxyl group (PMMA-OH) was performed by using a Du Pont Instruments chromatographic pump with a Lichrosorb Si 60 (5 μm) packed (E. Merck) column 4.0 × 250 mm with a Waters Associates differential refractometer Model R401 using ethyl acetate solvent as described by Andrews and Vatvars.[6] The retention volume for PMMA was 2.7 mL, and the retention volume for PMMA-OH was 3.8 mL at a flow rate of 1 mL/min.

General Procedure for Polymerization of MMA with Alternating Feeds of Monomer and Chain-Transfer Agent. Chain-Transfer with α-Phenylpropionitrile. To a stirred solution of 0.4 mL (2 mmol) of 1 and 10 μL of tetrabutylammonium *m*-chlorobenzoate (0.46 M in THF) in 30 mL of THF was added dropwise at a rate such that the reaction temperature did not exceed 44 °C (with the occasional aid of an ice bath) 10 mL of a solution of MMA (100 mL of 5 M solution in THF). Then 2 mL of a solution of α-phenylpropionitrile (18 mL of 1 M solution in THF) was added rapidly with development of a yellow color. In a similar manner, the remaining solutions were added by alternating nine more additions of MMA solution with eight more additions of α-phenylpropionitrile solution. After the reaction temperature had cooled to room temperature, 1 mL of methanol was added to quench the reaction, and a small sample was removed for analysis. NMR showed a trace of residual monomer. The polymer was isolated in nearly quantitative yield by precipitation with 1:1 aqueous methanol in a blender followed by drying at 80 °C (0.1 Torr). Gel permeation chromatography (GPC) showed that the PMMA had $\bar{M}_n = 2550$, $\bar{M}_w = 5550$, and $\bar{M}_w/\bar{M}_n = 2.18$.

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† Contribution no. 4251.

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General Procedure for Polymerization of MMA with Chain-Transfer Agent Introduced in Monomer Feed. Chain Transfer with α-Phenylpropionitrile. To a solution of 0.4 mL (2 mmol) of 1 and 10 μL of tetrabutylammonium *m*-chlorobenzoate (0.46 M in THF) in 30 mL of THF was added a solution of 50 g (0.5 mol) of MMA and 1.64 g (12.5 mmol) of α-phenylpropionitrile in 30 mL of THF at a rate such that the temperature remained at 40 °C. When the addition of the monomer solution was complete, the temperature began to fall. When the temperature had fallen to room temperature, 1 mL of methanol was added to quench the reaction and a small sample was removed for analysis. NMR showed no residual monomer. Precipitation with aqueous methanol in a blender and drying at 80 °C (0.1 Torr) gave 49.7 g of PMMA. GPC showed that the PMMA had $\bar{M}_n$ = 3120, $\bar{M}_w$ = 6410, and $\bar{M}_w/\bar{M}_n$ = 2.08.

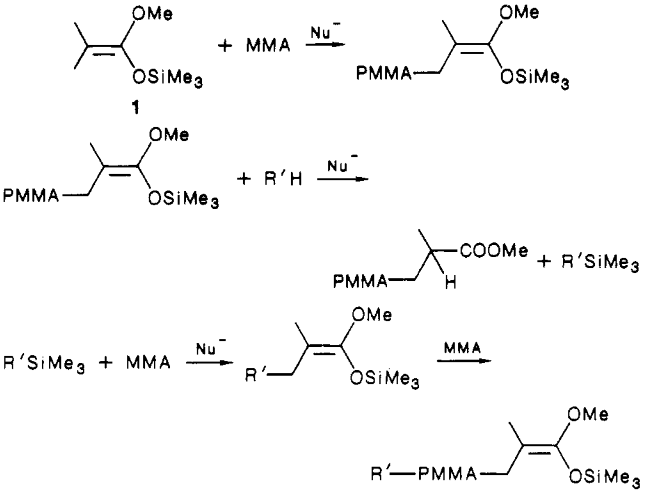
α-(Trimethylsilyl)-α-phenylpropionitrile, 6. To a stirred solution of 11 mL (78.5 mmol) of diisopropylamine in 100 mL of THF at 0 °C was added 78.5 mmol of butyllithium (1.6 M in hexane). After 30 min, the solution was cooled to −78 °C, and 10.3 g (78.5 mmol) of α-phenylpropionitrile was added dropwise while the temperature was kept below −70 °C. Then 10 mL (78.5 mmol) of chlorotrimethylsilane was added. The mixture was allowed to warm to room temperature and filtered under argon, and the filtrate was evaporated under reduced pressure. The residue was treated with hexane and filtered under argon. The filtrate was concentrated and distilled in a 25-cm spinning-band column to give 9.9 g of α-(trimethylsilyl)-α-phenylpropionitrile as a pale yellow liquid, bp 70–72 °C (0.12 Torr). Anal. Calcd for $C_{12}H_{17}NSi$: C, 70.87; H, 8.43; N, 6.89; Si, 13.81. Found: C, 70.24; H, 8.07; N, 6.70; Si, 13.20. NMR (80 MHz, $CDCl_3$, δ): 0.03 (s, 9 H, CSiMe), 1.73 (s, 3 H, CMe), 7.30 (s, 5 H, ArH). IR (CCl_4): 2200 cm^{-1} (CN).

