Group Transfer Polymerization. Polymerization of Acrylic Monomers†

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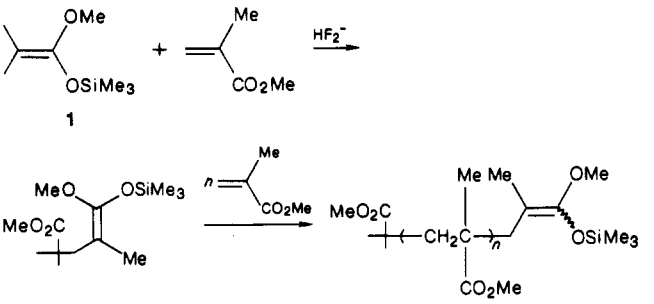
ABSTRACT: "Living" polymerization of methacrylates was achieved over a broad range of polymerization temperatures by using ketene silyl acetals as initiators in the presence of fluoride, bifluoride, cyanide, or azide salts as catalysts. Polymers with narrow molecular weight distribution were obtained. The process was named "group transfer polymerization" (GTP). Other monomers polymerized by GTP are alkyl acrylates, *N,N*-dimethylacrylamide, acrylonitrile, methacrylonitrile, and 2-methylene-4-butyrolactone. Block copolymers with controlled sequence lengths were prepared from methyl methacrylate (MMA), *n*-butyl methacrylate (BMA), and allyl methacrylate (AMA); MMA, 2-hydroxyethyl methacrylate (HEMA), and lauryl methacrylate (LMA); and MMA and LMA. The corresponding α-stannyl and α-germyl esters gave polymers of broader molecular weight distribution than did the ketene silyl acetals. Isothermal polymerizations of MMA by GTP provided detailed information on the temperature dependence of tacticity. The calculated differences in activation parameters ($m - r$) are $\Delta\Delta H^{\ddagger}$ = 1 kcal/mol, $\Delta\Delta S^{\ddagger}$ = 1.1 eu, and $\Delta\Delta G^{\ddagger}_{273}$ = 0.7 kcal/mol.

Introduction

Anionic polymerization provides a methodology for controlled polymerization of styrenes and dienes to living polymers, but for controlled polymerization of most acrylic monomers to living polymers low temperatures are required, with the result that commercial applications to methacrylate polymers have been inhibited.[1] Preliminary communications reported the controlled polymerization of acrylic monomers at ambient temperatures initiated by ketene silyl acetals in the presence of a catalyst according to Scheme I. The name "group transfer polymerization" (GTP) was suggested for the process.[2,3] This paper provides details of our studies of the polymerization of several acrylic monomers with a variety of initiators and catalysts.

Scheme I



Experimental Section

Materials and Methods. Tetrahydrofuran (THF) was distilled from sodium and benzophenone immediately prior to use. Acetonitrile (MeCN), methylene chloride, and 1,2-dichloroethane were purified by distillation from P_2O_5. *N,N*-Dimethylformamide (DMF) and propylene carbonate were distilled through a Vigreux column under reduced pressure. The water content of all solvents was determined with a Karl Fischer titrator. Initiators were distilled with a 12-in. spinning-band column. Commercially available monomers were passed through a short column of neutral alumina under an argon atmosphere to remove inhibitors and protonic impurities.

General classes of solvents that are suitable for anion-catalyzed GTP are hydrocarbons, ethers, carbonates, amides, nitriles, and tertiary amines. Specific examples of solvents that have been used are toluene, THF, glyme, ethyl acetate, cellosolve acetate, DMF, *N,N*-dimethylacetamide (DMAC), acetonitrile, and propylene carbonate. For best results, moisture and protic impurities must be kept to a minimum. Dimethylketene methyl trimethylsilyl acetal (1) was prepared by the procedure of ref 9a. Unless otherwise specified, elemental analyses were within 0.30% of calculated values.

Polymerizations were performed in glass reaction flasks under an argon atmosphere using syringe techniques for introduction of liquid reactants and solvents. Stirring was effected by a magnetic stirrer, unless otherwise specified. All glassware was dried prior to assembly by storing overnight in a 125–180 °C oven. The argon was passed over 4-Å molecular sieves and reduced nickel oxide catalyst G33RS obtained from United Catalysts, Inc.

The catalysts, zinc iodide (99.99%), zinc bromide (99.999%), and zinc chloride (99.999%) were used as obtained from Aldrich Chemical Co. They were weighed under dry nitrogen atmosphere in a drybox. In the absence of a drybox, zinc bromide of satisfactory activity could be prepared in situ by the reaction of diethylzinc (as a 15% solution in toluene obtained from Morton Thiokol, Inc., Alfa Products) with 2 molar equiv of bromine in dichloromethane or toluene with cooling. Diethylaluminum chloride was obtained as a 1.8 M solution in toluene from Morton Thiokol, Inc., Alfa Products. Tetrabutylammonium fluoride was purchased from Aldrich Chemical Co. as a 1 M solution in THF. Tetrabutylammonium fluoride trihydrate was purchased from the same source.

^{1}H NMR spectra were recorded with a Nicolet 360WB spectrometer, Varian Associates EM390, or an IBM NR/80 spectrometer. Molecular weights and polydispersities ($D = \bar{M}_w/\bar{M}_n$) were determined by gel permeation chromatography (GPC) using a Waters Associates GPC with a 590 pump, 401 refractive index detector and four μStyragel columns, 100 000, 10 000, 500, and 100, connected in series. Unless otherwise indicated, the standard was PMMA. Theoretical molecular weight was calculated from (wt monomer)/(mol initiator) + (formula wt initiator fragment). GC/MS data were obtained with a Varian 3700 GC with a V.G. Micromass 16-F mass spectrometer or a Du Pont 21-491 mass spectrometer.

Tris(dimethylamino)sulfonium Bifluoride ($TASHF_2$).[4a] Tris(dimethylamino)sulfonium difluorotrimethylsiliconate (TASF) was prepared from the reaction of (dimethylamino)trimethylsilane and sulfur tetrafluoride as described by Middleton,[8] taking care to use sulfur tetrafluoride of good purity. Crystalline TASF (27.5 g, 100 mmol) was dissolved in 24.5 mL of distilled acetonitrile under an argon atmosphere at ambient temperature. Then 1.0 mL (55 mmol) of water was added. The acetonitrile was removed under reduced pressure, and the crystalline residue was stirred overnight with 250 mL of anhydrous THF. Filtration under argon followed by drying at room temperature and 0.1 Torr for 3 days gave 20.1 g (99.7%) of crystalline tris(dimethylamino)sulfonium bifluoride ($TASHF_2$): mp 153–153.5 °C. Anal. Calcd for $C_6H_{19}F_2N_3S$: C, 35.47; H, 9.42; F, 18.68; N, 20.66; S, 15.77. Found: C, 35.45; H, 9.36; F, 17.52; N, 20.99; S, 16.15. ^{19}F NMR (CD_3CN, 200 MHz, 0 °C, $CFCl_3$ standard) δ −145.8 (d, J_{HF} = 120 Hz). ^{1}H NMR (CD_3CN, 80 MHz, −30 °C, Me_4Si standard) δ 2.88 (s, 18 H, CH_3N), −16.4 (t, J_{HF} = 120.9 Hz, 1 H, FHF). Proton NMR

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spectral data for other bifluorides are given in ref 5c. $TASHF_2$ was recrystallized by dissolving in a threefold (w/v) excess of anhydrous acetonitrile, adding THF until turbidity was apparent, adding acetonitrile until a clear solution was obtained, and storing overnight at 4 °C. The resulting crystals were collected by filtration under argon and washed with THF. Samples of the hygroscopic solid were weighed in a drybox. Samples of $TASHF_2$ that became contaminated with moisture could be restored to full activity by pumping at 0.01 Torr overnight. $TASHF_2$ was conveniently used as a catalyst for GTP as a 1 or 0.1 M solution in anhydrous acetonitrile, benzonitrile, or propylene carbonate.

Initiators. Ketene Trialkylsilyl Acetals. These compounds were prepared by modifications of published procedures.[9a] The preparation of **15a** is an illustrative general procedure.

1-(2-(Trimethylsiloxy)ethoxy)-1-(trimethylsiloxy)-2-methyl-1-propene (15a). General Procedure for the Synthesis of Ketene Trialkylsilyl Acetals. Into a three-necked 1-L flask fitted with a stirrer and thermometer were added 300 mL of tetrahydrofuran and 56 mL (0.40 mol) of diisopropylamine under argon. The resulting solution was cooled to 0 °C and 250 mL of *n*-butyllithium (1.5 M in hexane) was added dropwise with stirring. After 30 min of stirring at 0 °C, 26.4 g (0.20 mol) of 2-hydroxyethyl isobutyrate was added dropwise, the temperature being maintained as close to 0 °C as possible. The reaction mixture was stirred for 30 min and 76.2 mL (0.60 mol) of trimethylsilyl chloride was added. The mixture was stirred for 1 h at 0 °C and then allowed to warm slowly to 25 °C. It was then filtered under argon. Dry ether (150 mL) was added and the inorganic salts were removed by filtration under argon. Evaporation of the solvent gave an oily residue that was distilled (spinning-band column) to give 35.8 g of **15a**: bp 62–63 °C (1.0 Torr). ^1H NMR ($CDCl_3$, 360 MHz) δ 0.1 (s, 9 H, Me_3Si), 0.2 (s, 9 H, Me_3Si), 1.52, 1.60 (2 s, 6 H, CH_3), 3.77 (broad s, 4 H, C_2H_2). IR 1705 cm^{-1} (C=C).

***tert*-Butyl 2-(Trimethylsilyl)acetate.** The above general procedure was followed with 34.9 g (0.30 mol) of *tert*-butyl acetate (Aldrich Chemical Co.). Normal workup gave, after spinning-band distillation, both the C-silylated and O-silylated products (combined yield of 66%) shown below:

1-*tert*-Butoxy-1-(trimethylsiloxy)ethylene: 12.2 g (33%); bp 56 °C (20 Torr). ^1H NMR ($CDCl_3$, 90 MHz) δ 0.25 (s, 9 H, CH_3Si), 1.36 (s, 9 H, CH_3C), 3.45 (s, 2 H, CH_2). IR 1650 cm^{-1} (C=C).

***tert*-Butyl 2-(Trimethylsilyl)acetate**: 24.8 g (67%); bp 69–70 °C (20 Torr). ^1H NMR ($CDCl_3$, 90 MHz) δ 0.13 (s, 9 H, CH_3Si), 1.45 (s, 9 H, CH_3C), 1.80 (s, 2 H, CH_2Si). IR 1710 cm^{-1} (C=O of ester). GC/MS M^+ 188 (*m/e*).

1-Methoxy-1-(dimethyloctadecylsiloxy)-2-methyl-1-propene. This compound was prepared in quantitative yield from 14.3 g (0.14 mol) of methyl isobutyrate and dimethyloctadecylchlorosilane using the above procedure. ^1H NMR ($CDCl_3$, 80 MHz) δ 0.20 (s, 6 H, OSiMe), 0.6–1.0 (m, 5 H, CMe, CH_2Si), 1.28 (s, 32 H, CH_2), 1.55 (s, 3 H, C=CMe), 1.60 (s, 3 H, C=CMe), 3.53 (s, 3 H, OMe).

Bis(1-methoxy-2-methyl-1-propenoxy)methylsilane. This compound was obtained in 16% yield from methyl isobutyrate and methyldichlorosilane: bp 55–57 °C (0.5–0.7 Torr). ^1H NMR ($CDCl_3$, 80 MHz) δ 0.67 (d, J = 3 Hz, SiMe), 1.55 (2 s, CMe), 3.55 (s, OMe), 4.88 (q, J = 3 Hz, SiH).

1,2-Bis(1-(trimethylsiloxy)-2-methylprop-1-enoxy)ethane (17). To a stirred solution of 0.30 mol of lithium diisopropylamide (LDA) in 220 mL of THF and 193 mL of hexane at 0 °C was added 30 g (0.15 mol) of ethylene glycol diisobutyrate. After 30 min at 0 °C, 39.7 mL (0.31 mol) of chlorotrimethylsilane was added at 0 °C. After the mixture was warmed to room temperature, it was filtered under argon. The filtrate was evaporated under reduced pressure, and the residue was treated with hexane and filtered under argon, and the filtrate was evaporated. The residue was stirred at 55 °C at 0.05 Torr to give 50 g of **17**. ^1H NMR ($CDCl_3$, 90 MHz) δ 0.1 (s, 18 H, SiMe), 1.40 (s, 6 H, CMe), 1.49 (s, 6 H, CMe), 3.77 (s, 4 H, OCH_2).

2-(Trimethylsilyl)isobutyronitrile. Following the procedure for the synthesis of ketene silyl acetals, the desired product was obtained in 74% yield from 20 g (0.29 mol) of isobutyronitrile as a pale yellow solid. Sublimation in vacuo gave a colorless solid. Anal. Calcd for $C_7H_{15}NSi$: C, 59.50; H, 10.70; N, 9.92. Found: C, 59.60; H, 11.07; N, 9.74. IR (CCl_4) 2220 cm^{-1} (CN). ^1H NMR ($CDCl_3$, 90 MHz) δ 0.22 (s, 9 H, SiMe), 1.35 (s, 6 H, CMe).

Tin- and Germanium-Containing Initiators. These were prepared from dimethylketene methyl trimethylsilyl acetal (1) as illustrated for methyl 2-(trimethylgermyl)isobutyrate (5).

To a stirred solution of 27.7 g (31.8 mL, 0.16 mol) of 1 in 200 mL of THF at 0 °C was added 100.6 mL of 1.58 M *n*-butyllithium/hexane. The resulting solution was stirred for 1 h at room temperature and then treated with 24.38 g (0.16 mol) of trimethylgermyl chloride at a rate such that the temperature did not exceed 32 °C. After 30 min at room temperature, the solution was filtered and the filtrate distilled in a spinning-band column to give 22.9 g of **5**: bp 46–49 °C (4.5–6 Torr). IR 1713 cm^{-1} (ester C=O). ^1H NMR ($CDCl_3$, 90 MHz) δ 0.0 (s, 9 H, GeMe), 1.09 (s, 6 H, CMe), 3.46 (s, 3 H, OMe).

Methyl 2-(Tributylstannyl)isobutyrate (6). With 17.4 g (0.10 mol) of **1**, 21.2 g of **6** were prepared following the above procedure. Anal. Calcd for $C_{17}H_{36}O_2Sn$: C, 52.27; H, 9.29; Sn, 30.25. Found: C, 52.11; H, 9.35; Sn, 28.71. IR 1705 cm^{-1} (ester C=O). ^{H} NMR ($CDCl_3$, 90 MHz) δ 1.2 (s, CMe), 3.34 (s, OMe).

Methyl 2-(Trimethylstannyl)isobutyrate (7). This compound was prepared from methyl isobutyrate (25.6 g, 0.25 mol), lithium diisopropylamide, and trimethyltin chloride at −78 °C in 11% yield following the general procedure for the preparation of corresponding ketene silyl acetals: bp 61 °C (0.8 Torr). ^1H NMR ($CDCl_3$, 360 MHz) δ −0.03 (s, 2d, $J_{^{119}Sn}$ = 53.3 Hz, $J_{^{117}Sn}$ = 50.7 Hz, 9 H, SnMe), 1.25 (s, 2d, $J_{^{119}Sn}$ = 56 Hz, $J_{^{117}Sn}$ = 53.3 Hz, 6 H, CMe), 3.43 (s, 3 H, OMe).

