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Synthesis of PMMA Star Polymers with Siloxane Cores via Group-Transfer Polymerization Using Silyl Ketene Acetal Functionalized Cyclic Siloxanes

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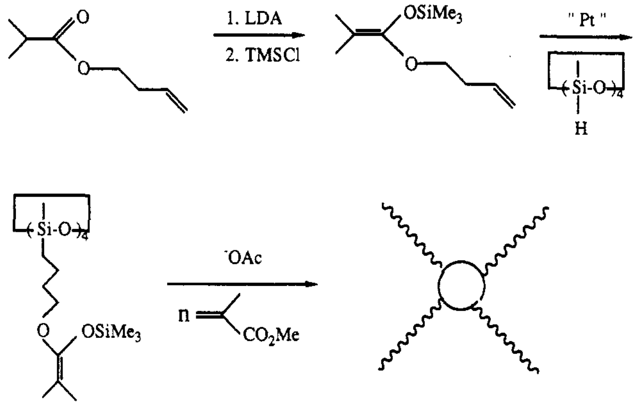
ABSTRACT: Four-arm, poly(methyl methacrylate) star polymers having cyclic siloxane cores were prepared by group-transfer polymerization (GTP). In this core-first approach, a cyclic hydromethylsiloxane tetramer was hydrosilated with a terminal olefin bearing a silyl ketene acetal, and methyl methacrylate polymerization was initiated in THF using acetate ion as a catalyst. Star polymers having between 20 and 150 methyl methacrylate repeat units per arm were prepared, and had polydispersities of ca. 1.2–1.3, as determined by gel permeation chromatography (GPC). The polymerizations were quantitative. The star topology was confirmed by cleavage of the cyclic siloxane cores with triflic acid in the presence of an excess of hexamethyldisiloxane. The number-average molecular weights of the resulting arms were determined relatively by GPC with PMMA standards and absolutely by end group analysis via ^{1}H NMR of the heptamethyltrisiloxane termini. The results are in reasonable agreement with the predicted arm molecular weights based on the ratios of methyl methacrylate to silyl ketene acetal employed during synthesis.

Introduction

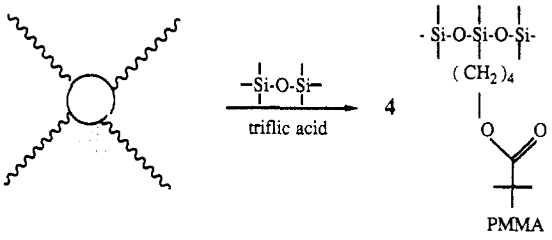
Group-transfer polymerization (GTP) has proven to be an attractive method for preparing low-polydispersity poly(alkyl methacrylates) and related polymers. GTP typically involves the use of silyl ketene acetals as initiators with Lewis bases or acids as catalysts.[1–3] While there currently exists a debate about whether the silyl ketene acetals themselves or a small, equilibrium concentration of enolate ions is the actual propagating species,[4] advantage can be taken of the living nature of the propagating ends to prepare block and end-functionalized polymers, as well as interesting architectures such as stars.[5–7]

Star polymers are of interest in part because their smaller hydrodynamic volumes afford lower viscosities compared with linear polymers of the same molecular weight. In general, the synthesis of star-shaped polymers can be accomplished by either preparing the arms first followed by coupling or preparing a core containing multiple initiator sites from which the arms grow.[8,9] The former method, using GTP, has been applied successfully to the synthesis of poly(methyl methacrylate) (PMMA) star polymers by reaction of living PMMA chains with core-forming monomers such as ethylene glycol dimethacrylate.[5] In this paper we report a "core-first" approach to PMMA star polymers using silyl ketene acetal-functionalized cyclic siloxanes as the initiators. These are readily synthesized by hydrosilation of a silyl ketene acetal bearing a terminal olefin such as 1-[(but-3-en-1-yl)oxy]-1-(trimethylsiloxy)-2-methyl-1-propene (BTMP), as outlined in Scheme I. Polymerization of MMA to afford the star polymers is rapid and quantitative in THF in the presence of acetate ion as a catalyst. The sensitivity of cyclic siloxanes toward acid cleavage afforded the opportunity to cleave the cores (Scheme II) and characterize the resulting arms. A similar approach has been used to selectively degrade silicone copolymers and networks.[10] The use of hexamethyldisiloxane as a capping agent yielded arms with heptamethyltrisiloxane termini, enabling the determination of absolute number-average molecular weights of the arms by ^{1}H NMR.