Initiation of Polymerization of MMA with α-(Trimethylsilyl)-α-phenylpropionitrile, 6. To a stirred solution of 0.15 g (0.75 mmol) of 6 and 20 μL of tetrabutylammonium *m*-chlorobenzoate (0.45 M in THF) in 30 mL of THF was added 10.8 mL (0.1 mol) of MMA. After all of the MMA had been added, a feeble exothermic reaction began. After an additional 40 μL of tetrabutylammonium *m*-chlorobenzoate (0.45 M in THF) was added, a slow temperature rise to 36 °C occurred. The reaction mixture was stirred for 18 h, and an aliquot was removed for analysis by NMR which showed that conversion to PMMA was complete. After the mixture was quenched with 1 mL of methanol, the polymer was precipitated into 1:1 aqueous methanol to give PMMA with $\bar{M}_n$ = 17500, $\bar{M}_w$ = 20300, and $\bar{M}_w/\bar{M}_n$ = 1.16 (theory, $\bar{M}_n$ = 13450).

2-(Trimethylsiloxy)ethyl Isobutyrate, 7. To a stirred solution of 13.2 g (0.1 mol) of 2-hydroxyethyl isobutyrate[8] and 13.9 mL (0.1 mol) of triethylamine in 100 mL of methylene chloride was added dropwise 12.7 mL (0.1 mol) of chlorotrimethylsilane. The mixture was concentrated on a rotary evaporator and treated with hexane. The mixture was filtered, and the filtrate was concentrated and distilled in a spinning-band column to give 6.7 g of 7, bp 37 °C (0.2 Torr) to 40 °C (0.7 Torr). ^1H NMR (80 MHz, $CDCl_3$, δ): 0.13 (s, 9 H, OSiMe), 1.2 (d, J = 6.7 Hz, 6 H, CMe), 2.58 (septet, J = 6.7 Hz, 1 H, CH), 3.77 (m, 2 H, $SiOCH_2$), 4.17 (m, 2 H, $COOCH_2$).

General Procedure for Polymerization of MMA in the Presence of a Reagent Containing a Protected Hydroxyl Label. Polymerization of MMA in the Presence of α-Phenylpropionitrile and 2-(Trimethylsiloxy)ethyl Isobutyrate. To a stirred solution of 0.5 mL (2.5 mmol) of 1, 0.33 mL (2.5 mmol) of α-phenylpropionitrile, 3, and 0.51 g (0.567 mL, 2.5 mmol) of 2-(trimethylsiloxy)ethyl isobutyrate, 7, in 30 mL of THF was added 50 μL of tetrabutylammonium *m*-chlorobenzoate (0.1 M in THF). After 1 min, 10.8 mL (0.1 mol) of MMA was added, the first 2 mL being added rapidly and the remainder slowly. The temperature did not rise above 43 °C. After the reaction had cooled to room temperature, an aliquot was removed for NMR analysis, which showed 100% conversion to PMMA. The reaction mixture was treated with 15 mL of methanol and 2 mL of tetrabutylammonium fluoride (1 M in THF) and refluxed for 2 h. Precipitation of the polymer with aqueous methanol containing 0.5 g of silver nitrate gave 8 g of PMMA, $\bar{M}_n$ = 2670, $\bar{M}_w$ = 3920, and $\bar{M}_w/\bar{M}_n$ = 1.47 (theory for initiation of 66% of the MMA by 1 and consumption of all of the 3 in chain transfer: $\bar{M}_n$ = 2500). NMR analysis of the polymer shows 40 MMA units per phenyl group. HPLC in ethyl acetate[6] showed only PMMA, no PMMA-OH was detected.

Scheme I



2-(Trimethylsiloxy)ethyl Phenylacetate. To a stirred solution of 65.13 g (0.36 mol) of 2-hydroxyethyl phenylacetate (prepared by the reaction of 0.9 mol of phenylacetic acid with 1 mol of ethylene oxide and a catalytic amount of tetraethylammonium bromide at 100 °C for 8 h in a stainless-steel tube) and 69.6 mL (0.5 mol) of triethylamine in 150 mL of methylene chloride was added dropwise 63.5 mL (0.5 mol) of chlorotrimethylsilane. The mixture was refluxed for 15 min, cooled, and treated with 100 mL of petroleum ether and filtered. The filtrate was concentrated, treated with petroleum ether, and filtered. The filtrate was concentrated and distilled in a Vigreux column to give 36 g of 2-(trimethylsiloxy)ethyl phenylacetate, bp 86–91 °C (0.15 Torr). Anal. Calcd for $C_{13}H_{20}O_3Si$: C, 61.86; H, 7.99; Si, 11.13. Found: C, 61.63; H, 7.81; Si, 11.85. NMR (80 MHz, $CDCl_3$, δ): 0.13 (s, 9 H, OSiMe), 3.67 (s, 2 H, $ArCH_2C{=}O$), 3.78 (m, 2 H, $SiOCH_2$), 4.20 (m, 2 H, $COOCH_2$), 7.27 (s, 5 H, ArH).

Initiation of Polymerization of MMA with 1-(Trimethylsilyl)indene. To a solution of 0.24 g (1.25 mmol) of 1-(trimethylsilyl)indene,[7a] **15**, and 63 μL of tetrabutylammonium bibenzoate[4] (0.1 M in THF) in 30 mL of THF was added 10.8 mL (0.1 mol) of MMA. The addition of 0.19 mL of additional tetrabutylammonium bibenzoate (0.1 M in THF) was required to obtain a slow rate of polymerization. After the solution was stirred 18 h, an aliquot was removed for analysis. NMR showed quantitative conversion to PMMA. GPC showed $\bar{M}_n$ = 12300, $\bar{M}_w$ = 15600, and $\bar{M}_w/\bar{M}_n$ = 1.26 (theory, $\bar{M}_n$ = 8100). After the mixture was quenched with 1 mL of methanol, 10.3 g of polymer was obtained by precipitation with aqueous methanol. A similar experiment using 300 μL of tetrabutylammonium acetate (0.1 M in THF) instead of tetrabutylammonium bibenzoate gave a similarly slow polymerization with quantitative conversion to PMMA with $\bar{M}_n$ = 10400, $\bar{M}_w$ = 15500, and $\bar{M}_w/\bar{M}_n$ = 1.50 (theory, $\bar{M}_n$ = 8100). After purification of the polymer by precipitation with hexane and then with aqueous methanol, UV analysis of the polymer showed strong absorption at 254 nm.