Other Initiators. Bis(trimethylsilyl) 3-Methoxy-3-(trimethylsiloxy)-2-methylprop-2-ene-1-phosphonate (10c). To 13.12 g (15 mL, 44 mmol) of tris(trimethylsilyl) phosphite (**9b**)[28] at 115 °C was added 4.76 mL (44 mmol) of MMA during 30 min. The resulting solution was heated at 115–120 °C for 2 h, after which time ^1H NMR showed that all of the MMA had reacted. Distillation gave 6 g of **10c**: bp 96 °C (0.05 Torr). Anal. Calcd for $C_{14}H_{35}O_5PSi_3$: C, 42.18; H, 8.85; P, 7.77; Si, 21.14. Found: C, 42.17; H, 8.54; P, 8.07; Si, 21.12. ^1H NMR ($CDCl_3$, 360 MHz) δ 0.25 (s, 9 H, OSiMe), 0.3 (s, 18 H, POSiMe), 1.74 (d, J_P = 4 Hz, 3 H, CMe), 2.45 (d, J_P = 21.3 Hz, 2 H, CH_2), 3.55 (s, 3 H, OMe). ^{31}P NMR ($CDCl_3$, ref trimethyl phosphite) δ −130.85 (m). NOEs in the ^1H NMR spectrum were quite weak. However, irradiation of the OMe produced a small NOE in C–Me resonance consistent with probable *Z* stereochemistry.

Bis(trimethylsilyl) 3-Methoxy-3-(trimethylsiloxy)prop-2-ene-1-phosphonate (10b). A mixture of 7.4 mL (22 mmol) of tris(trimethylsilyl) phosphite and 2.0 mL (22 mmol) of methyl acrylate was heated at 95 °C for 30 min, at which time NMR showed no residual methyl acrylate. Anal. Calcd for $C_{13}H_{33}O_5PSi_3$: C, 40.60; H, 8.65; P, 8.05; Si, 21.91. MW = 384.64. Found: C, 40.66; H, 8.28; P, 8.10; Si, 21.79. GC/MS M^+ 384. ^1H NMR ($CDCl_3$, 360 MHz) δ 0.16 (s, 9 H, $COSi(CH_3)_3$), 0.24 (s, 18 H, $POSi(CH_3)_3$), 2.40 (dd, J = 20 Hz, J = 7 Hz, 2 H, P–CH_2), 3.44 (dt, J = 7 Hz, J = 8 Hz, 1 H, C=CH), 3.49 (s, 3 H, OCH_3).

Tetramethyl 3-Methoxy-3-(trimethylsiloxy)-2-methylprop-2-ene Phosphonamide Oligomers 11a. Bis(dimethylamino)(trimethylsiloxy)phosphine (**9c**), bp 50–51 °C (7 Torr), was prepared by the reaction of sodium with bis(dimethylamino)-phosphorochloridate in ether followed by reaction at 0 °C with chlorotrimethylsilane. ^1H NMR ($CDCl_3$, 360 MHz) δ 2.45 (d, J = 9.3 Hz, 12 H, PNMe), 0.2 (s, 0 H, SiMe). To 16.64 g (80 mmol) of **9c** at 50 °C was added 8 g (8.6 mL, 80 mmol) of MMA. After the mixture was heated for 30 min at 60 °C, NMR showed residual MMA. After 1 h at 80 °C, NMR showed no residual MMA. Distillation at 26–31 °C (1.4 Torr) gave a mixture of MMA and **9c**, identified by NMR. The composition of the product, **11a**, prior to distillation was determined by quenching with methanol and analyzing the adducts, **12**, by GC/MS, which showed 21.6% **12a**, 75.7% **12b**, and 2.7% **12c**.

Tetramethyl 3-Methoxy-3-(trimethylsiloxy)prop-2-ene Phosphonamide Oligomers (11b). To 3.89 g (20 mmol) of **9c** was added 1.72 g (1.8 mL, 20 mmol) of methyl acrylate. After a brief induction period, an exothermic reaction ensued, accompanied by a rise in temperature to 69 °C. ^1H NMR showed that all of the methyl acrylate had been consumed. The presence of more than one resonance at 3.7 ppm (OMe) indicated that oligomers, **11b**, were present as in the reaction of **9c** with MMA.

$TASHF_2$-Catalyzed Isomerization of 1-Methoxy-1-(trimethylsiloxy)prop-1-ene to Methyl α-(Trimethylsilyl)propionate. A solution of 93 μL (0.5 mmol) of 1-methoxy-1-(trimethylsiloxy)prop-1-ene[29] in 0.7 mL of THF-d_8 was analyzed by ^1H NMR and found to be 85% *E* and 15% *Z* (360 MHz, ppm). *E*: δ 0.20 (s, 9 H, SiMe), 1.44 (d, *J* = 6 Hz, 3 H, CMe), 3.46 (s, 3 H, OMe), 3.60 (q, *J* = 6 Hz, 1 H, C=CH). *Z*: 0.175 (s, 9 H, SiMe), 1.47 (d, *J* = 6 Hz, 3 H, CMe), 3.44 (s, 3 H, OMe), 3.59 (q, *J* = 6 Hz, 1 H, C=CH). To this solution was added 10 μL of $TASHF_2$ (0.1 M in propylene carbonate). The ^1H NMR spectrum determined after 10 min showed 83% 1-methoxy-1-(trimethylsiloxy)prop-1-ene (87% *E*, 13% *Z*) and 17% methyl α-(trimethylsilyl)propionate.[30] NMR 0.05 (s, 9 H, CSiMe), 1.14 (d, *J* = 7 Hz, 3 H, CMe), 2.04 (q, *J* = 7 Hz, 1 H, C=CH), 3.56 (s, 3 H, OMe). After 4.5 h, NMR showed the composition to be 69% ketene silyl acetal (83% *E*, 17% *Z*) and 31% C-silyl isomer.

$TASHF_2$-Catalyzed Isomerization of 1 and Methyl α-(Trimethylsilyl)isobutyrate.[31] With the same procedures, ^1H NMR (360 MHz) was used to follow separately the changes in solutions in 0.7 mL of THF-d_8 of 80 μL (0.4 mmol) of 1 and 80 μL of methyl α-(trimethylsilyl)isobutyrate after addition of 40 μL of $TASHF_2$ (0.1 M in propylene carbonate) to each solution.

Equilibration of 1 and Methyl α-(Trimethylsilyl)isobutyrate Catalyzed by Tetrabutylammonium *m*-Chlorobenzoate.[13] With the same procedure, but with substitution of 40 μL of tetrabutylammonium *m*-chlorobenzoate (0.1 M in THF) for 40 μL of $TASHF_2$, ^1H NMR was used to determine the composition starting with methyl α-(trimethylsilyl)isobutyrate at time (s) = 22 800 (79% C–silyl, 21% **1**), 47 800 (59%, 41%), 85 600 (33%, 67%), 123 700 (28%, 72%), and 177 800 (26%, 74%), and starting with 1 at time (s) 19 100 (19% C–silyl, 81% 1), 48 500 (24%, 76%), and 86 100 (24%, 76%).

Polymerizations. Polymerization of Ethyl Acrylate with Zinc Iodide and 1. A 100-mL three-necked flask containing 6.48 g (20 mmol) of zinc iodide was heated to 300 °C in vacuo for 30 min and then allowed to cool under argon. Then 50 mL of dichloromethane was added followed by 1.4 mL (4.71 mmol) of 1. After the mixture was cooled to −78 °C, 10 mL (92.2 mmol) of ethyl acrylate was added. The mixture was allowed to warm to −15 °C, whereupon the temperature rose to +38 °C during 3 min. The temperature was allowed to fall to 20 °C. The solvent was evaporated, and the residue was dissolved in 100 mL of ethyl acetate and washed 3 times with 100-mL portions of water. The organic layer was dried over magnesium sulfate, filtered, and evaporated to give 9.91 g of poly(ethyl acrylate). GPC $\bar{M}_n$ = 2200, $\bar{M}_w$ = 2300, and *D* = 1.05 (theoretical $\bar{M}_n$ = 2160).

Polymerization of Ethyl Acrylate with Diethylaluminum Chloride and 1. To a solution of 0.87 g (1 mL, 5 mmol) of 1 in 20 mL of dichloromethane at −78 °C was added 0.28 mL (0.5 mmol) of 1.8 M diethylaluminum chloride/toluene. Then 10 g (10.8 mL, 0.10 mol) of ethyl acrylate was added at such a rate that the temperature of the reaction mixture did not exceed −70 °C. After 15 min at −78 °C, 5 mL of methanol was added and the mixture was allowed to warm to room temperature. Evaporation gave 10.7 g of poly(ethyl acrylate) as a viscous liquid. GPC $\bar{M}_n$ = 2130, $\bar{M}_w$ = 2580, and *D* = 1.21 (theoretical $\bar{M}_n$ = 2100).

Polymerization of Methyl Methacrylate to $\bar{M}_n$ = 60 000. A 500-mL, four-necked round-bottomed flask, fitted with a magnetic stirring bar, argon inlet, thermocouple well, serum cap, and 125-mL pressure-equalizing dropping funnel equipped with a serum cap, was assembled under argon while hot. The entire apparatus was then heated with a heat gun while being flushed with argon. The argon flush was continued until the apparatus was cool. The assembly was then maintained under a slight positive pressure of argon. THF (225 mL) was transferred to the flask via a cannula. MMA (75 mL, 0.69 mol) was transferred to the dropping funnel via a cannula. Then 0.37 mL (1.16 mmol) of **15a** and 58 μL of tetrabutylammonium fluoride trihydrate (0.02 M in THF) were introduced to the flask with syringes. MMA was then added dropwise over a period of 90 min. After stirring for 16 h, the reaction was quenched with 10 mL of methanol, stirred for 1 h, and poured very slowly into a fivefold volume of hexane that was being agitated strongly in a blender. After filtration and washing with hexane, the polymer was air-dried at room temperature and then dried for 48 h to constant weight in a vacuum oven at 65 °C, under a slight nitrogen purge. Recovered PMMA weighed 71.2 g (quantitative conversion), which is slightly more than theory due to the presence of traces of solvent (observed only in TGA). GPC gave $\bar{M}_n$ = 62 300, $\bar{M}_w$ = 71 500, and *D* = 1.15 (theoretical $\bar{M}_n$ = 60 180).

Polymerization of Methyl Methacrylate with 11a. To a solution of 0.93 g (3 mmol) of undistilled reaction product of **9c** and MMA and 10 μL of $TASHF_2$ (1 M in acetonitrile) in 20 mL of THF was added dropwise 10 g (100 mmol) of MMA, producing an exothermic polymerization. The resulting solution was evaporated to give a quantitative yield of PMMA, $\bar{M}_n$ = 6610, $\bar{M}_w$ = 6930, and *D* = 1.05 (theoretical $\bar{M}_n$ = 3250).

Block Copolymerization of Methyl Methacrylate and Butyl Methacrylate with 10c. To a solution of 0.8 g (2 mmol) of **10c** and 20 μL of $TASHF_2$ (1 M in acetonitrile) in 20 mL of THF was added dropwise 10 g (100 mmol) of MMA. Prior to addition of the final 5 g of MMA, 0.1 mL of $TASHF_2$ (1 M in acetonitrile) was added, resulting in a gradual temperature rise to 54 °C during 15 min. After 30 min, a sample was removed for GPC analysis: $\bar{M}_n$ = 5100, $\bar{M}_w$ = 5340, and *D* = 1.05 (theoretical $\bar{M}_n$ = 5300). Then 4.55 g (32 mmol) of *n*-butyl methacrylate was added (slight exotherm), and the solution was stirred for 18 h. The resulting solution was treated with 5 mL of methanol and stirred at reflux for 1 h to the cleavage of all the trimethylsilyl groups. Evaporation gave 17.4 g of solid polymer. After dissolution in methylene chloride, washing with water, drying ($MgSO_4$), and precipitation with hexane, there was obtained 15 g of block poly(MMA-*co*-BMA). ^1H NMR showed the presence of a terminal phosphonic acid group with a resonance at 8.9 ppm (P–OH). GPC showed $\bar{M}_n$ = 7050, $\bar{M}_w$ = 7260, and *D* = 1.03 (theoretical $\bar{M}_n$ = 7572).

Polymerization of Methyl Methacrylate with Trimethylsilyl Methyl Sulfide and Tetraethylammonium Cyanide. To a solution of 0.71 mL (5 mmol) of trimethylsilyl methyl sulfide and 30 μL of tetraethylammonium cyanide (1 M in acetonitrile) in 20 mL of acetonitrile was added 10 g (100 mmol) of MMA. A few minutes after all of the monomer had been added polymerization began, and the temperature rose to 57 °C. After 1 h, an additional 5 g (50 mmol) of MMA was added. An additional 20 μL of tetraethylammonium cyanide (1 M in acetonitrile) was required to obtain a slow exotherm to 37 °C. After 18 h the solution was treated with 3 mL of methanol and evaporated to 15.2 g of PMMA, $\bar{M}_n$ = 11 800, $\bar{M}_w$ = 19 400, and *D* = 1.64 (theoretical $\bar{M}_n$ = 3065). The polymer was precipitated from methylene chloride with hexane for purification. Anal. Calcd for $(C_5H_8O_2)_{118}SCH_3$: S, 0.27; N, 0.00. Found: S, 0.24; N, 0.00.

Polymerization of Methyl Methacrylate with Trimethylsilyl Cyanide and TAS Cyanide. To a stirred solution of 0.99 g (1.3 mL, 10 mmol) of trimethylsilyl cyanide in 20 mL of anhydrous acetonitrile was added 10 g (100 mmol) of MMA. No temperature increase was observed, and NMR analysis of an aliquot after 18 h showed that no polymer was present. Addition of 1 mL of TAS cyanide (1 M in acetonitrile) caused a slow temperature rise of about 1 °C, and after 45 min a rapid exothermic reaction ensued with a temperature increase to above 60 °C. After the solution had cooled to room temperature, evaporation gave 10.4 g of PMMA, $\bar{M}_n$ = 800, $\bar{M}_w$ = 800, and *D* = 1.00 (theoretical $\bar{M}_n$ = 1026).

Polymerization of Acrylonitrile. To a mechanically stirred mixture of 6.6 mL (5.3 g, 100 mmol) of acrylonitrile and 20 μL of $TASHF_2$ (1 M in acetonitrile) in 60 mL of DMF at −50 °C was added rapidly a solution of 7 μL (35 μmol) of 1 in 1 mL of THF. The temperature rose rapidly to 3 °C, and the solution became viscous. After 10 min a solution of 2 drops of sulfuric acid in 10 mL of DMF was added, and poly(acrylonitrile) was precipitated with aqueous methanol in a blender and dried to give 4.8 g (91%) of colorless polymer, η_{inh} 3.13 (DMF, 25 °C, $\bar{M}_v$ = 422 000), $\bar{M}_n$ = 128 000, $\bar{M}_w$ = 486 000, and *D* = 3.79 (DMAC at 135 °C). ^{13}C NMR (100.6 MHz, quaternary carbon) shows essentially random tacticity.

Polymerization of Methacrylonitrile. To a solution of 2.8 mL of 2-(trimethylsilyl)isobutyronitrile (0.88 M in acetonitrile) and 20 μL of $TASHF_2$ (1 M in acetonitrile) in 20 mL of DMAC was added 10 mL (12.6 mL, 150 mmol) of methacrylonitrile. After stirring for 1.5 h, 20 μL of $TASHF_2$ (1 M in acetonitrile) was added, resulting in a rapid temperature increase to 63 °C and an increase in viscosity. NMR and GPC analyses of a sample of the reaction

mixture showed that 87% of the monomer had been converted to polymer with $\bar{M}_n$ = 5800, $\bar{M}_w$ = 11 800, and D = 2.04 (theoretical $\bar{M}_n$ for 87% conversion 3570). The polymer was precipitated with methanol. ^{13}C NMR at 100.6 MHz shows essentially random tacticity.

Polymerization of α-Methylene-γ-butyrolactone. To a solution of 6 g (61 mmol) of freshly distilled α-methylene-γ-butyrolactone and 50 μL of $TASHF_2$ (1 M in acetonitrile) in 40 mL of anhydrous propylene carbonate was added 0.5 mL (1.6 mmol) of **15a**, which resulted in a rapid exotherm to 50 °C. Precipitation with THF gave 4 g (67%) of poly(α-methylene-γ-butyrolactone), $\bar{M}_n$ = 31 500, $\bar{M}_w$ = 47 900, D = 1.52 (in hexafluoro-2-propanol, PMMA calibration), $[\eta]^{25°}_{DMF}$ = 0.0716, $[\eta]^{25°}_{Me_2SO}$ = 0.0824 g/dL, T_g = 112 °C (DSC).