Scheme I



Scheme II



Experimental Section

Materials. Tetrahydrofuran (THF) was distilled from sodium benzophenone prior to use. Diisopropylamine, trimethylchlorosilane, 1,3,5,7-tetramethylcyclotetrasiloxane, and bis(trimethylsiloxy)methylsilane were distilled prior to use. The last was a gift from GE Silicones. 3-Buten-1-ol, methyl isobutyrate, potassium carbonate, *n*-butyllithium (2.5 M in hexane), hexamethyldisiloxane, trifluoromethanesulfonic acid, sodium carbonate, methylene chloride (anhydrous) (all from Aldrich) and platinum divinyltetramethyldisiloxane complex (Petrarch) were used without further purification. Tetrabutylammonium acetate (Aldrich) was dried on a vacuum line prior to use. Methyl methacrylate (Aldrich) was purified by first passing it through neutral alumina under dry argon and then distilling under reduced pressure from CaH_2 prior to use. ^{1}H NMR spectra were obtained on a Varian XL-200 spectrometer and resonance positions were referenced to TMS. GPC measurements were performed on a Waters chromatographic system (Model 600E), with commercial μ-Styragel columns and poly(methyl methacrylate) standards.

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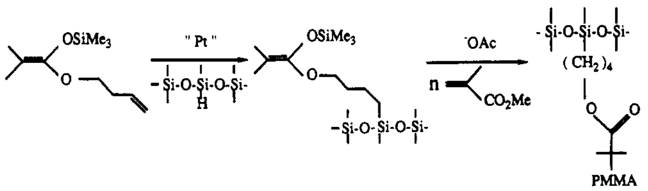
Scheme III



Preparation of Initiators. 2-Methylpropanoic Acid But-3-en-1-yl Ester. To a one-necked, 200-mL, round-bottomed flask fitted with a Dean-Stark trap and a condenser were added 25 g (0.35 mol) of 3-buten-1-ol, 71 g (0.70 mol) of methyl isobutyrate, and 4 g of K_2CO_3. The flask was heated to 110 °C. The solution was stirred for 24 h, while CH_3OH was distilled out. The product was filtered and distilled. The distillate having a boiling point of 145 °C was collected. ^1H NMR (200 MHz, $CDCl_3$): δ 5.78 (m 1 H, C=CH), 5.08 (m, 2 H, CH_2=C), 4.11 (t, J = 6.6 Hz, 2 H, CH_2O), 2.53 (m, 1 H, $HCMe_2$), 2.38 (m, 2 H, CH_2), 1.16 (d, J = 6.9 Hz, 6 H, CH_3).

1-[(But-3-en-1-yl)oxy]-1-(trimethylsiloxy)-2-methyl-1-propene (BTMP). This compound was prepared by modifications of published procedures. In a typical procedure, 250 mL of THF and 30 mL (214 mmol) of diisopropylamine were added to a three-necked 500-mL flask fitted with a stirrer and a reflux condenser under argon. The resulting solution was cooled to 0 °C and 86 mL (214 mmol) of *n*-butyllithium (2.5 M in hexane) was added dropwise. After 30 min of stirring, 30.5 g (214 mmol) of 2-methylpropanoic acid but-3-en-1-yl ester was added over a 10-min period, and the temperature was cooled to −78 °C. The reaction mixture was stirred for 1 h, and 65 mL (512 mmol) of trimethylsilyl chloride was added. The mixture was warmed to room temperature and stirred for 2 h. It was then filtered under argon. A 200-mL aliquot of pentane was added, and the inorganic salts were removed by filtration under argon. The solvent was evaporated, and the residue was distilled. The product was collected at 70 °C under reduced pressure. ^1H NMR (200 MHz, $CDCl_3$): δ 5.80 (m, 1 H, C=CH), 5.10 (m, 2 H, CH_2=C), 3.74 (t, J = 6.6 Hz, 2 H, CH_2O), 2.46 (m, 2 H, CH_2), 1.57, 1.51 (2s, 6 H, CH_3), 0.20 (s, 9 H, $Si(CH_3)_3$).