Results and Discussion

Compounds that have been found to chain transfer in group-transfer polymerization (GTP) are moderate carbon acids (pK_a in DMSO generally less than 25) which become silated by the silyl ketene acetal of a living GTP polymer in the presence of an anion catalyst[4] at a reasonably fast rate to give a new silicon compound capable of initiating GTP (see Scheme I). Among the most effective chain-transfer agents are methyl arylacetates and arylacetonitriles. The recently reported oxyanion catalysts for GTP[4] are also effective catalysts for chain transfer in GTP.

Chain-transfer activity was detected by GPC measurement of molecular weights ($\bar{M}_n$) substantially lower than the predicted value for initiation by silyl ketene acetal

Table I
Chain Transfer by Arylacetonitriles in GTP of MMA in THF

	transfer agt (mmol)	init (mmol)	MMA[a], mmol	cat,[b] %	$\bar{M}_n$	$\bar{M}_w$	D	predicted $\bar{M}_n$	transf const
1	3 (12.5)[c]	1 (2)	500	0.2 M	3120	6410	2.05	25100	1.1
2	3 (18)[d]	1 (2)	500	0.2 M	2550	5550	2.18	25100	1.0
3	3 (2.55)[d]	1 (0.85)	100	2.3 M	3000	4830	1.61	11865	1.0
4	4 (1)[d]	1 (0.5)	50	7.3 M	4030	6980	1.73	10100	0.7
5	3 (1.7)[d]	1 (0.85)	100	1.8 F	4720	6900	1.46	11860	0.7
6	2 (1.7)[d]	1 (0.85)	100	3.2 F	4300	6970	1.62	11500	0.9
7	3 (2.5)[e]	8 (2.5)	100	0.16 A	2970	4390	1.48	4100	
8	3 (2.5)[e]	8 (2.5)	100	0.2 M	3010	4470	1.49	4100	
9	2 (2.5)[e]	8 (2.5)	100	0.2 M	2990	3890	1.30	3590	

[a] Yields of PMMA are 100%, except 98% in entry 4, 97% in 6, and 87% in 9. [b] Catalysts are as follows: M, tetrabutylammonium *m*-chlorobenzoate; A, tetrabutylammonium acetate; F, tris(dimethylamino)sulfonium bifluoride. [c] Chain-transfer agent in monomer feed. [d] Alternating feeds of monomer and chain-transfer agent. The number of feeds of chain-transfer agent is equal to the millimoles of chain-transfer agent divided by the millimoles of initiator. [e] Monomer added to a solution of chain-transfer agent, initiator, and catalyst.

initiator alone. Additional evidence for chain transfer was obtained by the use of labeled initiator or labeled chain-transfer agent followed by end-group analysis of the polymer. Among the compounds that were found to have chain-transfer activity in GTP of methyl methacrylate are benzyl cyanide, **2**, α-phenylpropionitrile, **3**, 2-(β-naphthyl)propionitrile,[5] **4**, methyl phenylacetate, methyl (*p*-methoxyphenyl)acetate, methyl α-phenylpropionate, indene, fluorene, and γ-thiobutyrolactone. Of these chain-transfer agents, α-phenylpropionitrile, **3**, gave the best overall results in terms of efficiency and freedom from interference with catalyst activity. To facilitate the comparison of effectiveness of chain-transfer agents and reaction conditions, chain-transfer constants were estimated from the GPC measurements of $\bar{M}_n$. Transfer constants, the dimensionless ratios of rates of chain transfer:rates of polymerization, were calculated from the equation[1c,d]

$$1/X_n = 1/X_{n,o} + C_t([RH]/[M])$$

in which X_n = observed degree of polymerization in the presence of chain-transfer agent, RH, $X_{n,o}$ = predicted degree of polymerization in the absence of RH, calculated as [(moles of monomer + moles of initiator)/moles of initiator]Y, where Y is the observed conversion to polymer (Y = 1 for 100% conversion), C_t = transfer constant to transfer agent, RH, [RH] = moles of RH, and [M] = moles of monomer. One of the assumptions in using this equation is that RH does not react with the initiator. In experiments in which transfer agent and initiator are premixed with catalyst before adding monomer, the calculated transfer constants will have little significance. Figure 1 shows the linearity of a plot of [chain-transfer agent]/[MMA] vs $1/X_n - 1/X_{n,o}$ using the data for entries 2, 3, and 5 of Table I in which the slope, C_t, is 1.

A simple method of demonstrating chain transfer by α-phenylpropionitrile, **3**, in the GTP of MMA using 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene, **1**, as initiator and tetrabutylammonium *m*-chlorobenzoate[4] as catalyst is to provide the chain-transfer agent in the monomer feed. Thus, when a solution of 12.5 mmol of **3** and 500 mmol of MMA was fed to a solution of 2 mmol of **1** and 0.0046 mmol of tetrabutylammonium *m*-chlorobenzoate in THF at 41–43 °C, a quantitative yield of PMMA was obtained with $\bar{M}_n$ = 3120, $\bar{M}_w$ = 6410, and polydispersity 2.05 (see Table I, entry 1). Theory for no chain transfer predicts $\bar{M}_n$ = 25 100; for complete chain transfer, $\bar{M}_n$ = 3560. The calculated transfer constant, 1.1, is within experimental error of the maximum expected value of 1.0. To obtain PMMA with $\bar{M}_n$ = 3120 from 500 mmol of MMA in the absence of a chain-transfer agent would have required 16 mmol of **1**. While about 88% of the initiator was replaced with chain-transfer agent in this experiment to achieve a $\bar{M}_n$ of 3120, the polydispersity (2.05) is substantially higher than the 1.05–1.2 which is generally achieved in the absence of chain-transfer agent.[3]