Polymerization of Butyl Acrylate with $TASHF_2$. A 500-mL three-necked flask, fitted with an argon inlet, a magnetic stirrer, and a thermocouple, was charged with THF (200 mL) and cooled to 0 °C using an ice bath. Then $TASHF_2$ (0.01 mL, 1 M in MeCN) was added followed by the addition of **1** (0.50 mL, 2.50 mmol). The mixture was allowed to equilibrate for 15 min and then treated dropwise with *n*-butyl acrylate (65 g, 0.51 mol), the rate of addition being adjusted such that the temperature of the reaction mixture was maintained at 0 ± 1 °C. An additional 0.01 mL of $TASHF_2$ (1 M in MeCN) was added when monomer addition was over. The mixture was stirred and allowed to warm to 25 °C. The resulting viscous mixture was evaporated and the residue dried at 100 °C (0.10 Torr) to give 59.5 g of polymer. This has an inherent viscosity of 0.24 g/dL. Gel permeation chromatography gave $\bar{M}_n$ = 27 200, $\bar{M}_w$ = 59 400, and D = 2.16 (theoretical $\bar{M}_n$ = 23 800).

Poly(lauryl methacrylate)-*block*-poly(methyl methacrylate). A three-necked 500-mL flask, equipped with an addition funnel, an argon inlet, and a thermocouple, was charged with THF (250 mL), lauryl methacrylate (46 g, 0.18 mol), and **1** (6 mL, 30 mmol). Then $TASHF_2$ (1.0 mL, 0.1 M in MeCN) was added. An exothermic reaction ensued, accompanied by a gradual temperature rise from 23.8 to 37.2 °C over a 10-min period. The mixture was stirred for 3 h and then treated with methyl methacrylate (162.4 g, 1.62 mol) at a 3 mL/min rate of addition. The temperature rose from 25 to 44.4 °C. After the mixture was stirred for 1.5 h, additional $TASHF_2$ (0.5 mL, 0.1 M in MeCN) was added and stirring was continued for 18 h. The viscous mixture was diluted with acetone (150 mL) and then poured into methanol (four 2.5-L batches) to precipitate the polymer. The precipitate was collected by filtration, dried, and weighed to give 186 g of polymer as a white powder: $\bar{M}_n$ = 6540, $\bar{M}_w$ = 7470, and D = 1.14 (theoretical $\bar{M}_n$ = 7120).

Poly(methyl methacrylate)-*block*-poly(lauryl methacrylate). A three-necked 1-L flask, equipped as above, was charged with **1** (4.66 mL, 23.3 mmol), THF (350 mL), and methyl methacrylate (5 mL). Then $TASHF_2$ (1.0 mL, 0.1 M in MeCN) was added. The temperature rose from 24.2 to 28 °C, at which point the addition of the rest of MMA (128.5 mL) was begun at approximately 3 mL/min with continued stirring. After the addition of MMA was completed, the mixture was stirred until the temperature dropped from the maximum of 45.2 to 24 °C. After the mixture was stirred for an additional 0.5 h, lauryl methacrylate (35.7 g, 0.14 mol) was added all at once. Stirring was continued for 15 min, followed by the addition of more $TASHF_2$ (2.0 mL, 0.1 M in MeCN). The mixture was stirred for an additional 3 h, treated with methanol (50 mL), concentrated in vacuo to 400 mL, and then poured into methanol (5 L). The precipitate was collected, dried, and weighed to give 159 g of polymer: $\bar{M}_n$ = 6650, $\bar{M}_w$ = 7070, and D = 1.06 (theoretical $\bar{M}_w$ = 7140).

Poly(methyl methacrylate)-*block*-poly(butyl methacrylate)-*block*-poly(allyl methacrylate). To a solution of 1.25 mL (6.25 mmol) of **1** and 50 μL $TASHF_2$ (1 M in acetonitrile) in 50 mL of THF was added 10.7 g (106.9 mmol) of MMA during 15 min. The temperature rose from 24.8 to 51.6 °C. After the reaction mixture had cooled to 38.6 °C, 9.0 g (63.3 mmol) of *n*-butyl methacrylate was added during 15 min with an increase in temperature to 43.2 °C. After the temperature had dropped to 33 °C, 5.34 g (42.5 mmol) of allyl methacrylate was added with an increase in temperature to 39.2 °C. When the reaction mixture had cooled to 23 °C, 10 mL of methanol containing 1.0 mg of phenothiazine was added. Removal of solvent in vacuo gave 23.72 g (95%) of block terpolymer, $\bar{M}_n$ = 3800, $\bar{M}_w$ = 4060, and D = 1.07 (theoretical $\bar{M}_n$ = 4100).

Poly(methyl methacrylate-*co*-2-hydroxyethyl methacrylate)-*block*-poly(lauryl methacrylate)-*block*-poly(methyl methacrylate-*co*-2-hydroxyethyl methacrylate). Lauryl methacrylate was purified as follows: 160 g of lauryl methacrylate that had been passed through a column of neutral alumina was stirred for 2 h with 0.1 g of phenothiazine, 8.9 mL of triethylamine, and 6.2 mL of methacrylyl chloride. Then 200 mL of hexane was added, and the mixture was filtered. The filtrate was washed with water, dilute sodium bicarbonate solution, and water, dried ($MgSO_4$), passed through a column of basic alumina, and distilled over phenothiazine. To a solution of 1.45 g (1.59 mL, 4.17 mmol) of **17** and 0.2 mL of $TASHF_2$ (1 M in acetonitrile) in 100 mL of THF was added 25 g (98 mmol) of purified lauryl methacylate. One hour after the end of the exotherm, a mixture of 13.5 mL (125 mmol) MMA, 19.4 g (19.9 mL, 96 mmol) of 2-(trimethylsiloxy)ethyl methacrylate, and 30 μL of $TASHF_2$ (1 M in acetonitrile) was added, accompanied by a less than 1 °C increase in temperature. Addition of 0.2 mL of $TASHF_2$ (1 M in acetonitrile) gave a slow temperature rise to 50 °C. After 18 h analysis of an aliquot by GPC showed $\bar{M}_n$ = 9340, $\bar{M}_w$ = 11 200, and D = 1.20 (theoretical $\bar{M}_n$ = 13 800). The solution was refluxed for 1.5 h with 25 mL of methanol and 2 mL of tetrabutylammonium fluoride (1 M in THF) and evaporated to give 55 g of polymer. ^1H NMR analysis showed no residual monomer and no trimethylsilyl groups. The polymer was dissolved in methylene chloride, washed with water, dried ($MgSO_4$), and evaporated. The polymer was precipitated from THF with water to give 40 g of copolymer. DSC showed two T_gs at −43 and +95 °C.

Poly(methyl methacrylate-*co*-*n*-butyl methacrylate). To a stirred mixture of 0.51 g (1.85 mmol) of **15a** and 20 mg (0.1 mmol) of $TASHF_2$ in 100 mL of THF were added simultaneously during 20 min 11 mL (103.7 mmol) of MMA and 30 mL (188.5 mmol) of *n*-butyl methacrylate. The temperature rose from 20.6 to 48.6 °C. Evaporation of solvent and drying of the resultant residue gave 38.6 g of poly(MMA-*co*-BMA). ^1H NMR analysis showed that the polymer consisted of 35 mol % MMA and 65 mol % butyl methacrylate units. GPC: $\bar{M}_n$ = 22 100, $\bar{M}_w$ = 24 500, and D = 1.11 (theoretical $\bar{M}_n$ = 20 215).

Methyl Methacrylate, Butyl Methacrylate, and Glycidyl Methacrylate Terpolymer. To a solution of 15 mL (13.07 g, 75 mmol) of **1** and 7.5 mL of $TASHF_2$ (0.1 M in acetonitrile) in 300 mL of THF at 0 °C was added 8.1 mL (7.5 g, 75 mmol) of MMA. Then a solution of 153.9 mL (142.5 g, 1.43 mol) of MMA, 66 mL (60 g, 0.42 mol) of *n*-butyl methacrylate, and 83.7 mL (90 g, 0.63 mol) of glycidyl methacrylate (purified by vacuum distillation) was added during 45 min while maintaining the reaction mixture at 0 ± 2 °C. The solution was then allowed to warm to room temperature, and 10 mL of methanol was added. Evaporation under reduced pressure gave a quantitative yield of solid terpolymer containing 50 wt % MMA, 20 wt % butyl methacrylate, and 30 wt % glycidyl methacrylate: $\bar{M}_n$ = 3910, $\bar{M}_w$ = 4290, and D = 1.10 (theoretical $\bar{M}_n$ = 4092), T_g = −13, + 47 °C.

Poly(methyl methacrylate)-*block*-poly(caprolactone)-*block*-poly(methyl methacrylate). A solution of 50 g of poly(caprolactone-α,ω-diol) (MW 1000, CAPA 210, Union Carbide Corp.) in 300 mL of toluene was refluxed under a Dean and Stark water separator for 18 h. Then 20 mL (150 mmol) of triethylamine was added followed by 10.2 g (110 mmol) of acrylyl chloride at a rate to keep the temperature from exceeding 50 °C. After the solution was stirred for 30 min at 50 °C, it was cooled and filtered under argon. The solution was concentrated in vacuo and passed over a column of neutral alumina under argon. The ^1H NMR spectrum of the resulting solution (230 g) showed 67.7% by wt of poly(caprolactone diacrylate) (**23**) with a formula weight of 992 and 32.4% toluene. GPC: $\bar{M}_n$ = 1250, $\bar{M}_w$ = 2200, and D = 1.76.

To a solution of 0.6 g (0.75 mL, 6.04 mmol) of trimethylsilyl cyanide and 0.5 mL of tetraethylammonium cyanide (1 M in acetonitrile) in 20 mL of acetonitrile was added 4.44 g (3.02 mmol) of 67.6% **23** in toluene. After 20 min, 10.8 mL (10 g, 100 mmol) of MMA was added. A slow exothermic reaction occurred during 90 min. After 18 h, 2 mL of methanol was added and the solution was evaporated in vacuo to 13.5 g of solid **25**, $\bar{M}_n$ = 4120, $\bar{M}_w$ =

7340, and D = 1.78 (theoretical $\bar{M}_n$ = 4303). ^{1}H NMR shows 4.24 MMA units per caprolactone unit (theory, 4.36).

Isolation and Characterization of Living Poly(methyl methacrylate). To a stirred mixture of 16 mg (0.1 mmol) of anhydrous tetraethylammonium cyanide and 2 mL (10 mmol) of **1** in 20 mL of THF was added 10 g (100 mmol) of MMA during 30 min, during which time the temperature rose to 55.4 °C. The reaction mixture was allowed to cool to 22 °C, and the solvent was removed under vacuum at 25 °C. The resulting colorless residue was transferred to a drybox, and samples were removed for analysis by ^{13}C NMR in $CDCl_3$ and GPC: $\bar{M}_n$ = 777, $\bar{M}_w$ = 1010, and D = 1.30 (theoretical $\bar{M}_n$ = 1102). The remaining polymer was dissolved in 20 mL of THF, and 10 mL (94 mmol) of MMA was added. The temperature rose from 19 to 29.4 °C. After 3 h, the mixture was quenched with 10 mL of methanol and evaporated to 22.65 g of PMMA: $\bar{M}_n$ = 1430, $\bar{M}_w$ = 1900, and D = 1.32 (theoretical $\bar{M}_n$ = 2042).

Reaction of Living Poly(methyl methacrylate) with Benzaldehyde. A four-necked, 250-mL round-bottom flask, equipped with an argon inlet, a thermocouple well, a reflux condenser, a serum cap, and a magnetic stirring bar, was charged with THF (75 mL), **15a** (2.5 mL, 7.9 mmol), and $TASHF_2$ (0.040 mL, 1 M in MeCN). After 20 min, MMA (25 mL) was added at 0.5 mL/min by syringe pump. The temperature rose to 44 °C. After the solution was stirred an additional 2 h, benzaldehyde (0.88 mL, 8.7 mmol) and $TASHF_2$ (0.040 mL, 1 M in MeCN) were added. The temperature rose from 26 to 30 °C. The solution was stirred overnight, a 5-mL aliquot was removed, and polymer was precipitated by adding to a 20-fold excess of well-stirred hexane. The polymer was filtered, washed with hexane, and dried in a vacuum oven first at room temperature overnight and then at 65 °C for 8 h to a weight of 1.3 g. ^{1}H NMR ($CDCl_3$, 360 MHz, ref $CHCl_3$) revealed Me_3SiO singlets in the ratio of 2.0:1.1:0.9 at δ 0.15, 0.02, and −0.1. Comparison of their peak areas with the methacrylate MeO at δ 3.6 (broad s) gave a MeO:Me_3SiO (incorporated monomer:end group) value of 18.4; theoretical dp of the polymer is 29.4 and monomer/end group is expected to be 14.7. GPC: $\bar{M}_n$ = 2800, $\bar{M}_w$ = 3000, and D = 1.04 (theoretical $\bar{M}_n$ = 3300).

To convert terminal $OSiMe_3$ to OH, Bu_4NF (8 mL, 1 M in THF) and methanol (30 mL) were added to the remaining polymer solution, and the mixture was brought to and held at reflux for 1.5 h. The polymer solution was then concentrated to one-third its volume and PMMA precipitated by addition to a 20-fold excess of stirred hexane. The polymer was isolated and dried as above (48 h at 65 °C) to a weight of 24.4 g. The combined yield of PMMA was quantitative. Me_3Si resonances were completely absent in the ^{1}H NMR spectrum of hydroxy-PMMA. GPC: $\bar{M}_n$ = 3200, $\bar{M}_w$ = 3800, and D = 1.18 (theoretical $\bar{M}_n$ = 3200).

Three-Armed Star Poly(ethyl acrylate). To a solution of 0.93 mL (1 mmol) of 25% triisobutylaluminum/toluene in 20 mL of methylene chloride was added 9 μL (0.5 mmol) of water. The resulting solution was cooled to −78 °C, and 1.8 mL (9 mmol) of **1** was added followed by 0.89 g (0.86 mL, 3 mmol) of trimethylolpropane triacrylate (purified by extraction with hexane and passage of the hexane extract over a column of neutral alumina). After 10 min, 9.7 mL (90 mmol) of ethyl acrylate was added at a rate to maintain the temperature below −70 °C. After 10 min at −78 °C, 2 mL of methanol was added, and the solution was evaporated to 10.4 g of viscous poly(ethyl acrylate), $\bar{M}_n$ = 2190, $\bar{M}_w$ = 3040, and D = 1.39 (theoretical $\bar{M}_n$ = 3300).

Four-Armed Star Poly(ethyl acrylate). The same procedure was followed with 12 mmol of **1**, 3 mmol of pentaerythritol tetraacrylate (purified by fractional dissolution in hexane–methylene chloride), and 120 mmol of ethyl acrylate. There was obtained 16.2 g of crude poly(ethyl acrylate), $\bar{M}_n$ = 2400, $\bar{M}_w$ = 2970, and D = 1.24 (theoretical $\bar{M}_n$ = 4752).

Coupling of Living Polymer with Bis(iodomethyl)benzene. A three-necked 250-mL flask, equipped with a stirrer, an argon inlet, a thermocouple, and a syringe pump, was charged with THF (100 mL) and **15a** (3.27 mL, 11.0 mmol) at 25 °C. After $TASHF_2$ (0.02 mL, 1 M in CH_3CN) was added, MMA (25 g, 0.25 mol) addition was performed at 1.0 mL/min via the syringe pump. The mixture was stirred for 1 h and a 11.5-mL aliquot was removed. This aliquot was quenched with methanol (5 mL), evaporated, dried, weighed (2.44 g), and analyzed by GPC [$\bar{M}_n$ = 2570, $\bar{M}_w$ = 2750, $\bar{M}_n$(calcd) = 2500, D = 1.07]. The remaining mixture was cooled to −78 °C in a dry ice/acetone bath and treated with solid TASF (2.75 g, 10 mmol). Then bis(iodomethyl)benzene (1.79 g, 0.50 mmol) was added as a solution in THF (10 mL). The mixture was stirred at −78 °C for 5 h, quenched with 10 mL of methanol, and evaporated, and the residue was dried and weighed (19.89 g). Proton NMR showed complete loss of the trimethylsilyl group. The residue was dissolved in 20 mL of dichloromethane (20 mL) and added to 1 L of hexane/methanol (100/2, (v/v)) to precipitate the polymer: yield, 26.3 g. GPC gave $\bar{M}_n$ = 4720, $\bar{M}_w$ = 5600, and D = 1.19. $\bar{M}_n$(calcd) = 4910. Molecular weight at peak (M_p) was found by GPC to be 5200 for the final polymer.