1,3,5,7-Tetrakis{[(1-(trimethylsiloxy)-2-methyl-1-propenyl)oxy]butyl}-1,3,5,7-tetramethylcyclotetrasiloxane (D4-BTMP). To a 50-mL one-necked round bottom flask were added with stirring under argon 2.0 g (8.3 mmol) of 1,3,5,7-tetramethylcyclotetrasiloxane and 7.8 g (36.4 mmol) of BTMP. (A 10 mol % excess of BTMP was used.) Then three drops of platinum divinyltetramethyldisiloxane complex was added. The flask was immersed in an oil bath at 60 °C for 24 h. The extent of reaction was followed by IR and NMR spectroscopy. After the Si–H peak in the IR and NMR spectra disappeared, the excess BTMP was removed under vacuum. ^1H NMR (200 MHz, $CDCl_3$): δ 3.68 (t, J = 6.4 Hz, 2 H, CH_2O), 1.62 (m, 2 H, OCH_2), 1.56, 1.50 (2s, 6 H, CH_3), 1.40 (m, 2 H, CH_2CSi), 0.52 (t, J = 8.3 Hz, 2 H, CH_2Si), 0.20 (s, 9 H, $OSi(CH_3)_3$), 0.07 (s, 3 H, $Si(CH_3)O$).

Bis(trimethylsiloxy){[(1-(trimethylsiloxy)-2-methyl-1-propenyl)oxy]butyl}methylsilane (BMS-BTMP). The same procedure as described above was employed, using bis(trimethylsiloxy)methylsilane instead of tetramethylcyclotetrasiloxane. ^1H NMR (200 MHz, $CDCl_3$): δ 3.68 (t, J = 6.4 Hz, 2 H, CH_2O), 1.65 (m, 2 H, OCH_2), 1.58, 1.52 (2s, 6 H, CH_3), 1.41 (m, 2 H, CH_2CSi), 0.48 (t, J = 8.3 Hz, 2 H, CH_2Si), 0.20 (s, 9 H, $OSi(CH_3)_3$), 0.09 (s, 18 H, $Si(CH_3)_3$), −0.01 (s, 3 H, $OSi(CH_3)O$). This initiator was used to prepare PMMA's with heptamethyltrisiloxane end groups (see Scheme III) following the general procedure for star polymer synthesis below.

General Procedure for the Core-First Synthesis of PMMA Star Polymers. To a three-necked, 50-mL, round-bottomed flask fitted with a septum, thermocouple well, and condenser was added under argon a solution of 0.55 g (2.0 mmol) of D4-BTMP in 15 mL of THF, and 2.0 mL (18.7 mmol) of MMA. To the stirred solution was added 0.008 mmol (0.4 mol % relative to initiator) of the catalyst solution (tetrabutylammonium acetate 0.03–0.05 M in THF), after which an exothermic reaction occurred. Then 4.4 mL (41.3 mmol) of MMA was added dropwise via a syringe at a rate to keep the temperature below 50 °C. One hour after the maximum temperature was reached, the polymerization was quenched with methanol. After an additional 1 h of stirring, the polymer was precipitated in hexane, collected by filtration, and dried in a vacuum oven.

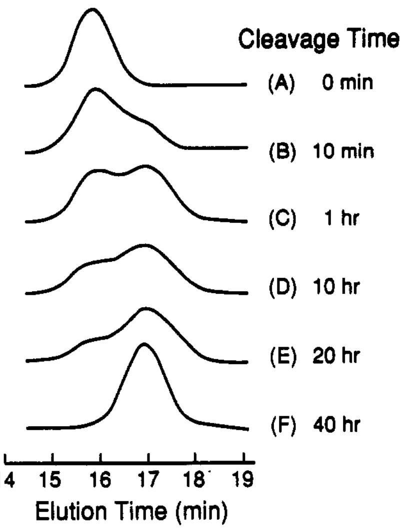


Figure 1. GPC traces following the progress of star20 cleavage as outlined in Scheme II.

General Procedure for the Cleavage of the Star Polymer. To an one-necked flask were added 0.6 g of star PMMA, 10 g of hexamethyldisiloxane, and 50 mL of methylene chloride, followed by adding six drops of trifluoromethanesulfonic acid, with stirring. The mixture was refluxed for 40 h. The product solution was neutralized with sodium carbonate and then filtered. The cleaved polymer was precipitated in hexane, collected by filtration, and dried in a vacuum oven. The dried polymer was analyzed by GPC and NMR.