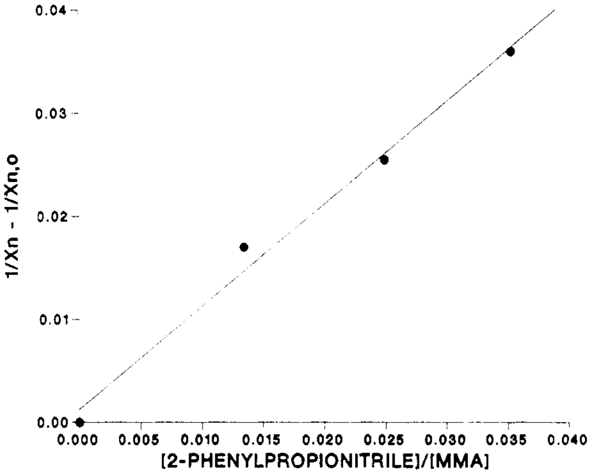
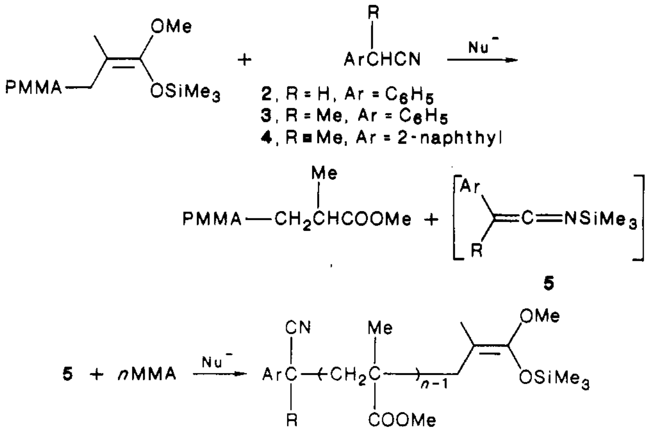


Figure 1. Plot of [chain-transfer agent]/[monomer] vs (observed degree of polymerization, X_n)$^{-1}$ − (degree of polymerization in the absence of chain transfer)$^{-1}$. The slope, which is the chain-transfer constant, C_t = 1. Experimental data from entries 2, 3, and 5 of Table I are used.

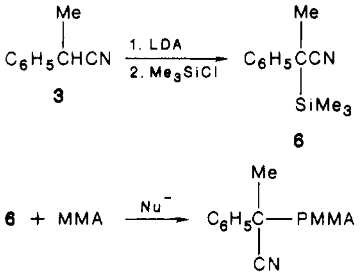
Efficient chain transfer by **3** can also be carried out by using alternate feeds of monomer and chain-transfer agent. Thus, alternating ten 50-mmol feeds of MMA with nine 2-mmol feeds of **3** to a solution of 2 mmol of **1** and 0.0046 mmol of tetrabutylammonium *m*-chlorobenzoate gave quantitative conversion to PMMA with $\bar{M}_n$ = 2550, $\bar{M}_w$ = 5550, and polydispersity 2.18. Theory for no chain transfer predicts $\bar{M}_n$ = 25 100; for complete chain transfer, $\bar{M}_n$ = 2600 (Table I, entry 2). Alternating feeds of monomer and chain-transfer agent produces molecular weight reduction, polydispersity, and a transfer constant rather similar to the common feed method. The presence of the α-phenylpropionitrile residue in the polymer prepared in the presence of α-phenylpropionitrile chain-transfer agent is readily confirmed by UV detection of the aromatic ring and by elemental analysis for nitrogen (see Scheme II).

2-(β-Naphthyl)propionitrile,[5] **4**, is also an effective chain-transfer agent for GTP of MMA, and the results of an alternating feed experiment with **4** and tetrabutylammonium *m*-chlorobenzoate catalyst are summarized in Table I, entry 4. An unusually high level of catalyst was required to maintain a rapid rate of polymerization. Phenylacetonitrile, **2**, is an effective chain-transfer agent in GTP, but it often leads to less than quantitative polymerization of MMA, and higher levels of catalyst are required to maintain a high rate of polymerization. A direct comparison of a TASHF$_2$-catalyzed GTP of MMA