Reaction of Poly(methyl acrylate) with *p*-Nitrobenzyl Bromide. A three-necked 50-mL flask fitted with a stirrer, an argon inlet, and a thermocouple, was charged with a solution of TASF (33 mg, 0.12 mmol) in MeCN (50 μL) and THF (8.0 mL). The reactor was cooled to 0 °C and the initiator **1** (2.0 mL, 10 mmol) was added, immediately followed by distilled methyl acrylate (5.0 mL, 55 mmol) as a solution in THF (5.0 mL). The mixture was stirred at 0 °C for 15 min and a 10-mL aliquot removed and quenched with methanol (2 mL). The aliquot was evaporated and the residue dried to give 1.80 g of polymer ($\bar{M}_n$ = 500, $\bar{M}_w$ = 700). The rest of the mixture was cooled to −5 °C and treated with *p*-nitrobenzyl bromide (1.65 g, 6.32 mmol) dissolved in THF (10 mL). After the mixture was stirred at 0 °C for 1 h, it was treated with methanol (2 mL) and evaporated. The residue was redissolved in ethyl acetate, washed successively with $NaHSO_3$ (5% in water, 50 mL), 50 mL HCl (0.1 N HCl), water (100 mL), and brine (100 mL). After drying over $MgSO_4$, the organic layer was filtered and evaporated to give 5.52 g of polymer ($\bar{M}_n$ = 700, $\bar{M}_w$ = 900). The proton NMR spectrum recorded in $CDCl_3$ showed peaks consistent with poly(methyl acrylate) structure. Integration of the two sets of peaks at 4.55 ppm (broad s, CH_2Ar) and 4.70 (broad m, CH_2Ar) gave a ratio of 9:1.

Results and Discussion

The reaction of α,β-unsaturated esters with ketene silyl acetals occurs only in the presence of a catalyst. When the α,β-unsaturated ester is a methacrylate, the reaction of **1** with an excess of the methacrylate in the presence of $TASHF_2$ (<1 mol % of **1**) is rapid and exothermic. As the molecular weight of the polymer that is formed increases with successive additions of the methacrylate, the molecular weight distribution remains narrow, and, with careful attention to exclusion of moisture, poly(methyl methacrylate) with a molecular weight of 50 000 (DP = 500) is readily obtained. The living polymer thus obtained has a narrow molecular weight distribution and is still susceptible to further molecular weight increase by addition of more monomer. The degree of polymerization is controlled by the ratio of monomer to initiator. Two types of catalysts for GTP have been recognized—certain anions and Lewis acids. Anions that catalyze GTP are cyanide, fluoride, bifluoride, difluorotrimethylsiliconate and azide. Typical of the Lewis acid catalysts are zinc iodide, zinc bromide, zinc chloride, and diethylaluminum chloride.[3]

Anion Catalysts for GTP. Tris(dimethylamino)-sulfonium bifluoride[4] ($TASHF_2$) is the GTP catalyst that has been studied most thoroughly. $TASHF_2$ is readily prepared from tris(dimethylamino)sulfonium difluorotrimethylsiliconate by addition of 0.5 molar equiv of water. The potency of bifluoride ion as a catalyst for GTP is quite surprising. Although there are numerous studies (mostly theoretical, spectroscopic, and structural) on bifluoride ion reported in the literature,[5a-c] only recently have reports of the use of this species in catalysis of reactions involving organosilicon reagents appeared.[5d] Prior to the present work, no catalytic applications are reported in the area of silicon-mediated organic reactions. Yet, bifluoride can be used effectively at a level of less than 0.1 mol % relative to ketene silyl acetal initiator in the catalysis of GTP of methyl methacrylate. While the pentacoordinate silico-

Table I
PMMA Prepared by GTP Using Anion Catalysts[a]

entry	cat.	mol 1/mol cat.	solvent	theor $\bar{M}_n \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	D
1	KHF_2	83	CH_3CN	20.2	18.0	21.4	1.17
2	KHF_2	10.4	DMF	5.1	5.95	6.63	1.12
3	$TASHF_2$	21[b]	THF	10.1	10.2	11.9	1.17
4	$TASHF_2$	125	THF	4.1	3.80	4.04	1.06
5	$TASHF_2$[c]	1	THF	10.1	9.37	20.0	2.13
6	Bu_4NF[d]	1023	THF	15.1	17.5	19.9	1.14
7	$Bu_4NF{\cdot}3H_2O$[e]	1003[f]	THF	60.0	62.3	71.5	1.15
8	TASCN[g]	25	9% DMF in THF	10.1	10.5	12.0	1.14
9	Et_4NCN	33	9% DMF in THF	10.1	11.5	12.2	1.06
10	$TASN_3$[g]	6.7	CH_3CN	3.8	3.00	3.10	1.03

[a] Polymerization temperatures were between 20 and 50 °C, with slow addition of monomer to a solution of 1 and catalyst. [b] Solid $TASHF_2$ used, most of which did not dissolve in the reaction medium. [c] Batch polymerization with catalyst added last as 1 M solution in acetonitrile. [d] Bu_4NF as 1.0 M solution in THF with <5% water as obtained from Aldrich Chemical Co. [e] $Bu_4NF{\cdot}3H_2O$ obtained from Aldrich Chemical Co. [f] Initiator is **15a** instead of 1. [g] Preparation of TASCN and $TASN_3$ are described in ref 8.

Table II
Lewis Acid Catalyzed Group-Transfer Polymerization[a]

entry	monomer	cat.	solvent	theor. $\bar{M}_n \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	D	yield, %
1	**2**	$ZnBr_2$	CH_2Cl_2		1.6	2.6	1.6	13
2	EA[b,c]	ZnI_2	CH_2Cl_2	3.36	3.3	3.4	1.03	100
3	EA[c]	ZnI_2	$(ClCH_2)_2$	1.195	1.25	1.38	1.10	100
4	MMA	$ZnBr_2$	$(ClCH_2)_2$	3.4	6.02	7.24	1.20	100
5	EA	$ZnCl_2$	Toluene	4.1	5.8	11.3	1.96	100
6	EA	$ZnBr_2$	$(ClCH_2)_2$	10.1	17	26.6	1.57	100
7	EA[d]	$(i\text{-}Bu_2Al)_2O$[e]	Toluene	2.1	1.33	1.58	1.19	100
8	MMA	$i\text{-}Bu_2AlCl$	CH_2Cl_2	1.465	3	8.5	2.43	21
9	BA[f]	$i\text{-}Bu_2AlCl$	CH_2Cl_2	2.66	2.37	2.52	1.06	100
10	EA[f]	$(i\text{-}Bu_2Al)_2O$[a]	2:1 $MeCN:CH_2Cl_2$	2.1	1.98	2.38	1.20	97
11	EA[f]	Et_2AlCl	CH_2Cl_2	2.1	2.34	2.74	1.17	100

[a] Initiator is 1. [b] EA indicates ethyl acrylate. [c] Initiator is **15a**. [d] Temperature is 20–58 °C. [e] Mixed oligomers prepared by the addition of 0.5 equiv of water to triisobutylaluminum in toluene solution. [f] Temperature is −78 °C.

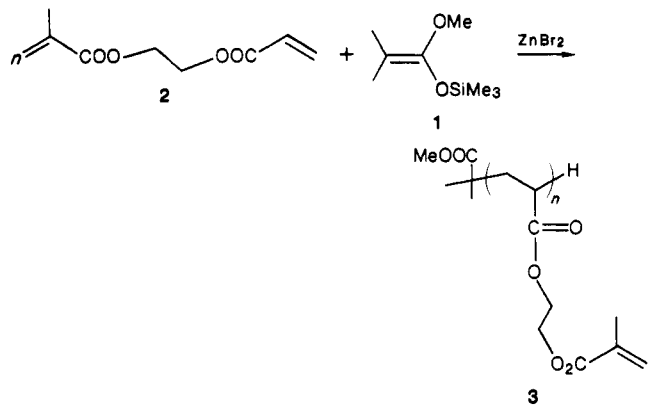
nate, $F_2SiMe_3^-$, has been reported[6] to react with silyl enolates of aldehydes, ketones, and esters with cleavage to fluorosilane and enolate, bifluoride, in contrast, coordinates with the ketene silyl acetals to give a pentacoordinate siliconate that reacts directly with the α,β-unsaturated ester with transfer of the trialkylsilyl group.[7] Examples of bifluoride and fluoride salts that have been used to catalyze the homopolymerization of methyl methacrylate initiated by 1 are listed in Table I. $TASHF_2$ has given good overall results and has been the most generally used bifluoride salt. A satisfactory alternative to $TASHF_2$ as a catalyst for GTP is commercially available tetrabutylammonium fluoride hydrate.

Although the solubility of potassium bifluoride in organic solvents is low, a mixture of the solid catalyst with reaction mixtures containing either acetonitrile or dimethylformamide as solvent gives a quantitative formation of PMMA with low polydispersity as seen in entries 1 and 2 of Table I. More soluble catalysts were generally required when less polar solvents than these were used. Thus, $TASHF_2$ (entries 3 and 4, Table I) and tetrabutylammonium fluoride (entries 6 and 7) provide efficient catalysis of GTP in tetrahydrofuran (THF) solution. $TASHF_2$ was usually introduced as a 1 or 0.1 M solution in acetonitrile because of low solubility in THF. However, a heterogeneous mixture of solid $TASHF_2$ in THF (entry 3) gave satisfactory results. To minimize termination reactions and to obtain polymer of lowest polydispersity, it is best to use the smallest amount of catalyst consistent with the desired rate of reaction, particularly when preparing a polymer of $\bar{M}_n$ above about 20 000. Thus, in the preparation of PMMA of $\bar{M}_n$ = 60 000 (entry 7) using tetrabutylammonium fluoride catalyst, only 0.1% catalyst (based on initiator) was used, resulting in a sluggish polymerization, but the polydispersity was only 1.15. When high levels of the fluoride catalyst are used, higher polydispersities are obtained, and incomplete monomer conversions are encountered when the usual monomer-feed process is used, particularly for the preparation of polymers of high molecular weight. In a batch polymerization of MMA using equimolar amounts of $TASHF_2$ and initiator 1, complete conversion of monomer was obtained, but the resulting polymer had a high polydispersity (entry 5). Further, addition of more monomer after 30 min gave no polymerization, indicating that the polymer formed in the presence of a high level of catalyst was no longer living. In contrast, living GTP PMMA prepared at normal levels of catalyst can be stored under an inert atmosphere in a drybox for 18 h or more while retaining its ability to undergo further molecular weight increase upon addition of monomer. Catalyst level is less important in determining polydispersity when preparing lower molecular weight polymers ($\bar{M}_n$ <20 000) than when preparing higher molecular weight polymers. The nature of the termination processes is currently under investigation.

Other anions that catalyze GTP of MMA are cyanide and azide. Good control of $\bar{M}_n$ and low polydispersity resulted from catalysis of GTP of MMA with cyanide ion (Table I, entries 8 and 9). Because the solubility of tetraethylammonium cyanide in THF is low, dimethylformamide was added to obtain a homogeneous polymerization medium. Catalysis with TAS azide also produced monodisperse PMMA (Table I, entry 10).

Lewis Acid Catalysts. Lewis acids that catalyze GTP, presumably by activating the monomer through coordination, are zinc chloride, zinc bromide, zinc iodide, dialkylaluminum chlorides, and dialkylaluminum oxides.[3] While the zinc halide catalysts are best used at or above room temperature, the aluminum catalysts give living polymers only at low temperatures due to a rapid, temperature-dependent destruction of the living end. Molecular weight control in acrylate polymerization is better

Scheme II



2 1 3

with zinc iodide than with zinc chloride or bromide (compare entries 2 and 3 with 5 and 6 in Table II). In zinc halide catalyzed GTP initiated by 1, acrylates are much more reactive than methacrylates. This is exemplified by the zinc bromide catalyzed polymerization of 2-(acryloxy)ethyl methacrylate (**2**) to a soluble polyacrylate containing pendant methacrylate groups, **3** (Scheme II and entry 1 in Table II). Since conversion in this reaction was only 13% (11% isolated yield), it is not known whether at higher conversion cross-linking would occur. The ^1H NMR spectrum of the resulting polymer shows the absence of unpolymerized acrylate, and only "monomeric" methacrylate is present. In contrast to anion catalysts, which catalyze GTP at levels of less than 1 mol %, based on *initiator*, zinc halide catalysts are best used at about 10 mol % based on *monomer*. Aluminum catalysts can be used at about 10 mol % relative to *initiator*.

The aluminum catalysts can be used at ambient temperature in a batch process to obtain complete polymerization of ethyl acrylate (Table II, entry 7), but under the same conditions, MMA is only polymerized to the extent of 21% (Table II, entry 8), presumably due to the effective competition of destruction of the living end with propagation. At −78 °C, acrylates undergo well-controlled GTP with aluminum catalysts to give acrylates with low polydispersities (Table II, entries 9–11). For polymerization of acrylates to monodisperse polymers, GTP with Lewis acid catalysts is the method of choice.

Initiators. Ketene Silyl Acetals and Other Organosilicon Reagents. A great variety of organosilicon reagents serves as GTP initiators. Many of the ketene silyl acetals investigated as initiators for GTP were prepared by the general procedure of Ainsworth, Chen, and Kuo.[9a] For the selection of an initiator for GTP, it is important that its rate of reaction with monomer (k_i) be at least as great as the rate of reaction of the resulting living polymer with monomer (rate of propagation, k_p) in order to maintain control of molecular weight and to minimize polydispersity (i.e., $k_i \geq k_p$). Preliminary results of GTP kinetics studies in our laboratories indicate that the rate of initiation of MMA polymerization by **1** exceeds the rate of propagation.[10] Several factors affect the relative rates of initiation and propagation and some of these factors are discussed below.

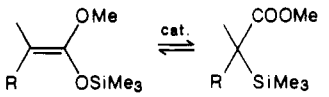
Rate-retarding effects of larger substituents on the silicon atom of the ketene silyl acetal do not become apparent, qualitatively, until the steric requirements of the substituents become quite large. Thus, the apparent rate of GTP of MMA initiated with 1-methoxy-1-(triethylsiloxy)-2-methylprop-1-ene[11] (Table III, entry 2) is comparable to the rate observed when using **1** as the initiator. However, the highly hindered ketene silyl acetal, 1-methoxy-1-(dimethyl-*tert*-butylsiloxy)-2-methylprop-1-ene (Table III, entry 3), initiates a very slow polymerization of MMA, giving PMMA with higher than normal polydispersity and $\bar{M}_n$ much higher than theory. Although several causes of the loss of control of molecular weight with this initiator may be imagined, one possibility is that the rate of catalyst exchange between living polymer molecules may be slower than the rate of propagation. Because less than stoichiometric amounts of catalyst are used, molecular weight control is only possible when the rate of catalyst transfer between living ends is greater than the propagation rate. Further work is in progress to determine the reasons for poor molecular weight control. The ponderous, but less sterically demanding, dimethyloctadecylsilyl analogue (Table III, entry 4) gives PMMA with good molecular weight control but high polydispersity. Good control of molecular weight and low polydispersity are achieved with the bis ketene silyl acetal, bis(1-methoxy-2-methylprop-1-enoxy)methylsilane (Table III, entry 5), indicating that the SiH functionality is tolerated by GTP.