Results and Discussion

Four-arm star polymers having between ca. 20 and 150 MMA repeat units per arm were prepared according to Scheme I, and each was cleaved as outlined in Scheme II. A set of GPC traces recorded as a function of time during a cleavage experiment on a four-arm star polymer with 20 MMA repeat units per arm is shown in Figure 1. The peak from the original polymer is progressively replaced by one at higher elution times (and lower relative molecular weight) during the experiment. Control experiments with linear PMMA prepared using 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene as the initiator showed virtually no change in the GPC peak maximum and molecular weight distribution when treated in an identical manner, which suggests that the arms remain intact during the cleavage reaction. Figure 2a shows a ^1H NMR spectrum of the cleavage products, which are anticipated to be "released" PMMA arms having heptamethyltrisiloxane end groups. The peaks at ca. 0.09 and 0 ppm, which integrate in a ratio of 6:1, are consistent with the presence of this end group. In order to further confirm this assignment, a few linear PMMA's were prepared from the initiator bis(trimethylsiloxy){[(1-(trimethylsiloxy)-2-methyl-1-propenyl)oxy]butyl}methylsilane, bearing a heptamethyltrisiloxane group, which was obtained by hydrosilation of bis(trimethylsiloxy)methylsilane with BTMP (Scheme III). A ^1H NMR spectrum of PMMA formed by GTP with this initiator is shown in Figure 2b. Indeed, the peaks from the initiator fragment at ca. 0.09 and 0 ppm are identical to those of a cleaved star PMMA (Figure 2a).

A listing of the star and heptamethyltrisiloxane-capped polymers prepared and accompanying characterization data are given in Table I. The number associated with the star polymer in the first column of the table refers to

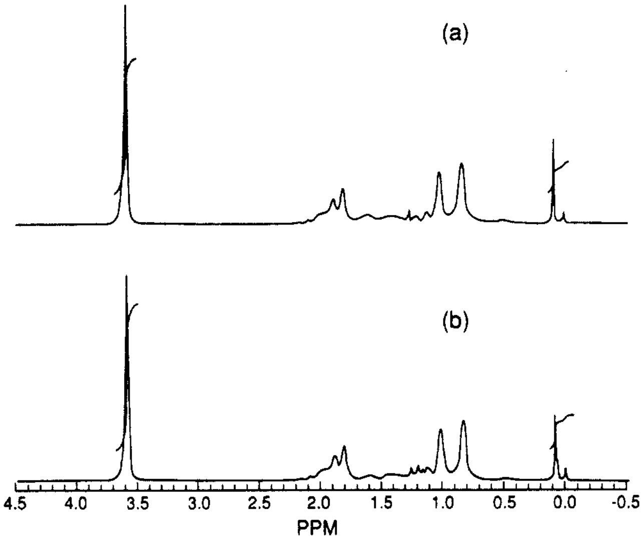


Figure 2. (a) 200-MHz ^1H NMR spectrum of cleaved star20. Solvent is $CDCl_3$. (b) 200-MHz ^1H NMR spectrum of capped PMMA with ca. 20 repeat units prepared according to Scheme III. Solvent is $CDCl_3$.

Table I
Number-Average Molecular Weights (M_n's) and Polydispersities (D's) of Star PMMA's and Cleaved Arms[a]

polymer	M_n (theory)	M_n (GPC)	D	M_n (NMR)
star19	8408	6260	1.21	
star19 cleaved	2262	2060	1.19	2680
star20	8808	6360	1.21	
star20 cleaved	2362	2130	1.25	2760
star30-1	12808	9130	1.22	
star30-1 cleaved	3362	3200	1.19	3970
star30-2	12808	9510	1.29	
star30-2 cleaved	3362	3230	1.21	3690
star45	18808	11860	1.30	
star45 cleaved	4862	4390	1.17	5200
star59	24408	17950	1.22	
star59cleaved	6262	5580	1.17	6120
star98	40008	30550	1.22	
star98 cleaved	10162	9620	1.16	8430
star150	60808	50870	1.22	
star150 cleaved	15362	15720	1.53	13530
capped PMMA20	2362	2670	1.20	3050
capped PMMA43	4662	4690	1.25	4710
capped PMMA66	6962	6750	1.27	7250

[a] GPC data are relative to PMMA standards. Capped PMMA's were prepared according to Scheme III.

the number of MMA repeat units per arm. The number associated with the heptamethyltrisiloxane-capped polymers (capped PMMA) is simply the number of MMA repeat units. The relative number-average molecular weights (M_n's) of the PMMA stars and the cleaved arms were determined by GPC and are summarized in Table I. Also included are absolute molecular weights obtained from the ^1H NMR spectra from integration ratios of the 21 end group protons to those of the methoxy groups (δ = 3.60 ppm) in the PMMA repeat unit. For comparative purposes, we include similar data for a few PMMA's prepared as outlined in Scheme III.