Scheme II

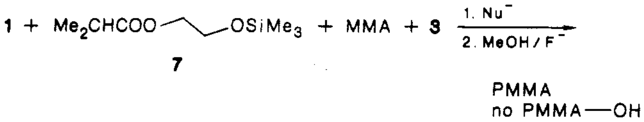


Scheme III

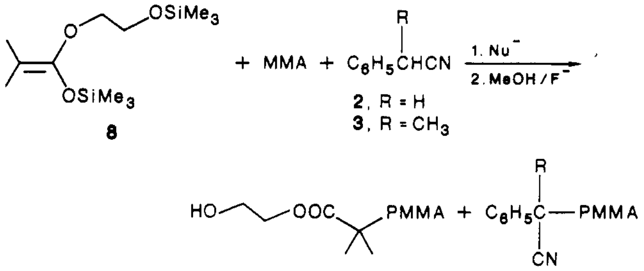


with phenylacetonitrile as chain-transfer agent (entry 6) and with α-phenylpropionitrile as chain-transfer agent (entry 5) is included in Table I. The results are remarkably similar, but a higher level of catalyst was needed for the phenylacetonitrile. Under similar conditions, the transfer constant for **2** is slightly greater than that for **3** (compare Table I, entries 5 and 6). When diphenylacetonitrile was evaluated as a chain-transfer agent in GTP of MMA with tetrabutylammonium *m*-chlorobenzoate catalyst, termination occurred and the MMA failed to polymerize. Presumably the transfer of the trimethylsilyl group occurred, but the resulting silylated diphenylacetonitrile either failed to initiate polymerization of MMA or deactivated the catalyst in some manner. Although there is no direct evidence that the *N*-silylketene imine structure **5** is formed from the exchange of hydrogen and trialkylsilyl group between silyl ketene acetal and α-phenylpropionitrile, in the alternating feed process a yellow color is observed each time the chain-transfer agent is added, and the yellow color fades when the MMA feed is added. The yellow color may be due to **5**. Silylation of **3** with LDA and chlorotrimethylsilane gave the α-(trimethylsilyl)nitrile, **6**, rather than **5** (see Scheme III). Although **6** can be used as an initiator of GTP of MMA with anion catalysts, higher levels of catalyst are required to obtain even a slow rate of polymerization than are required for GTP of MMA in the presence of chain-transfer agent **3**. This suggests that **6** is not the active intermediate in the chain-transfer process. Since *N*-silyl compounds can be expected to be more reactive than *C*-silyl compounds[8] by analogy to the greater reactivity of silyl ketene acetals relative to α-silyl esters,[3] it is reasonable to assume that the chain-transfer process leads to kinetically controlled formation of **5** which efficiently initiates new polymer chains. Since anion-catalyzed equilibration of silyl ketene acetals and α-silyl esters has been documented,[3] it would not be surprising if there were a similar equilibration of **5** and **6**, perhaps at a rate which is slower than the rate of initiation by **6**. Neither the rate nor the position of such an equilibration has been established.

Scheme IV



Scheme V



To demonstrate that chain transfer by **3** in GTP of MMA is not accompanied by chain transfer between **5** or silyl ketene acetal end groups and isobutyrate units of "dead" PMMA chains (resulting from chain transfer or termination by extraneous protic sources), a chain-transfer experiment was performed in the presence of a "labeled" isobutyrate, **7**, (see Scheme IV). Since **7** contains a protected hydroxyl group, any polymer formed by an initiator resulting from chain transfer to **7** would contain a protected hydroxyl group at its terminus. After the resulting polymer was treated with fluoride ion to remove any trimethylsilyl groups, HPLC analysis by the method of Andrews and Vatvars[6] showed that none of the PMMA contained a terminal hydroxyl group. Thus, we conclude that the α-hydrogen of an isobutyrate species does not participate to a significant extent in chain-transfer processes. This can be attributed to the weak carbon acidity of isobutyrates, with a pK_a greater than 25.

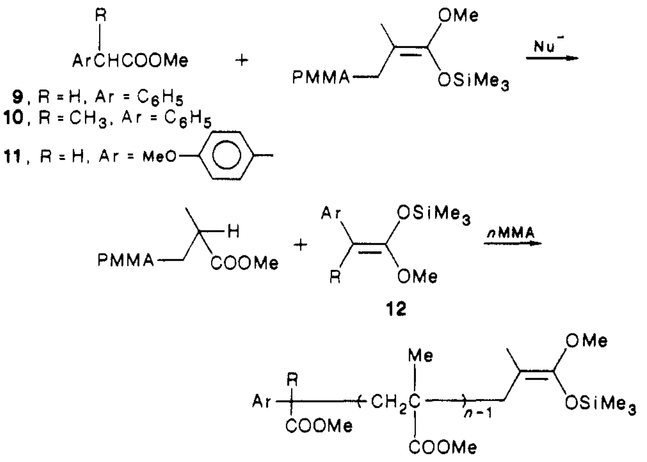
Use of the "labeled" silyl ketene acetal initiator **8** in a chain-transfer experiment with α-phenylpropionitrile permits the direct determination of the amount of monomer polymerized directly by the silyl ketene acetal and the amount polymerized by chain transfer. As shown in Scheme V, the polymer formed by direct initiation by **8** will contain a protected hydroxyl group at the end of the polymer chain, while the polymer formed by chain transfer will not. Thus, "batch-type" GTP of MMA by an equimolar mixture of **8** and **3** in the presence of tetrabutylammonium acetate catalyst followed by deprotection of the terminal hydroxyl group with methanolic tetrabutylammonium fluoride gave a mixture of PMMA and PMMA-OH. Analysis of the mixture by HPLC using the technique of Andrews and Vatvars[6] showed that 60% of the mixture was PMMA-OH (derived from direct initiation by **8**) and 40% was PMMA derived from chain transfer. Thus, from end-group analysis, we can estimate a chain-transfer efficiency of 80%. As seen in Table I, entry 7, the observed $\bar{M}_n$ of 2970 when compared with the predicted value of 4100 for the absence of chain transfer suggests a chain transfer constant of 0.71. In this experiment it is not certain how much of the transfer occurred with the initiator and how much occurred with polymer, so a chain-transfer constant for this "batch-type" polymerization was not included in Table I. In a similar experiment using tetrabutylammonium *m*-chlorobenzoate instead of tetrabutylammonium acetate (Table I, entry 8), the product consisted of 66% PMMA-OH and 34% PMMA indicating a chain-transfer constant of 0.68. The observed and predicted $\bar{M}_n$ values indicate a chain-transfer constant of 0.70. When phenylacetonitrile, **2**, was used as the chain-transfer agent in a batch polymerization of MMA