Table III
PMMA Prepared by Group-Transfer Polymerization[a] With $TASHF_2$ Catalyst

entry	init	theor $\bar{M}_n \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	D
1	**1**	60	53.7	85.38	1.59
2[b]	$Me_2C{=}C(OMe)$-$OSiEt_3$	10.1	10.2	14.7	1.45
3	$Me_2C{=}C(OMe)$-$OSiMe_2t$-C_4H_9	1.99	17.9	37.9	2.12
4	$Me_2C{=}C(OMe)$-$OSiMe_2C_{18}H_{37}$	7.6	8.28	17.1	2.07
5	$[Me_2C{=}C(OMe)$-$O]_2SiHMe$[c]	1.6	1.41	1.55	1.10
6	$MeCH{=}C(OMe)$-$OSiMe_3$[d]	10.1	14.2	21.1	1.48
7	$Me_2C{=}C$-$(OSiMe_3)O$-$(CH_2)_2OSiMe_3$	123	262	371	1.42
8	$Me_3SiCH_2CO_2Et$	5.1	28.6	103	3.61
9	$Me_3SiCH_2CO_2t$-Bu	2.1	13.0	54.0	4.0
10	$Me_2C(CN)SiMe_3$[e]	10.1	47.5	188	3.96

[a] Solvent was tetrahydrofuran; yields are all greater than 99%. [b] Prepared according to ref 11. [c] Molecular weight values for polymer after removal of silicon by methanolysis. [d] Batch polymerization, initiator added last. Initiator 85% *E*, 15% *Z*. [e] Prepared by an improved procedure over ref 9b–d (see Experimental Section).

Scheme III



a, R = H
b, R = Me

Initiation of GTP of MMA with the ketene silyl acetal 1-methoxy-1-(trimethylsiloxy)prop-1-ene (Table III, entry 6) generally leads to PMMA with $\bar{M}_n$ greater than theory and higher polydispersity than is obtained with **1** as the initiator. This may be due to the fact that the GTP catalyst $TASHF_2$ also catalyzes isomerization of the ketene silyl acetal to methyl α-(trimethylsilyl)propionate (see Scheme III). As indicated later in this section, C-silyl compounds are not efficient GTP initiators and tend to give polymers whose molecular weights are not as well controlled as in the case of ketene silyl acetals.

We used ^1H NMR to observe the isomerization of 1-methoxy-1-(trimethylsiloxy)prop-1-ene (initially 85% *E*, 15% *Z*, **a** in Scheme III) to the C-silyl isomer, methyl

α-(trimethylsilyl)propionate, catalyzed by 0.2% $TASHF_2$. The initial observation, after about 10 min, showed that 17% O-to-C isomerization had occurred, but that the initial *E*:*Z* ratio of the starting material remained essentially unchanged. Further O-to-C isomerization occurred, but the process became progressively slower, showing 54% isomerization after 3 days. The reported[12] equilibrium composition of 100% methyl α-(trimethylsilyl)propionate (achieved by mercuric iodide catalyzed equilibration) was never achieved, probably as a result of slow deactivation of the catalyst by some side process that is not identified. Interestingly, changes in the *E*:*Z* ratio appeared to be slower than the O-to-C isomerization process. Since C-silyl isomers of ketene silyl acetals are generally less reactive than ketene silyl acetals and initiate GTP more slowly, this would account for the observed molecular weight results (Table III, entry 6) if the rate of isomerization were great enough for appreciable isomerization to occur during the time that catalyst is in contact with ketene silyl acetal in a GTP reaction. Since we do not have rate measurements for the isomerization process, this analysis is speculative.

A similar study of the $TASHF_2$-catalyzed isomerization of 1 (b in Scheme III) to methyl α-(trimethylsilyl)isobutyrate showed clearly that the rate of isomerization in this case was much slower in the initial stages than the isomerization of 1-methoxy-1-(trimethylsiloxy)prop-1-ene. After 133 min only 5% O-to-C isomerization had occurred even though the catalyst level was 5 times greater (1%). Similarly, the C-to-O isomerization of methyl α-(trimethylsilyl)isobutyrate to 1 proceeded only to the extent of 3% after 116 min. In this study we also found that the catalyst became deactivated with time, and the isomerizations in both directions did not reach equilibrium (vide infra). Because of the apparent slowness of the O-to-C isomerization of 1 relative to the GTP process under catalysis by $TASHF_2$, it is safe to assume that such isomerization processes are not able to occur within the time frame of a polymerization reaction and, thus, do not cause an increase in polydispersity or loss of control of molecular weight. In order to determine the equilibrium composition of 1 and methyl α-(trimethylsilyl)isobutyrate, the O-to-C and C-to-O isomerizations were studied with tetrabutylammonium *m*-chlorobenzoate[13] as the catalyst, which for such isomerizations retains activity over the course of the reaction. At a catalyst level of 1%, equilibration of 1 was complete in about 800 min, giving an equilibrium composition of 76% 1 and 24% methyl α-(trimethylsilyl)isobutyrate. Under similar conditions, the C-to-O isomerization reached the same equilibrium composition in about 2000 min. This corresponds to an equilibrium constant of 0.32 for the C ⇌ O process, which translates to ΔG = 700 cal·mol^{-1}.

$$\underset{\mathbf{C1}}{Me_2C(COOMe)(SiMe_3)} \underset{k_{-1}[B^-]}{\overset{k_1[B^-]}{\rightleftharpoons}} \underset{\mathbf{1}}{Me_2C{=}C(OMe)(OSiMe_3)} \quad (1)$$

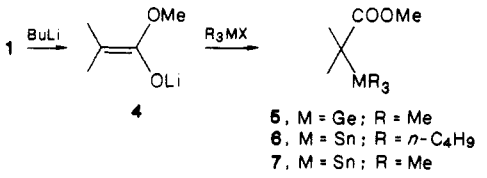
In order to obtain information about the rate of the C ⇌ O isomerization, tetrabutylammonium *m*-chlorobenzoate, a slower catalyst than bifluoride, was used. The rate at which the isomerization of methyl α-(trimethylsilyl)isobutyrate (**C1**) to 1 approached equilibrium was measured by following both the appearance of 1 and disappearance of **C1** using ^1H NMR. Assuming that the concentration of 1 at time infinity, $[1]_\infty$, represents its equilibrium concentration, $[1]_e$, which is constant, the rate expression of eq 2 (derived for the process of eq 1) can be

$$\ln [[1]_e/([1]_e - [1]_t)] = (k_f + k_r)t \quad (2)$$

Table IV
Properties of α-Trialkylmetallo (Germyl and Stannyl) Esters

compd	bp, °C (press, Torr)	^1H NMR ($CDCl_3$), ppm
5	46–49 (4.5–6)	3.46 (OCH_3) 1.09 (CCH_3) 0.0 ($GeMe_3$)
6	85–95 (0.3)	3.34 (OCH_3) 1.20 (CCH_3) 0.95–1.5 (CH_2) 0.54–0.9 (CH_2CH_3)
7	61 (0.8)	3.43 (OCH_3) 1.25 (CCH_3) −0.03 ($SnCH_3$)

Scheme IV



used to calculate $(k_f + k_r)$, where $k_f = k_1[B^-]$, $k_r = k_{-1}[B^-]$, $[1]_t$ is the concentration of 1 at time **t**, and $[B^-]$ is the concentration of the anion catalyst, e.g., *m*-chlorobenzoate.

With methyl α-(trimethylsilyl)isobutyrate and tetrabutylammonium *m*-chlorobenzoate initial concentrations of 0.49 and 0.0049 M, respectively, $(k_f + k_r)$ is found to be 1.9×10^{-5} s^{-1}. Since the equilibrium constant $K = k_f/k_r = 0.32$, the values of k_f and k_r are calculated to be 4.7×10^{-6} and 1.5×10^{-5} s^{-1}, respectively. Similarly, the second-order catalytic constants, k_1 and k_{-1}, for C ⇌ O isomerization are calculated to be 9.6×10^{-4} and 3.0×10^{-3} M^{-1} s^{-1}, respectively. These values are less by 2–3 orders of magnitude than the independently determined GTP initiation and propagation rate constants for catalysts of similar reactivities in GTP.[10] Hence, O-to-C isomerizations of 1 and, possibly, methacrylate living polymers are not competitive with initiation and propagation of GTP.

Initiation of GTP of MMA with the C-silyl compounds, ethyl (trimethylsilyl)acetate, *tert*-butyl (trimethylsilyl)acetate, and 2-(trimethylsilyl)isobutyronitrile, gives poor control of molecular weight and polydispersities greater than 3 (Table III, entries 8–10). These compounds are believed to have initiation rates much slower than the propagation rate of MMA in GTP.

Organostannane and Organogermane Initiators. Organotin and organogermanium analogues of silicon-containing GTP initiators were studied in order to evaluate the effect of these metals on initiation and propagation of group-transfer polymerization. The tin and germanium analogues of 1 (**5** and **6**) were prepared by the reaction of 1 with butyllithium to give the lithium enolate **4**, which was then metallated with trialkylmetal chloride to give the α-trialkylmetallo ester (see Scheme IV). Methyl α-trimethylstannyl isobutyrate (**7**) was prepared by reaction of lithium diisopropylamide (LDA) with methyl isobutyrate followed by metallation with chlorotrimethylstannane. There is no evidence for the presence of any of the O-metal analogues (ketene stannyl or germyl acetals) in these products. This contrasts with the silicon analogue, 1, as prepared by the LDA–methyl isobutyrate–chlorotrimethylsilane method, in which none of the α-silyl ester is detected. The tin and germanium initiators were purified by distillation, and their properties are summarized in Table IV.

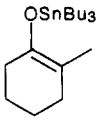
Compounds **5**–**7** of Table IV and the known[14] tributyltin enol ether **8** initiate GTP of MMA in the presence of

Table V
GTP of Acrylic Monomers with Methyl 2-(Trimethylstannyl)isobutyrate (7)[a]

cat. $\bar{M}_n \times 10^{-3}$	mol 7/mol cat.	monomer	theor $\bar{M}_n \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	D
$TASHF_2$	40	MMA[b]	5.26	8.51	12.8	1.51
Et_4NCN	40	MMA	5.26	6.88	12.4	1.78
$TASHF_2$	20	EA[c]	4.2	3.88	6.35	1.64
$TASHF_2$	1.0	EA[c]	4.40	6.23	8.36	1.34

[a] Solvent was THF. [b] Addition of more MMA after 1 h produced an increase in molecular weight to $\bar{M}_n$ = 11 400, D = 1.45 (theoretical $\bar{M}_n$ = 7760). [c] EA indicates ethyl acrylate.

$TASHF_2$ catalyst. With **5**, **6**, and **8**, control of molecular weight was poor and polydispersities were quite high. A



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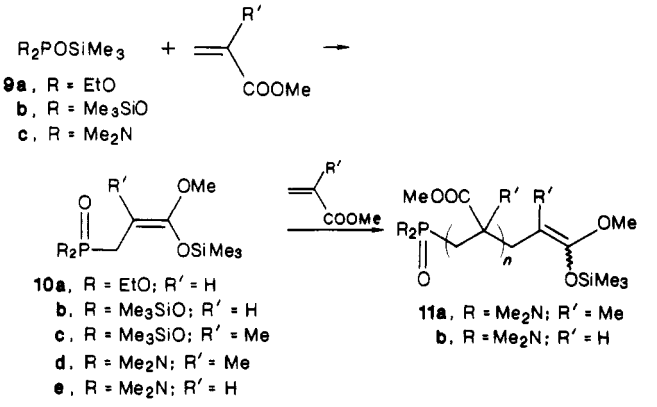
possible explanation of the poor control of molecular weight is that, during polymerization, the change of steric environment at the living end is such that the O-metal isomer is stabilized relative to the C-metal isomer with a consequent acceleration of the rate of propagation relative to the rate of initiation by the C-metal initiator. This would lead to loss of control of molecular weight. The results of initiation of GTP of MMA and ethyl acrylate with **7** are summarized in Table V. If we compare the PMMA obtained with **7** and $TASHF_2$ with PMMA obtained with the silicon analogue **1** and $TASHF_2$ (see Table I, entries 3 and 4), it is apparent that the PMMA prepared by initiation with **1** has a lower polydispersity and the $\bar{M}_n$ is closer to theory than is the case with PMMA prepared by initiation with **7**. The same trend is seen when the catalyst is cyanide ion (compare Table V with entry 9 of Table I), in which case initiation by **1** provides PMMA with a lower polydispersity and $\bar{M}_n$ closer to theory than initiation by **7**. The stereochemical outcome of MMA polymerization using tin and germanium initiators **5**–**8** is qualitatively similar to that observed with **1** under similar conditions (vide infra). Initiation of GTP of ethyl acrylate with **7** and $TASHF_2$ produced poly(ethyl acrylate) with a polydispersity of 1.64 (at 5% catalyst) and 1.34 (at 100% catalyst), but the conversion in the former case was only 41% and in the latter case only 43% (see Table V).

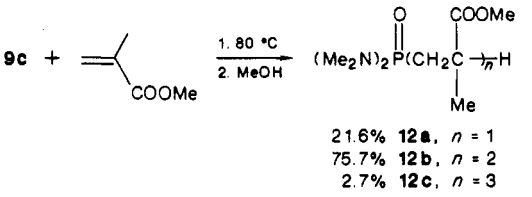
Our studies do not permit us to conclude whether the reacting form of the tin and germanium initiators and living polymers is the O- or the C-metal intermediate. However, treatment of **7** with a catalytic amount of $TASHF_2$ in a polar solvent (propylene carbonate) did not lead to any observable (by ^1H NMR) isomerization to the O–Sn derivative.

Functionalized Initiators. When functionalized ketene silyl acetals are used to initiate GTP, polymers with terminal functionality are obtained. A variety of phosphorus-terminated polymers were synthesized by the use of phosphorus-containing ketene silyl acetals prepared by the thermal addition of silyl phosphites to α,β-unsaturated esters in the absence of solvent. The diethyl phosphonate **10a** was prepared by the method of Okamoto and Sakurai.[15a] Although **10a** can be distilled,[15a] we found the purity of the distilled product to be lower (by NMR spectroscopy) than that of the crude product. Therefore, crude **10a** was used in initiation studies. The bis(trimethylsilyl) phosphonates **10b** and **10c** were prepared by the thermal reaction of tris(trimethylsilyl) phosphite (**9b**) with MMA at 110–120 °C and with methyl acrylate at 95 °C (Scheme V). Nakano, Okamoto, and Sakurai[15b] have reported the analogous thermal addition of **9b** to acrylonitrile. Although

Scheme V



Scheme VI



10c could be purified by distillation, **10b** could not, and **10b**, therefore, was used without purification in the initiation studies. ^1H NOE analysis of **10c** indicates probable Z stereochemistry. The tetramethyl phosphonamide initiators **10d** and **10e** were not obtained by addition of **9c**[16] to MMA at 80 °C and to methyl acrylate at 25 °C (see Scheme V). Instead, it was found that oligomers **11a** and **11b** were formed from the thermal reaction of **9c** with MMA and methyl acrylate.

Apparently the rate of reaction of **10d** and **10e** with α,β-unsaturated esters is not greatly different from the rate of reaction of **9c** with α,β-unsaturated esters. The composition of oligomeric **11a** was estimated by GC/MS analysis of the products obtained by methanolysis of the reaction mixture resulting from reaction **9c** with MMA at 80 °C for 1 h (see Scheme VI). Products **12b** and **12c** correspond to reaction of **9c** with 2 and 3 equiv of MMA, respectively. Interestingly, the principal product of this reaction is not **10d** but the product of the reaction of **10d** with another equivalent of MMA. In the initiation studies (vide infra), the oligomeric mixtures of phosphonamides **11a** and **11b** were used.

Although reversibility of the thermal addition reaction of silyl phosphites to α,β-unsaturated esters was not encountered in the preparation of **10a**–**c**, attemped vacuum distillation of the phosphonamide **11a** led to reversion to MMA and **9c**.