Several points merit discussion. First, the M_n's of the PMMA star polymers, relative to linear PMMA standards, are smaller than the theoretical M_n's calculated from the monomer/initiator ratio. This is expected, as the hydrodynamic volume of a star will be smaller than that of a linear polymer of similar molecular weight. Second, the average polydispersity of the stars is ca. 1.24, comparable to polydispersities of linear PMMA's prepared by GTP. Third, cleavage of the star polymers according to Scheme II affords lower molecular weight fragments as expected, and in fact, the GPC-derived molecular weights are in reasonable agreement with the theoretical molecular weights (including the heptamethyltrisiloxane end cap) of the arms. Note that the arm M_n's are approximately one-fourth of the theoretical M_n's of the stars and that the polydispersities of the arms are generally similar to those of the stars from which they were derived. Fourth, the NMR-derived M_n's, while slightly higher than the GPC-derived and most of the theoretical M_n's, also confirm that the stars have been cleaved to the individual arms. The NMR-derived M_n's are lower than the theoretical M_n's for the cleaved stars 98 and 150. However, in these cases, the NMR integrations are becoming less reliable due to the diminishing end group concentration. The reproducibility of the star synthesis and cleavage is quite good, as exemplified by the data for the two star 30 samples which were prepared and cleaved separately.

We have observed by GPC that the cleavage of star 150 is incomplete, even at longer reaction times and higher concentrations of triflic acid. Also, the polydispersity of the cleaved star 150 arms is rather high (ca. 1.5) even though the star polymer itself has a polydispersity of 1.22. We believe that the relatively long arms in this star polymer sterically interfere with the cleavage reaction.

We conclude this section by noting that a modification of Scheme I can be employed to prepare PMMA star polymers by an "arm-first" method. BTMP can be used to initiate MMA polymerization first, followed by hydrosilation of the hydromethylsiloxane tetramer with the resulting vinyl-capped PMMA. We have in fact explored this route. However, the initial, vinyl-capped PMMA arms are never fully converted to the desired star polymer, as monitored by GPC, and therefore any resulting stars are contaminated with unattached linear polymer. Also, the reaction between the vinyl end groups and Si–H's was incomplete even when an excess of cyclic siloxane was used, though the Si–H IR band disappeared, suggesting that competitive reactions such as H_2 elimination and the formation of Si–Si coupled products may be occurring.[11] Therefore, this particular approach appears to be inferior to the core-first method discussed above.

Conclusions

This investigation has demonstrated that four-arm star polymers of methyl methacrylate ($M_n = 8 \times 10^3$–6×10^4) can be synthesized via group-transfer polymerization using silyl ketene acetal functionalized cyclic siloxanes. The demonstration of the star architecture was confirmed by the cleavage of the siloxane cores followed by GPC and NMR characterization of the cleaved arms. Due to the living nature of the propagating silyl ketene acetals, it may be possible to obtain star polymers having functionality at the chain ends by adding appropriate end-capping reactants or block stars by sequential addition of different monomers.

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References and Notes

(1) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1983**, *105*, 5706.

(2) Dicker, I. B.; Cohen, G. M.; Farnham, W. B.; Hertler, W. R.; Laganis, E. D.; Sogah, D. Y. *Macromolecules* **1990**, *23*, 4034.
(3) Hertler, W. R.; Sogah, D. Y.; Webster, O. W. *Macromolecules* **1984**, *17*, 1415.
(4) Quirk, R. P.; Bidinger, G. P. *Polym. Bull.* **1989**, *22*, 63.
(5) Simms, J. A. *Rubber Chem. Technol.* **1991**, *64*, 139.
(6) Sogah, D. Y.; Hertler, W. R.; Webster, O. W.; Cohen, G. M. *Macromolecules* **1987**, *20*, 1473.
(7) Simms, J. A.; Spinelli, H. J. *J. Coat. Technol.* **1987**, *59*, 125.
(8) Rempp, P.; Lutz, P. *Polym. Prepr. (Am. Chem. Soc., Div. Poly. Chem.)* **1988**, *29* (2), 15.
(9) Tsitsilianis, C.; Lutz, P.; Graff, S.; Lamps, J.; Rempp, P. *Macromolecules* **1991**, *24*, 5897.
(10) Keohan, F. L.; Swint, S. A.; Buese, M. A. *J. Polym. Sci., Part A. Polym. Chem.* **1991**, *29*, 303.
(11) Lewis, L. N. *J. Am. Chem. Soc.* **1990**, *112*, 5998.

Registry No. BTMP, 144634-59-3; D-4–BTMP, 144667-08-3; BMS–BTMP, 144634-60-6; PMMA, 9011-14-7; $H_2C{=}CH(CH_2)_2OCOCH(CH_3)_2$, 144634-58-2; $HO(CH_2)_2CH{=}CH_2$, 627-27-0; $(CH_3)_2CHCO_2Me$, 547-63-7; TMSCl, 75-77-4; $MeSiH(OTMS)_2$, 1873-88-7; 1,3,5,7-tetramethylcyclotetrasiloxane, 2370-88-9.