Table II
Chain Transfer by 2-Arylacetates in GTP of MMA in THF

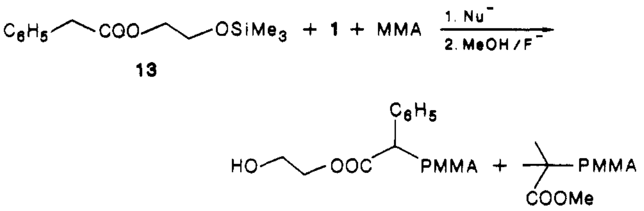
	transfer agt (mmol)	init (mmol)	HF_2^-,[a] %	$\bar{M}_n$[b]	$\bar{M}_w$	D	predicted $\bar{M}_n$	transf const
1	10 (7.5)[c]	1 (2.5)	0.8	1750	1930	1.11	4100	0.4
2	9 (7.5)[c]	1 (2.5)	0.8	1670	3090	1.85	4100	0.5
3	9 (10)[d-f]	1 (2.5)	0.4	2290	3450	1.51	5660	0.2
4	9 (7.5)[g]	1 (2.5)	1.6	1350	2070	1.53	4100	0.7
5	11 (7.5)[c]	8 (2.5)	1.2	1170	2340	1.99	4130	0.8
6	9 (10)[d,f]	8 (2.5)	0.4	1460	2810	1.93	5660	0.7
7	13 (3.75)[g]	1 (1.25)	0.8	3250	4490	1.38	7209	0.5

[a] Mole % $TASHF_2$ relative to initiator. [b] Yield of PMMA 100% except 89% in entry 7. [c] Chain-transfer agent in monomer feed. [d] Alternating feeds of chain-transfer agent and monomer. The number of feeds of chain-transfer agent is equal to the millimoles of chain-transfer agent divided by the millimoles of initiator. [e] The catalyst is present in the chain-transfer agent feed. [f] 139 mmol of MMA used. In all other entries, 100 mmol of MMA used. [g] Batch polymerization, catalyst added to all other ingredients.

Scheme VI



Scheme VII



with the labeled initiator 8 (Table I, entry 9), at the same level of *m*-chlorobenzoate catalyst as was used with α-phenylpropionitrile (Table I, entry 8), conversion to PMMA was 87%, and 44% of the product resulted from initiation by 8 (detected as PMMA-OH), while 56% resulted from chain transfer (detected as PMMA by HPLC). The apparent chain-transfer constant of 1.12 based on end-group analysis can, perhaps, be attributed to some loss of initiator, which would also be consistent with the higher $\bar{M}_n$ (2990) than the value predicted for 100% chain transfer (1760). These efficiencies of chain transfer for 3 may well apply specifically for this particular mode of polymerization, namely, adding monomer to premixed initiator and chain-transfer agent. But the experiments confirm the potency of phenylacetonitriles as chain-transfer agents in GTP.

Methyl arylacetates and propionates have also been found to be effective chain-transfer agents for GTP of MMA. Methyl phenylacetate, 9, methyl α-phenylpropionate, 10, and methyl *p*-methoxyphenylacetate, 11, were evaluated as chain-transfer agents using $TASHF_2$ as catalyst (see Scheme VI). The chain-transfer agents dissolved in MMA monomer were fed to a solution of catalyst and initiator, or alternating feed processes were used as in the case of 2 and 3. The results are summarized in Table II.

Both methyl α-phenylpropionate, 10, and methyl phenylacetate, 9, are efficient chain-transfer agents in the GTP of MMA using $TASHF_2$ catalyst, but it is apparent from the comparison of the data of entries 1 and 2 of Table II with entries 5 and 6 of Table I that 9 and 10 are less efficient than the arylacetonitriles 2 and 3. The polydispersity obtained with 10 is closer to that obtained in GTP of MMA in the absence of chain-transfer agents[3] than is that obtained with 9. Thus, the presence of the α-methyl group in the phenylacetic ester seems to have a beneficial effect on control of molecular weight parameters in the polymer. We can speculate that the additional alkyl substituent retards the rate of anion-catalyzed rearrangement of the intermediate silyl ketene acetal 12 to a less reactive isomeric α-silyl ester.[3] Alternating feeds of MMA and 9 (Table II, entry 3) resulted in a lower chain-transfer constant than was obtained by feeding 9 along with the monomer (Table II, entry 2). Performing the chain-transfer experiment as a batch polymerization (i.e., adding catalyst to a solution of MMA, initiator, and chain-transfer agent) produces PMMA in which the chain transfer is significantly higher than in the cases of feeding 9 with monomer or alternating the feed of 9 with monomer (see Table II, entry 4).

The use of the "labeled" initiator 8 with methyl (*p*-methoxyphenyl)acetate, 11, as chain-transfer agent in GTP of MMA (Table II, entry 5) following the procedures described in connection with α-phenylpropionitrile, 3, revealed that 52% of the polymer (PMMA-OH) was derived from direct initiation by 8, while 48% was derived from chain transfer by 11. The transfer constant indicates that more than 48% of the polymer weight should have been derived from chain transfer. However, the value of a transfer constant determined in a batch process where there is a high concentration of transfer agent in the presence of initiator cannot be considered to be very significant. Rather similar results were obtained in an alternating feed experiment with 9 and the labeled initiator 8 (Table II, entry 6), in which 47% of the PMMA (PMMA-OH) was derived from direct initiation by 8, while 53% of the PMMA was derived from chain transfer by 9. In this case, as well, the transfer constant is larger than would be expected from the polymer end-group analysis.