The phosphorus-containing ketene silyl acetals **10a**, **10b**, and **11a** initiated GTP of MMA in the presence of $TASHF_2$ to give PMMA with low polydispersity (Table VI, entries 1, 3, 6, and 7), but **10b** gave a higher polydispersity (Table VI, entry 2). In addition, block and random copolymers of MMA and butyl methacrylate with low po-

Table VI
GTP of MMA with Phosphorus-Containing Initiators in THF

entry	init	cat.[a]	monomer	theor $\bar{M}_n \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	D
1	**10a**	3% $TASHF_2$ 1% Et_4NCN	MMA	3.5	4.96	1.00
2	**10b**	4.7% $TASHF_2$	MMA	3.5	1.73[b]	2.42
3	**10c**	3.8% $TASHF_2$	MMA	6.65	5.9[b]	1.02
4	**10c**	6% $TASHF_2$	MMA/BMA[c]	7.57	7.05[b]	1.03
5	**10c**	11% $TASHF_2$	MMA/BMA[d]	11.36	11.2[b]	1.05
6	**11a**	3.3% $TASHF_2$	MMA	3.25	9.13	1.11
7	**11a**	0.33% $TASHF_2$	MMA	3.25	6.93	1.05
8	**11b**	0.33% $TASHF_2$	MMA	3.55	25.2	1.64
9	**9a**	10% $TASHF_2$	MMA	1.1	12.8	1.96
10	**9b**	6% $TASHF_2$	MMA	2.3	15.3	1.92
11	**9c**	0.8% $TASHF_2$	MA/MMA[e]	4.1	74.9	2.16

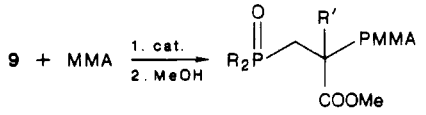
[a] Mole percent of initiator. [b] GPC MW determined after hydrolysis to phosphonic acid. [c] Block copolymer: 76 mol % MMA and 24 mol % *n*-butyl methacrylate. [d] Random copolymer: 42 mol % *n*-butyl methacrylate and 58 mol % MMA prepared by feeding MMA during 4 h to BMA/initiator/catalyst solution, T_g = 62 °C. [e] Block copolymer: 20 mol % methyl acrylate and 80 mol % MMA.

Table VII
Polymers Prepared with Trimethylsilyl Sulfide and Trimethylsilyl Cyanide Initiators in Acetonitrile Solution[a]

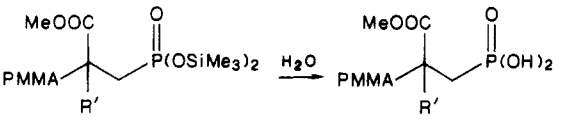
entry	init	monomer	cat.	theor $\bar{M}_n \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	D
1	Me_3SiSMe	MMA	Et_4NCN	3.07	11.8	19.4	1.64
2	$Me_3SiSC_6H_5$	EA[b]	Et_4NCN	2.1	2.27	4.16	1.83
3	Me_3SiCN	MMA	Et_4NCN	6.67	6.91	10.3	1.49
4	Me_3SiCN	MMA	TASCN	1.0	0.8	0.8	1.03

[a] Yields are quantitative in all runs. [b] EA indicates ethyl acrylate.

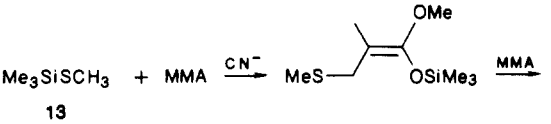
Scheme VII



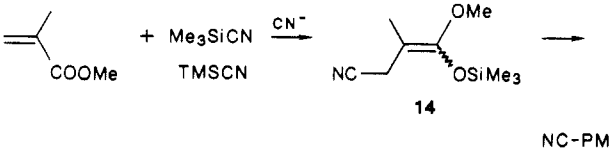
Scheme VIII



Scheme IX



Scheme X



lydispersity were obtained with **10c** as initiator (Table VI, entries 4 and 5). Good control of molecular weight (measured $\bar{M}_n$ close to theory) is obtained with **10c**, which was purifiable by distillation (Table VI, entries 3–5). The apparent lack of molecular weight control with the other initiators may simply reflect the fact that they could not be purified by distillation and that the theoretical $\bar{M}_n$s were calculated assuming 100% purity of the initiators.

Unusually high levels of catalyst (4–11% on initiator) were required for polymerizations with **10a–c**, presumably due to coordination of the catalyst with the phosphonate group. That the catalyst is tied up by coordination with phosphorus rather than the trimethylsilyl groups of the phosphonate ester of **10b** and **10c** is apparent from the high catalyst requirement for initiation of GTP by **10a** which does not contain any silyl group on phosphorus. This was further confirmed by adding dimethyl methylphosphonate to an ongoing $TASHF_2$-catalyzed polymerization of MMA initiated by **1**, which caused polymerization to cease until additional $TASHF_2$ was added. There was no such requirement for high levels of catalyst with **11a** and **11b**, since phosphonamides are less prone than phosphonates to coordinate with nucleophiles.[17]

Since the reaction of Scheme V is catalyzed by bifluoride ion (see ref 5d), compounds **9a** and **9b** may be used directly to initiate GTP of MMA in the presence of $TASHF_2$ (Scheme VII), but, since the rate of initiation is slower than the rate of propagation, molecular weight control is lost (see Table VI, entries 9 and 10). Similarly, **9c** was used with $TASHF_2$ to prepare a block copolymer of methyl acrylate and MMA (Table VI, entry 11).

Polymers containing a terminal silyl phosphonate group are easily converted into the corresponding polymer with a terminal phosphonic acid group. The silyl phosphonate ended polymers (from **10b**, **10c**, or **9b**) are readily hydrolyzed with dilute hydrochloric acid or methanolic tetrabutylammonium fluoride (Scheme VIII).

Trimethylsilyl methyl sulfide (**13**) in the presence of an anion catalyst (cyanide ion) initiates GTP of MMA via a catalyzed Michael addition to MMA to generate a ketene silyl acetal in a manner similar to **9a–c** (Scheme IX). This reaction showed a short induction period and poor control of molecular weight (Table VII, entry 1). Presumably the Michael addition of **13** to MMA is somewhat slower than the rate of propagation. Elemental analysis of the polymer verified the end group as methylthio. Trimethylsilyl phenyl sulfide with cyanide catalyst initiated the polymerization of ethyl acrylate, which was slower, qualitatively, than the initiation by **1** (Table VII, entry 2).

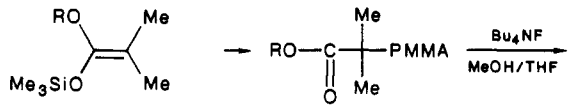
Initiation of GTP of MMA by trimethylsilyl cyanide (TMSCN)[2,18-20] is similar to initiation by **9a** and **9b** (see Scheme X) in that a catalyzed Michael addition of the TMSCN to monomer forms a ketene silyl acetal. Initiation by TMSCN gives rise to an induction period during which slow formation of **14** and slow oligomerization occur.[19b] This is followed by rapid exothermic polymerization. The

Table VIII
Non-Methacrylate Monomers Polymerized by GTP[a]

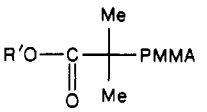
entry	monomer	init.	solvent	theor $\bar{M}_n \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	D	yield
1	acrylonitrile[b]	1	DMF	151	128[c]	3.79	91
2	methacrylonitrile	$Me_2C(CN)SiMe_3$	DMAC[d]	3.57	5.8	2.04	87
3	*N,N*-dimethylacrylamide	1	THF	5.0	2.05[e]	1.62	98
4	α-methylene-γ-butyrolactone	1	propylene carbonate				67
5	butyl acrylate	$Me_2C{=}C(OMe)OSiEt_3$[f]	THF	4.20	4.83	2.14	100
6	butyl acrylate[g]	1	THF	26.1	27.2	2.16	100

[a] Unless otherwise indicated, GPC $\bar{M}_n$ values are measured with a PMMA standard. [b] Batch polymerization beginning at −50 °C, 1 added last. [c] GPC in DMAC at 135 °C, polystyrene standard. $\bar{M}_v$ = 422 000, $[\eta]^{25°}_{DMF}$ 3.30. [d] DMAC indicates *N,N*-dimethylacetamide. [e] MW = 3800 by vapor phase osmometry in toluene (50 °C). [f] See ref 11. [g] Polymerization carried out at 0 °C.

Scheme XI



15a, R = $CH_2CH_2OSiMe_3$
b, R = $SiMe_3$



16a, R' = CH_2CH_2OH
b, R' = H

reasons for the induction period will be described in detail elsewhere.

Polymers with terminal hydroxyl or carboxyl groups are readily prepared by using the functionalized initiators **15a** or **15b**, respectively (Scheme XI), and then hydrolyzing the resulting polymer with refluxing methanolic tetrabutylammonium fluoride or with dilute methanolic HCl at ambient temperature to give PMMA–OH (**16a**) or PMMA–COOH (**16b**), respectively. The high degree of monofunctionality of the PMMA–OH thus prepared was determined by using the HPLC end-group analysis technique described by Andrews and Vatvars.[21] Methods for converting the living polymers prepared from functionalized initiators to telechelic polymers by coupling reactions have been described earlier.[22]

Monomers. A variety of methacrylates besides MMA have been polymerized by GTP, including lauryl methacrylate, *n*-butyl methacrylate, glycidyl methacrylate, 2-ethylhexyl methacrylate, 2-(trimethylsiloxy)ethyl methacrylate, sorbyl methacrylate, allyl methacrylate, and 2-(allyloxy)ethyl methacrylate. In most cases, copolymers (vide infra) rather than homopolymers were prepared. Because GTP is a much milder process than anionic polymerization, it is tolerant of the reactive functional groups in this group.

In addition to methacrylates, GTP was used for polymerization of acrylates, *N,N*-dimethylacrylamide, acrylonitrile, and methacrylonitrile (see Table VIII). Because of the solubility characteristics of poly(acrylonitrile), DMF is the solvent of choice for polymerization of acrylonitrile (AN). Since the polymerization rate of AN is very high compared with that of MMA, the normal technique of feeding the monomer resulted in uncontrolled localized polymerization of the monomer before complete mixing could be achieved. In a batch polymerization in which the $TASHF_2$ was added to a solution of AN and **1** in DMF, uncontrolled polymerization occurred in the vicinity of the catalyst before mixing could be achieved. Best results (see Table VIII, entry 1) were achieved with a batch polymerization in which the initiator, **1**, was added to a DMF solution of AN and $TASHF_2$ cooled to −50 °C. Although this procedure avoided gel formation, the molecular weight distribution is broad (D = 3.79) because the rate of initiation by **1** is slower than the rate of propagation.

Table IX
Configurational Sequences in Poly(α-methylene-γ-butyrolactone) Prepared by GTP from ^{13}C NMR[a]

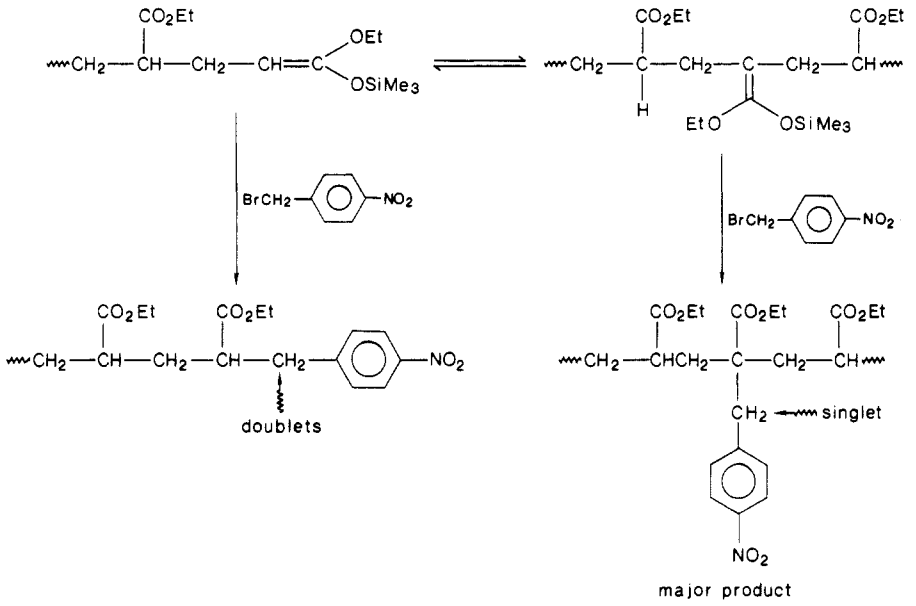
triads, %			diads, %				
mm	mr	rr	m	r	$P(m/r)$[b]	$P(r/m)$[c]	sum
37	36	27	55	45	0.327	0.400	0.727

[a] Based on triad assignments of quaternary carbon by Akkapeddi.[24a] [b] $P(m/r)$ is the calculated probability of an r diad following an m diad. [c] $P(r/m)$ is the calculated probability of an m diad following an r diad.

GTP of methacrylonitrile in *N,N*-dimethylacetamide solution using 2-(trimethylsilyl)isobutyronitrile[9b-d] as the initiator (Table VIII, entry 2) gave an 87% conversion to poly(methacrylonitrile) with $\bar{M}_n$ = 5800 and D = 2.04 (theoretical $\bar{M}_n$ = 3570). ^{13}C NMR studies of the resulting polymer showed nearly random tacticity.[23]

GTP of α-methylene-γ-butyrolactone by a batch process in propylene carbonate at 20–50 °C gave a 67% yield of poly(α-methylene-γ-butyrolactone), which was isolated by precipitation with THF. The polymer has an inherent viscosity of 0.072 g/dL, indicative of a substantially lower molecular weight than the polymers obtained by Akkapeddi[24a] from α-methylene-γ-butyrolactone by anionic and by free radical polymerization. Akkapeddi used the quaternary Cα carbon resonances in the ^{13}C NMR spectrum of the polymers in Me_2SO solution to assign triad populations. Since the high-field peak of the three Cα components predominated in the polymer prepared with phenylmagnesium bromide in toluene at −78 °C, this was assigned to the isotactic (mm) triad by analogy to the preferred formation of isotactic PMMA under these conditions. The central peak was assigned mr (heterotactic) and the low-field peak rr (syndiotactic). Poly(α-methylene-γ-butyrolactone) obtained by GTP at 20–50 °C has a triad composition of 27% rr, 36% mr, and 37% mm based on the ^{13}C NMR resonances for Cα at 44.21 and 43.99 ppm, respectively, by analogy with Akkapeddi's assignments[24a] (see Figure 1). This composition (see Table IX) differs from that of Akkapeddi's free radical polymer prepared at 60 °C (42% rr, 44% mr, 14% mm) mainly in the much greater mm content of the GTP polymer. The triads in the free radical polymer confirm Bernoullian statistics,[24a] i.e., $P(r/m) + P(m/r) = 1$; but the triads in the GTP polymer do not confirm Bernoullian statistics. In contrast, GTP PMMA (vide infra) prepared in the same temperature range features very low mm content, and Bernoullian statistics apply. Stille and co-workers[24b] have reported the GTP of racemic α-methylene-γ-methyl-γ-butyrolactone at −78 °C in THF, which gave a polymer

Scheme XII



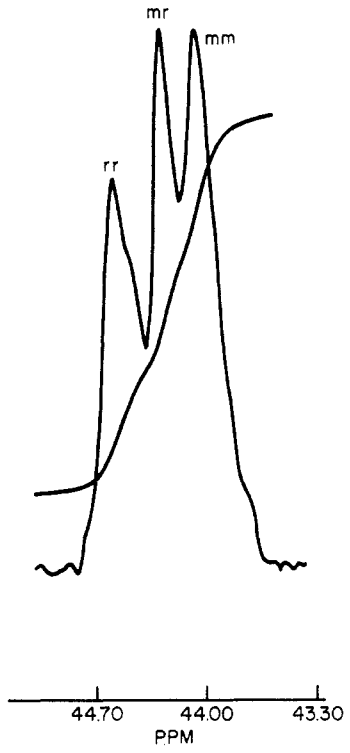


Figure 1. ^{13}C NMR of poly(α-methylene-γ-butyrolactone) in Me_2SO-d_6 (100.6 MHz), Cα region.

with low mm triad content. If normal temperature dependence applies, then the mm content would be expected to increase at higher temperatures.

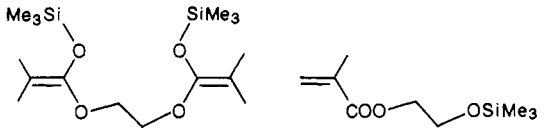
GTP of simple acrylates using a bifluoride catalyst generally leads to polymers with a broader molecular weight distribution than is observed in GTP of the corresponding methacrylate or GTP of acrylates using Lewis acid catalysts. Thus, polymerization of butyl acrylate in THF at 0 °C gave poly(butyl acrylate) with $\bar{M}_n$ = 27 200, $\bar{M}_w$ = 59 400, and D = 2.16 (theoretical $\bar{M}_n$ = 26 100). To obtain insight into the causes of the molecular weight broadening, living ethyl acrylate oligomer (degree of polymerization DP = 4) prepared by TASF-catalyzed GTP was treated with *p*-nitrobenzyl bromide at −78 °C. Chromatographic purification gave 60% yield of the benzylated product containing both *internal* and *terminal* *p*-nitrobenzyl groups in the ratio of 9:1 (Scheme XII). These results suggest that the trimethylsilyl group is capable of isomerizing to an internal position of the poly(acrylate) chain. However, ^{13}C NMR studies of GTP poly(ethyl acrylate) gave no evidence of branching, suggesting that the internal ketene silyl acetal, while capable of reacting with a benzyl halide, is too sterically hindered to initiate a branch point. We have no evidence to indicate whether or not O- or C-silyl intermediates are formed. The isomerization is presumably slower than chain propagation so that poly(acrylates) remain living, but the decrease in the concentration of "useful" living ends caused by the isomerization may be accountable for the observed broadening of molecular weight distribution. We have no evidence to indicate whether the migration of the trialkylsilyl group from the end of the chain to an internal position is intra- or intermolecular. But the process is clearly related to other chain-transfer processes in GTP which have been studied.[25] The problems encountered in the anion-catalyzed GTP of acrylates may be avoided by using Lewis acid catalysts (vide supra).

Copolymers. A useful attribute of "living" polymer systems is the ability to prepare block copolymers of predetermined block length and sequence. GTP provides a particularly facile methodology for the sequencing of both homopolymer blocks and random copolymer blocks. An AB block copolymer of lauryl methacrylate and MMA was prepared in two ways. First, MMA was polymerized with initiation by **1** and catalysis by $TASHF_2$ and then lauryl methacrylate was fed to give a quantitative conversion to polymer with $\bar{M}_n$ = 6650, $\bar{M}_w$ = 7070, and D = 1.06 (theoretical $\bar{M}_n$ = 7043). The same AB block copolymer was obtained by first polymerizing lauryl methacrylate and then changing the monomer feed to MMA to give a quantitative yield of polymer with $\bar{M}_n$ = 6540, $\bar{M}_w$ = 7470, and D = 1.14 (theoretical $\bar{M}_n$ = 7470). In each case the design composition of 10 mol % lauryl methacrylate was confirmed by NMR analysis of the copolymers.

An ABC block terpolymer of MMA, butyl methacrylate, and allyl methacrylate was prepared by sequential feeding of the three monomers in the order MMA, butyl methacrylate, allyl methacrylate. The resulting polymer, isolated in 95% yield, had $\bar{M}_n$ = 3800, $\bar{M}_w$ = 4060, and D = 1.07 (theoretical $\bar{M}_n$ = 4100). The expected composition

of 50 mol % MMA, 30 mol % butyl methacrylate, 20 mol % allyl methacrylate was confirmed by ^{1}H NMR analysis. The polymerization of allyl methacrylate to a soluble copolymer by GTP demonstrates an advantage of this relatively mild polymerization process. Radical polymerization of allyl methacrylate generally leads to gel formation.

An ABA block copolymer with A blocks consisting of a random copolymer of MMA and 2-hydroxyethyl methacrylate and a B block of lauryl methacrylate was prepared by GTP. With the difunctional initiator **17**, the B block



17 **18**

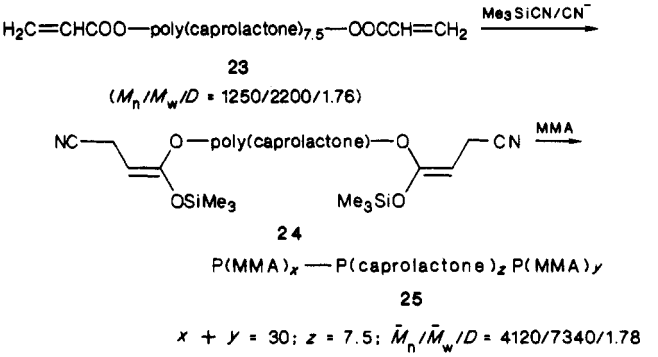
(lauryl methacrylate) was constructed first as a homopolymer with two living ends followed by addition of the random copolymer A blocks. Because direct polymerization of 2-hydroxyethyl methacrylate is not possible by GTP since the hydroxyl group would terminate the polymerization, the trimethylsilyl-protected monomer, **18**, was used in forming the A blocks. The resulting polymer had $\bar{M}_n$ = 9340, $\bar{M}_w$ = 11 200, and D = 1.20 (theoretical $\bar{M}_n$ = 13 600). Following deprotection of the hydroxyl groups with methanolic tetrabutylammonium fluoride, the polymer was found to have the expected composition: 31 mol % lauryl methacrylate, 39 mol % MMA, and 30 mol % 2-hydroxyethyl methacrylate. Differential scanning calorimetry showed two T_gs at −43 and +95 °C.

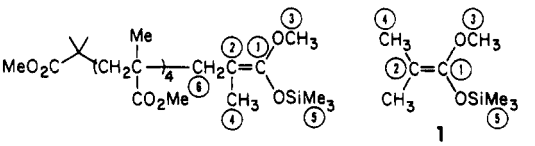
Random copolymers can be prepared by GTP by simultaneously feeding two different monomers or by feeding a mixture of monomers into the mixture of initiator and catalyst. Simultaneously feeding MMA and butyl methacrylate into a THF solution of initiator **15a** and solid TAS bifluoride gave a quantitative yield of copolymer of butyl methacrylate (65%) and MMA (35%) with $\bar{M}_n$ = 22 100, $\bar{M}_w$ = 24 500, and D = 1.11 (theoretical $\bar{M}_n$ = 20 215) which we presumed to be random. Under these conditions the reactivities of the two monomers are apparently sufficiently similar that random copolymerization is presumably achieved.

A random terpolymer of MMA (50 wt %), butyl methacrylate (20 wt %), and glycidyl methacrylate (30 wt %) was prepared by GTP. The only special precautions were that the polymerization temperature was kept near 0 °C and 1 equiv of MMA was added prior to beginning the feed of the mixed monomers. These precautions were intended to minimize the possibility of termination by reaction of the ketene silyl acetal with the epoxy group. It was assumed that the oligomers formed by the addition of 1 equiv of MMA, for steric reasons, would be less reactive than 1 toward the epoxy group. The resulting terpolymer, isolated in quantitative yield, had $\bar{M}_n$ = 3910, $\bar{M}_w$ = 4290, D = 1.10, and T_g = −13 and +47 °C. Thus, even as reactive a monomer as glycidyl methacrylate can be polymerized to a narrow molecular weight polymer by GTP.

Copolymerization of acrylates with methacrylates by GTP present special problems due, at least in part, to the disparate reactivities of the two types of monomer. When MMA is added to living GTP poly(ethyl acrylate), polymerization of the MMA generally does not proceed smoothly, although block copolymers of MMA and acrylates have been prepared. Competitive polymerizations of MMA and ethyl acrylate result in much greater incorporation of the acrylate than the methacrylate. Thus, random copolymers of acrylates and methacrylates are not readily achieved by GTP.

Scheme XIII





Carbon	^{13}C Peak (ppm)	^{13}C Peak (ppm)
1	151.99	149.50
2	89.78	90.40
3	55.42	56.17
4	29.56	16.61, 15.84
5	-0.11	-0.20
6	54.28	

Figure 2. ^{13}C NMR assignments for living GTP oligomer and model compound.

A block copolymer containing a nonacrylic block was prepared by first converting poly(caprolactone) to a GTP initiator, followed by initiation of MMA polymerization. The polymeric difunctional initiator **21** was prepared by the rapid reaction of trimethylsilyl cyanide with the diacrylate of poly(caprolactonediol) **20** ($\bar{M}_n$ = 1250, $\bar{M}_w$ = 2200, and D = 1.76) in the presence of tetraethylammonium cyanide catalyst. The resulting polymeric difunctional GTP initiator initiated polymerization of MMA to give a block copolymer, **22**, with $\bar{M}_n$ = 4120, $\bar{M}_w$ = 7340, and D = 1.78 (Scheme XIII).

Structure of the GTP "Living" End. A requisite for preparation of block copolymers by sequential monomer feed is that the polymer remain living long enough for initiation of the second or subsequent blocks to occur. To confirm the structure of the "living", or ketene silyl acetal, end group of PMMA, the ^{13}C NMR spectrum of the living oligomer was measured and the structural assignment was made by comparing the spectrum with that of a model compound (see Figure 2). The analysis confirms that in this oligomer the ketene silyl acetal function is still present, the silicon is on O, not C, and the group is at the end of the chain. ^{13}C NMR analysis of living PMMA prepared with tetraethylammonium cyanide catalyst shows that the structure of the living end group is the same as in living PMMA prepared with $TASHF_2$ catalyst.

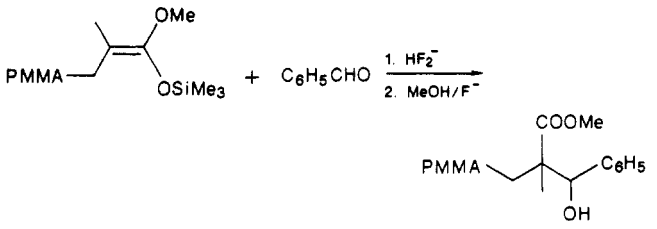
End-Capping Reactions. The reactivity of the ketene silyl acetal group of polymers prepared by GTP permits facile functionalization by end-capping reactions or coupling of polymer chains by reaction with polyfunctional terminating agents.[22] For example, reaction of GTP PMMA with benzaldehyde gives, after hydrolysis, a polymer with a terminal benzhydryl alcohol group (Scheme XIV). Alkylation with 0.5 equiv of *p*-xylylene dibromide and 1.0 equiv of TASF (F^- catalyst) gives a coupled polymer with twice the original molecular weight (Scheme XV).

Table X
Polymerization Temperature Dependence of Tacticity of GTP PMMA[a]

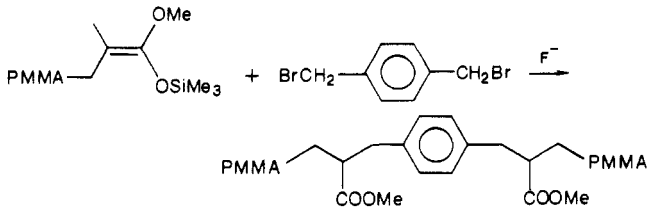
temp °C	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	triads, %			P(m/r)	P(r/m)	sum	diads, %	
			mm	mr	rr				m	r
−90	4550	1.11	0	19	81	1.00	0.11	1.11	9.5	90.5
−70	5540	1.38	1	26	73	0.93	0.15	1.08	14	86
−50	4020	1.26	2	29	69	0.88	0.18	1.06	16.5	83.5
−30	3530	1.28	2	30	68	0.88	0.18	1.06	17	83
−20	3760	1.03	3	32	65	0.84	0.20	1.04	19	81
−10	4140	1.08	4	31	65	0.80	0.19	0.99	19.5	80
0	3580	1.11	4	36	60	0.82	0.23	1.05	22	78
10	4940	1.04	5	36	59	0.78	0.23	1.01	23	77
20	3800	1.06	5	39	56	0.80	0.26	1.06	24.5	75.5
40	3860	1.15	6	40	54	0.77	0.27	1.04	26	74
60	4140	1.15	7	42	51	0.75	0.29	1.04	28	72

[a] The yield in each case is quantitative, theoretical $\bar{M}_n$ = 4100; solvent, THF; catalyst, $TASHF_2$; initiator, 1.

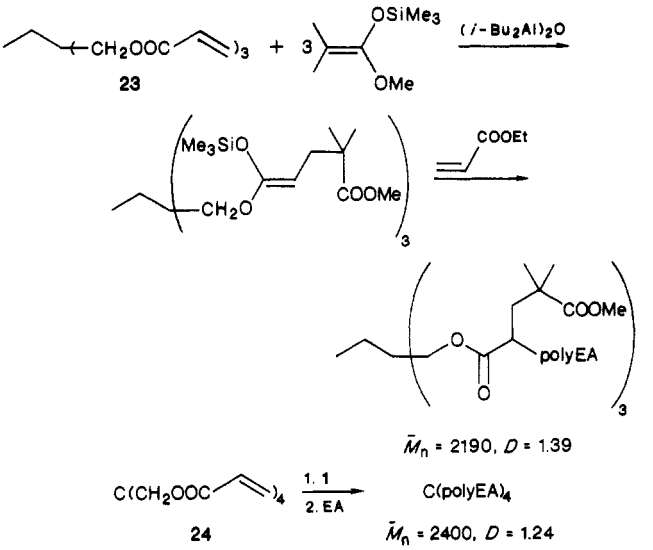
Scheme XIV



Scheme XV



Scheme XVI



The coupling of living polymer with either bis(bromomethyl)- or bis(iodomethyl)benzene is best carried out with 1.0 equiv of an anhydrous fluoride ion source (e.g., TASF) at low temperatures. This is because cleavage of each mole of ketene silyl acetal requires a mole of fluoride ion which, upon reaction, forms fluorotrimethylsilane. This process constantly consumes the catalyst. The reaction is further complicated by the fact that TASF is a very good fluorinating agent of benzyl halides.[8] Additionally, the leaving halide ion (e.g., Br^-, I^-) is a weak nucleophile which is usually not a catalyst for the reaction. The carbanion formed from the cleavage of the silyl group from the ketene silyl acetal is unstable at high temperatures. The solution must, therefore, be cooled (−78 °C) prior to the addition of TASF and the coupling agent.

Star Polymers. Initiation of GTP with polyfunctional initiators to produce star polymers presents the problem of synthesis of large, reactive, polyfunctional ketene silyl acetals. An alternative approach, which is described here, is to generate polyfunctional initiators in situ by the Michael addition reaction of polyfunctional monomers with silicon reagents. When 1 equiv of an n-functional monomer is allowed to react with n equiv of ketene silyl acetal initiator 1 in the presence of a Lewis acid catalyst[3] (especially a dialkylaluminum chloride or dialkylaluminum oxide) followed by addition of excess monofunctional monomer, cross-linking does not occur, but, instead, star polymers are formed. Thus, reaction of 1 with a 0.33 molar equiv of trimethylolpropane triacrylate (**23**) at −78 °C followed by 10 molar equiv of ethyl acrylate gave a quantitative yield of soluble star polymer containing no residual unsaturation with $\bar{M}_n$ = 2190, $\bar{M}_w$ = 3040, and D = 1.39 (theoretical $\bar{M}_n$ = 3300) (see Scheme XVI). Similarly, treatment of 1 at −78 °C with 0.25 molar equiv of pentaerythritol tetraacrylate (**24**) in the presence of diisobutylaluminum oxide followed by 10 equiv of ethyl acrylate gave a quantitative yield of soluble polymer with $\bar{M}_n$ = 2400, $\bar{M}_w$ = 2970, and D = 1.24 (theoretical $\bar{M}_n$ = 4752).