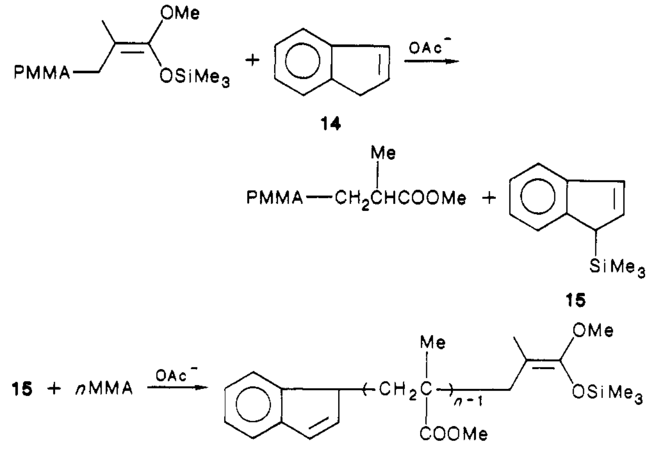
The use of the "labeled" chain-transfer agent 13 (Scheme VII) demonstrates conclusively that the chain transfer agent may be used to create a polymer with a functional end group. Analysis of the polymer produced in a batch process with 2-(trimethylsiloxy)ethyl α-phenylacetate, 13, and the initiator 1 following deprotection showed that 49% of the polymer was PMMA-OH derived from chain transfer with 13, while 51% of the polymer was PMMA derived from direct initiation by 1 (Table II, entry 7). In this case, the 49% chain transfer is consistent with the value calculated for the chain-transfer constant. The polydispersity in this example (1.38) is lower than in the

Table III
Chain Transfer by Hydrocarbons and Thioesters

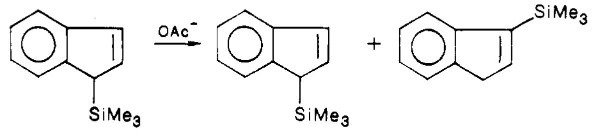
	transfer agt (mmol)	init (mmol)	cat,[a] %	$\bar{M}_n$	$\bar{M}_w$	D	yield, %	predicted M_n	transf const
1	14 (4)	1 (0.7)	4.0 B[b]	2730	8810	3.22	87	12520	0.7
2	14 (4)	1 (0.7)	4.0 M[c]	4310	10200	2.38	93	13960	0.4
3	14 (4)	1 (0.7)	4.0 A[d]	2380	5610	2.35	58	8340	0.2
4	14 (7.5)	8 (2.5)	0.8 F[e]	644	1350	2.10	35	1540	1.1
5	16 (7.5)	8 (2.5)	098 F[e]	2810	3250	1.16	100	4130	0.2
6	17 (4.5)	8 (1.5)	2.0 F[f,g]	2990	5710	1.91	59	6000	0.6

[a] Mole % of initiator. [b] B = tetrabutylammonium bibenzoate[4] (as 0.1 M solution in THF). [c] M = tetrabutyammonium *m*-chlorobenzoate (as 0.38 M solution in THF). [d] A = tetrabutylammonium acetate (as 0.1 M solution in THF). [e] F = TASHF$_2$ (as 1 M solution in benzonitrile). [f] F = TASHF$_2$ (as 1 M solution in acetonitrile). [g] 150 mmol of MMA used; in all other entries 100 mmol of MMA used.

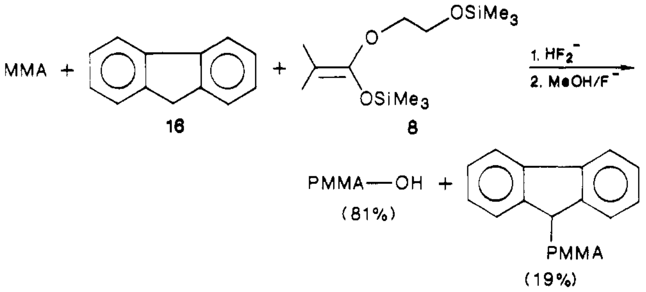
Scheme VIII



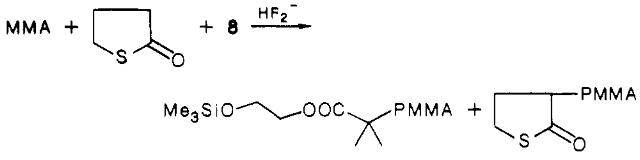
Scheme IX



Scheme X



Scheme XI



examples using 8 (Table II, entries 5 and 6), perhaps this is related to the smaller chain-transfer constant.

A particularly interesting chain transfer agent is the hydrocarbon, indene, 14. Chain transfer by indene was demonstrated in batch polymerizations of MMA initiated by 1 in the presence of 5.7 equiv of indene with catalysis by tetrabutylammonium bibenzoate,[4] tetrabutylammonium *m*-chlorobenzoate, and tetrabutylammonium acetate at a level of 4% of initiator (Table III, entries 1–3). Catalysis by TASHF$_2$ was studied at a level of 0.8% catalyst (relative to initiator 8, Table III, entry 4). The polymerizations proceeded quite slowly (for reasons which will be suggested below) and, in no case, was conversion to polymer quantitative. The molecular weight of the PMMA is consistent with chain transfer by 14. Among the oxyanion catalysts studied, the largest chain-transfer constant was obtained with bibenzoate (Table III, entry 1). The value of 1.1 for the transfer constant obtained with bifluoride is probably not meaningful because of the very low conversion. The portion of the PMMA that resulted from the chain transfer process has indene as an end group, readily detected by NMR and UV spectroscopy. Implicit in the fact of chain transfer by indene is the ability of the presumed intermediate, 1-(trimethylsilyl)indene, to initiate GTP of MMA under catalysis by acetate.