Stereochemistry of Group-Transfer Polymerization of Methyl Methacrylate. GTP of MMA using Lewis acid catalysts was reported to give PMMA with a ratio of 2:1 syndiotactic triads:heterotactic triads while PMMA prepared by GTP using bifluoride catalyst gave more nearly 1:1 syndiotactic:heterotactic composition.[3] The precise variation of tactic composition of GTP PMMA with polymerization temperature was determined by performing isothermal polymerizations of MMA using $TASHF_2$ as catalyst, 1 as initiator, and THF as solvent. The measurements cover the temperature range −90 to +60 °C. Slow feeding of monomer allowed temperature control of ±1 °C to be achieved. The composition of the PMMA as determined by measurement of isotactic (mm), heterotactic (mr), and syndiotactic (rr) triads in the C-methyl proton resonances at 1.2, 1.0, and 0.8 ppm at 360 MHz is shown in Figure 3, and the data are summarized in Table X. The fact that the sums of the probabilities of a meso following a racemic placement (P(r/m)) and a racemic following a meso placement ($P(m/r)$) differ from 1.0 by 10% or less indicates that the statistics are approximately Bernoullian for diad formation. The difference in activation enthalpy ($\Delta\Delta H^*$) and activation entropy ($\Delta\Delta S^*$) for m and r diad formation was determined from a plot of the natural logarithm of the ratio of m and r diads and the reciprocal of the polymerization temperature (see Figure 4). The $\Delta\Delta H^*$

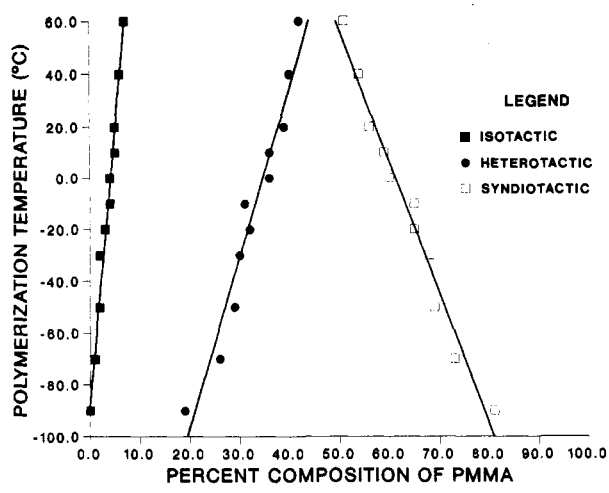


Figure 3. Variation of triad composition of GTP PMMA with polymerization temperature in THF solution with $TASHF_2$ catalysis as measured by ^1H NMR.

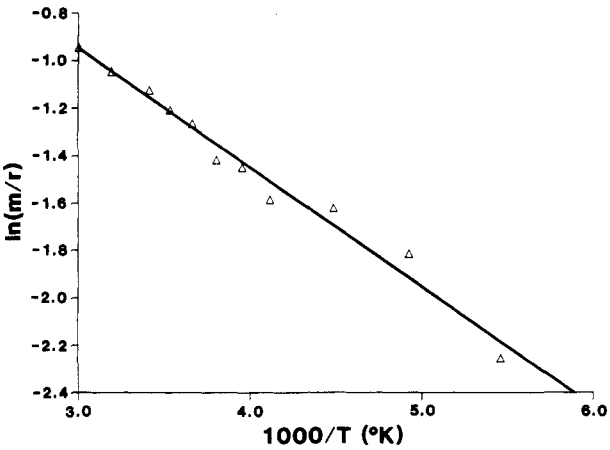


Figure 4. Arrhenius plot of meso/racemic diads in GTP PMMA prepared in THF with $TASHF_2$ catalysis.

favoring r formation is only 1.0 kcal/mol, while the $\Delta\Delta S^{\ddagger}$ favoring m formation is 1.1 eu. At 273 °C; $\Delta\Delta G^{\ddagger} = 0.70$ kcal/mol. After the manuscript was submitted for publication, Muller and Stickler[26] reported a similar study using TASF and TAS bifluoride, the results of which are in good agreement with our results. We would like to point out that it is extremely difficult to obtain TASF free of TAS bifluoride and that pure TASF (precursor to $TASHF_2$) at temperatures higher than 0 °C gives GTP polymers with much higher polydispersities than does TAS bifluoride. The fact that Muller and Stickler obtained excellent results at temperatures above 0 °C (7–50 °C) that were almost the same as their results obtained with $TASHF_2$ and our results suggests that, in fact, their TASF contained substantial amounts of $TASHF_2$. It is interesting to compare the data for group-transfer PMMA with free radical PMMA determined by various authors.[27] Fox and Schnecko[27a] and Otsu et al.[27c] found virtually the same values for $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ (1.07 kcal/mol and 0.99 eu)[27a] between the syndiotactic and isotactic propagation steps in MMA polymerization as we have found for group-transfer polymerization of MMA. Thus, in both GTP and radical polymerization of MMA a small positive $\Delta\Delta G^{\ddagger}$ disfavors m diad formation.

Conclusions. We have shown that acrylic monomers can be polymerized with group-transfer polymerization over a broad temperature range to give living polymers in which the molecular weight is controlled by the ratio of monomer to ketene silyl acetal initiator and the polydispersity is very low, providing that $k_i \geq k_p$. GTP is useful for preparation of both random and block copolymers of defined block size and sequence.

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References and Notes

(1) (a) For reviews see: Morton, M. *Anionic Polymerization: Principles and Practice*; Academic: New York, 1983. McGrath, J. E. Ed. *Anionic Polymerization: Kinetics, Mechanisms and Synthesis*, American Chemical Society: Washington, D.C., 1981; *ACS Symp. Series No. 166.* (b) A process for oligomerization of methacrylates to low molecular weight polymers with low polydisperisty using alkoxide initiators and alcohol chain-transfer agents at elevated temperatures has been described by: Haggard, R. A.; Lewis, S. N. *Prog. Org. Coat.* **1984**, *12*, 1.
(2) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; Rajanbabu, T. V. *J. Am. Chem. Soc.* **1983**, *105*, 5706. Also see: Webster, O. W. U.S. Patent 4 417 034, Nov 22, 1983; 4 508 880, April 2, 1985. Farnham, W. B.; Sogah, D. Y. U.S. Patent 4 414 372, Nov. 8, 1983; 4 524 196, June 18, 1985; 4 581 428, April 8, 1986.
(3) Hertler, W. R.; Sogah, D. Y.; Webster, O. W.; Trost, B. M. *Macromolecules* **1984**, *17*, 1415.
(4) (a) Farnham, W. B.; Middleton, W. J.; Sogah, D. Y. U.S. Patent 4 598 161, July 1, 1986. (b) For NMR spectra of other bifluorides see ref 5c.
(5) (a) Dixon, H. P.; Jenkins, H. D. B. *J. Chem. Phys.* **1971**, *56*, 4388. (b) Fujiwara, F. Y.; Martin, J. S. *J. Chem. Phys.* **1972**, *57*, 4091. (c) Fujiwara, F. Y.; Martin, J. S. *Can. J. Chem.* **1971**, *49*, 3071. (d) Sogah, D. Y., U.S. Patent 4 448 980, May 15, 1984.
(6) (a) Noyori, R.; Nishida, I.; Sakata, J. *J. Am. Chem. Soc.* **1983**, *105*, 1598. (b) See, however, ref 29.
(7) Sogah, D. Y.; Farnham, W. B. *Organosilicon and Bioorganosilicon Chemistry: Structures, Bonding, Reactivity and Synthetic Application*; H. Sakurai, Ed.; Wiley: New York, 1985; Chapter 20.
(8) Middleton, W. J. U.S. Patent 3 940 402, Feb. 24, 1976.
(9) (a) Ainsworth, C.; Chen, F.; Kuo, Y.-N. *J. Organomet. Chem.* **1972**, *46*, 59. (b) Ekouya, A.; Dunogues, J.; Duffaut, N.; Calas, R. *J. Organomet. Chem.* **1978**, *148*, 225. (c) Bush, R. D.; Golino, C. M.; Roark, D. N.; Sommer, L. H. *J. Organomet. Chem.* **1973**, *59*, C17. (d) Semmelhack, M. F.; Herndon, J. W. *Organometallics* **1983**, *2*, 363.
(10) Brittain, W. J. et al., unpublished results.
(11) (a) Yoshii, E.; Kobayashi, Y.; Koizumi, T.; Oribe, T. *Chem. Pharm. Bull.* **1974**, *22*, 2767. (b) Yoshii, E.; Takeda, K. *Chem. Pharm. Bull.* **1983**, *3*, 4586.
(12) Dicker, I. B. Presented at the 192nd National Meeting of the American Chemical Society, Anaheim, CA, September 1986; paper ORGN 91.
(13) Dicker, I. B.; Hertler, W. R.; Cohen, G. M.; Farnham, W. B.; Laganis, E. D.; Sogah, D. Y. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28(1)*, 106.
(14) Odic, Y.; Pereyre, M. *J. Organomet. Chem.* **1973**, *55*, 273.
(15) (a) Okamoto, Y.; Sakurai, H. *Synthesis* **1982**, 497. (b) Nakano, M.; Okamoto, Y.; Sakurai, H. *Synthesis* **1982**, 915.
(16) The facile reaction of diamino(trimethylsiloxy)phosphines (e.g., **9c**) with unsaturated aldehydes has been described by: Evans, D. A.; Hurst, K. M.; Takacs, J. M. *J. Am. Chem. Soc.* **1978**, *100*, 3467.
(17) See, for example: Kirby, A. J.; Warren, S. G. *The Organic Chemistry of Phosphorus*; Elsevier: New York, 1967; p 315.
(18) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; RajanBabu, T. V. *J. Macromol. Sci.—Chem.* **1984**, *A21*, 943.
(19) (a) Hertler, W. R.; Webster, O. W. *Int. Chem. Congr. Pacific Basin Socs., Abstr.* **1984**, 09059. (b) Hertler, W. R. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1986**, *27*(1), 165.
(20) Bandermann, F.; Speikamp, H. D. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 335.
(21) Andrews, G. D.; Vatvars, A. *Macromolecules* **1981**, *14*, 1603.
(22) Sogah, D. Y.; Webster, O. W. *J. Polym. Sci. Polym. Lett. Ed.* **1983**, *21*, 927.
(23) Ferguson, R. C., unpublished results.
(24) (a) Akkapeddi, M. K. *Macromolecules* **1979**, *12*, 546. (b) Suenaga, J.; Sutherlin, D. M.; Stille, J. K. *Macromolecules* **1984**, *17*, 2913.
(25) Hertler, W. R. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28(1)*, 108.

(26) Muller, M. A.; Stickler, M. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 575.
(27) (a) Fox, T. G.; Schnecko, H. W. *Polymer* **1962**, *3*, 575. (b) Bovey, F. A. *Chain Structure and Conformation of Macromolecules*; Academic: New York, 1982; p 62. (c) Otsu, T.; Yamada, B.; Imoto, M. *J. Macromol. Chem.* **1966**, *1*, 61.
(28) Sekine, M.; Olumoto, K.; Yamada, K.; Hata, T. *J. Org. Chem.* **1981**, *46*, 2097.
(29) RajanBabu, T. V. *J. Org. Chem.* **1984**, *49*, 2083.
(30) Emde, H.; Simchen, G. *Liebigs Ann. Chem.* **1983**, 816.
(31) Zaitseva, G. S.; Baukov, Yu. I.; Manukina, T. A.; Lutsenko, I. F.; Egorov, V. V. *Zh. Obshch. Khim.* **1975**, *45*, 86.

End Capping of Polynorbornene Produced by Titanacyclobutanes†

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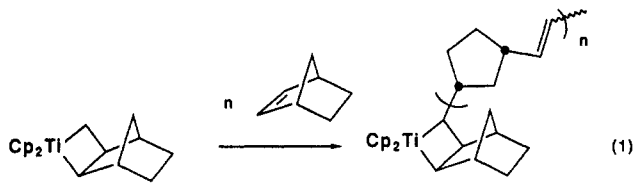
ABSTRACT: By use of **1** as a ring-opening olefin metathesis catalyst, norbornene was polymerized and the resulting living polymer allowed to react with benzophenone to give diphenylethylene-capped polymer **3**. The percentage of polymer chains end capped was 70–100% as determined independently by ^{1}H NMR and UV absorbance. Additionally, there was minimal change in the molecular weights and polydispersities of the polymers during the end-capping reaction.

The ring-opening olefin metathesis polymerization (ROMP) of cyclic olefins has been extensively studied,[1] and several ring-opened polymers are currently produced on an industrial scale.[2] A recent study[3] demonstrated that titanacyclobutanes polymerize norbornene to give the first well-defined living polymerization system reported for a ROMP catalyst (eq 1). This versatile system has been extended to the synthesis of block copolymers[4] and several novel conducting polymers.[4,5]



(1)

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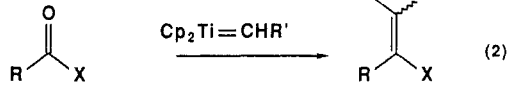
Previous work[6] has shown that titanium carbenes, generated from titanacyclobutanes and other sources, react with aldehydes, ketones, esters, amides, and imides to give Wittig-type products in excellent yields (eq 2). The novel



(2)

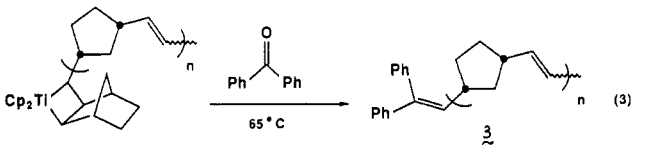
X= H, R'', OR'', NR''R''', N(R'')C(O)R'''

combination of the organic and polymer chemistry of titanium carbenes would make possible the synthesis of polymers with a variety of end groups. Among the potential uses are efficient removal of the catalyst, modification of the bulk properties of the original ROMP-derived polyalkenamer, and introduction of moieties for further chemical transformations and/or polymerization.

In our initial efforts in this area we report herein the end capping of polynorbornene with benzophenone, utilizing the Wittig-type chemistry of titanium carbenes. The efficiency of the end-capping reaction as well as the effect on polymer molecular weights and polydispersities is examined.

Results and Discussion

By use of **1** as a catalyst, norbornene was polymerized, and the resulting living polymer was allowed to react with benzophenone to give diphenylethylene-capped polymer **3** (eq 3). This capping group was chosen for its favorable



(3)

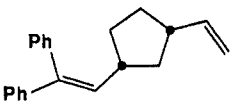
3

^{1}H NMR and UV properties to facilitate end group analysis. On the basis of model studies, benzophenone is also a good test of a sterically demanding ketone.

To establish the efficiency of the reaction, both ^{1}H NMR and UV analyses were used to determine the quantity of diphenylethylene end cap present in the isolated samples of end-capped polymer. Comparison of these values with the expected theoretical values (based on the molecular weights of the polymers derived from GPC and assuming 100% active catalyst) gave the percentage of chains containing the end cap.

A typical ^{1}H NMR spectrum of the capped polymer (in CD_2Cl_2) is given in Figure 1. Both the aromatic protons (δ 7.10–7.40, m, 10 H) and the olefinic proton (δ 5.95, d, J = 11 Hz, 1 H) of the end cap (Ph_2C=CH) are observable. The olefinic protons of the polymer (δ 5.10–5.40, m) overlap the residual solvent signal of the NMR solvent and could not be used for integration purposes. However, the allylic protons of the polymer (δ 2.40, 2.78) are well-resolved and were integrated and compared to the integration of the aromatic protons of the end cap. In this manner the ratio of monomer units of polymer to endcap was determined (Table I).

During GPC analysis (see Experimental Section) of the polymers, the UV trace (λ = 254 nm) was also recorded. Because of the much higher extinction coefficient of the end group compared to the polymer, the absorbance due to the polymer was minimal and could be easily subtracted from the trace by comparison to the UV trace of uncapped polymer samples of identical concentrations. The capped monomer **2** was synthesized as previously described[3] and the UV trace of a standard solution (1.02×10^{-4} M in



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