This was, in fact, confirmed by initiating GTP of MMA with 1-(trimethylsilyl)indene,[7] 15, in the presence of tetrabutylammonium acetate (2.4% of 15) to give, following a slow polymerization, a quantitative yield of PMMA with $\bar{M}_n$ = 10400 and D = 1.50 (theory, $\bar{M}_n$ = 8115, see Scheme VIII). At a catalyst level of 0.6% (of 15), polymerization was incomplete even after 18 h. Initiation of GTP by 15 demonstrates that a class of silicon compounds quite different from the silyl ketene acetals, silyl esters, and silyl nitriles reported earlier[2,3,9] is capable of reacting with acrylic monomers in the presence of anion catalysts to initiate GTP (see Scheme VIII). Investigation of the cause of the unusually slow GTP of MMA when initiated by 15 or initiated by 1 in the presence of indene led to the finding that tetrabutylammonium acetate in tetrahydrofuran solution caused the rapid isomerization of 15 to an equilibrium mixture containing 15 and 3-(trimethylsilyl)indene in a ratio of 9:1 (see Scheme IX). Thermal rearrangement of 1-(trimethylsilyl)indene to 2- and 3-(trimethylsilyl)indene has been well-documented in the literature.[10] Presumably, the 3-(trimethylsilyl)indene, which is formed in the anion-catalyzed equilibration of 1-(trimethylsilyl)indene, interfers with the availability of catalyst and retards the rate of GTP of MMA.

Less efficient as a chain-transfer agent is fluorene, 16. Initiation of GTP of MMA with the "labeled" initiator 8 in the presence of fluorene and TASHF$_2$ catalyst followed by deprotection of the hydroxyl group in the resulting polymer followed by HPLC analysis[6] showed that 81% of the polymer had a hydroxyl end group and was thus formed by direct initiation by 8. Only 19% of the polymer was formed by chain transfer (see Scheme X). The chain-transfer constant of 0.2 is consistent with the 19% chain transfer measured by HPLC. Another class of chain-transfer agents in GTP of MMA is thioesters, represented by γ-thiobutyrolactone, 17 (see Table III, entry 6). Chain transfer by 17 with 8 as initiator and TASHF$_2$ catalyst was accompanied by only 59% conversion to PMMA (Scheme XI). Elemental analysis of the polymer for sulfur and silicon showed that about 50% of the polymer was derived from direct initiation by 8 and 50% was derived from chain transfer by 17. This is in good agreement with the chain-transfer constant (0.6).

A variety of carbon acids has been shown to be effective as chain-transfer agents in GTP of MMA. Of the compounds studied, α-phenylpropionitrile and esters of phenylacetic acid are the most useful chain-transfer agents since they transfer efficiently and do not interfere with the activity of the anion catalysts used in the GTP process. The catalysts which are useful for GTP[4] also catalyze the chain-transfer process. Although our studies do not provide any direct evidence on the mechanism of silicon–proton exchange in the chain-transfer process, this process appears to be related to the tetrabutylammonium fluoride catalyzed silylation of aldehydes and ketones with ethyl (trimethylsilyl)acetate reported by Kuwajima and coworkers.[11] The mechanism proposed[11b] for this process involves the reaction of fluoride with ethyl (trimethylsilyl)acetate to form fluorotrimethylsilane and ester enolate which deprotonates the carbon acid. The resulting carbanion is then silylated by the fluorotrimethylsilane. We have no evidence to indicate whether, in the GTP chain-transfer process, a free enolate is an intermediate or whether an anion-activated silylenolate is the intermediate. Since the latter species has been proposed to be the reactive intermediate in the carbon–carbon bond-forming step of GTP[2,12] it seems reasonable that such an intermediate would have sufficient reactivity to undergo silicon–proton exchange with a carbon acid in the chain-transfer process. Although indene and phenylacetonitrile are chain-transfer agents in GTP exhibiting large chain-transfer constants, they both lead to slow polymerizations of MMA probably as a result of coordination with catalyst, and indene, in addition, leads to poor conversion to polymer. Thus, the most attractive chain-transfer agents are α-phenylpropionitrile and the α-arylacetates. Although the literature does not provide pK_a values for all of the carbon acids that have been evaluated as GTP chain-transfer agents in this study, all of the compounds that have good or moderate activity as chain transfer agents probably have pK_a (in DMSO) values of 25 or less.[13] Aliphatic esters, such as isobutyrates, which are estimated to have pK_a's in excess of 25,[13a] are not chain-transfer agents in GTP. Other, more acidic compounds with pK_a values below about 18, such as malonic esters, malononitrile, a diphenylacetonitrile, seem to produce termination of GTP for reasons not completely understood.

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"Immortal" Polymerization of ε-Caprolactone Initiated by Aluminum Porphyrin in the Presence of Alcohol

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ABSTRACT: The (5,10,15,20-tetraphenylporphinato)aluminum alkoxide–alcohol system is an excellent initiator for the polymerization of ε-caprolactone to give the corresponding polyester having a narrow molecular weight distribution, without the formation of cyclic oligomers. The number of polymer molecules produced exceeded that of aluminum porphyrin molecules, and the reaction thus has the character of "immortal" polymerization. ε-Caprolactone–ethylene oxide block copolymer with controlled chain lengths can also be synthesized.

Introduction

Polycaprolactone is widely used for the production of polyurethanes, and the synthesis of polycaprolactone with well-controlled molecular weight is very important in order to give a desired function to polyurethanes.

The polymerization of ε-caprolactone can be brought about with various initiators,[1,2] but examples of living polymerization have been very limited. Teyssiē and coworkers reported the living polymerization of ε-caprolactone catalyzed by soluble bimetallic μ-oxoalkoxide, to

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