physics and Photochemistry; Cambridge University Press: New York, Chapter 9, p 220.
(10) Johansen, O.; Mau, A. W.-H.; Sasse, W. H. F. *Chem. Phys. Lett.* **1983**, *94*, 113.
(11) Olmsted, J., III; McClanahan, S. F.; Danielson, E.; Younathan, J. N.; Meyer, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 3297.
(12) (a) Schaap, A. P.; Thayer, A. L.; Blossey, E. C.; Neckers, D. C. *J. Am. Chem. Soc.* **1975**, *97*, 3241. (b) Blossey, E. C.; Neckers, D. C.; Thayer, A. L.; Schaap, A. P. *J. Am. Chem. Soc.* **1973**, *95*, 5820. (c) Blossey, E. C.; Neckers, D. C. *Tetrahedron Lett.* **1973**, *14*, 1823.
(13) Cochet, X.; Mortreux, A.; Petit, F. *C.R. Seances Acad. Sci., Ser. C.* **1979**, 105.
(14) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.
(15) Bos, K. D.; Kraaijkamp, J. G.; Noltes, J. G. *Synth. Commun.* **1979**, *9*, 497.
(16) Maerker, G.; Case, F. H. *J. Am. Chem. Soc.* **1958**, *80*, 2745.
(17) Della Ciana, L.; Hamachi, I.; Meyer, T. J. *J. Org. Chem.*, in press.
(18) Arshady, R.; Reddy, B. S. R.; George, M. H. *Polymer* **1984**, *25*, 716.
(19) Johnstone, R. A.; Rose, M. E. *Tetrahedron* **1979**, *35*, 2169.
(20) Zook, H. D.; Gumby, W. L. *J. Am. Chem. Soc.* **1960**, *82*, 1386.
(21) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159. (b) Meyer, T. J. *Pure Appl. Chem.* **1986**, *25*, 2357. (c) Felix, F.; Ferguson, J.; Gudel, H. U.; Ludi, A. *Chem. Phys. Lett.* **1979**, *62*, 153. (d) Felix, F.; Ferguson, J.; Gudel, H. U.; Ludi, A. *J. Am. Chem. Soc.* **1980**, *102*, 4096. (e) Decurtins, S.; Felix, F.; Ferguson, J.; Gudel, H. U.; Ludi, A. *J. Am. Chem. Soc.* **1980**, *102*, 4102.
(22) Klopffer, W. *Introduction to Polymer Spectroscopy*; Springer-Verlag: New York, 1984; pp 139, 159.
(23) The loading of the metal complex on the polymeric chain is not equal to the fraction of modified methylene groups since two binding sites are possible starting with the difunctional bipyridine dicarboxylic acid. The degree of mono- and diester formation can be calculated by generating a second algebraic expression using the ratio of the integrated intensity of the total aromatic region to that of the benzylic protons. These two equations can be solved for a unique determination.
(24) Phelps, J.; Santhanam, K. S. V.; Bard, A. J. *J. Am. Chem. Soc.* **1967**, *89*, 1752.
(25) Parker, V. D. *Acta Chem. Scand.* **1970**, *24*, 2757, 2768.
(26) Hammerich, O.; Parker, V. D. *J. Am. Chem. Soc.* **1974**, *96*, 4289.

Termination in Group Transfer Polymerization†

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ABSTRACT: The major pathway for termination in group transfer polymerization (GTP) has been identified as a cyclization process analogous to backbiting in anionic polymerization. Rates of cyclization for oligomer mixtures prepared from methyl methacrylate (MMA) and [(1-methoxy-2-methyl-1-propenyl)oxy]trimethylsilane (P_1*) were determined by FT-IR spectroscopy. A stopped-flow FT-IR study of a discrete cyclization process involving an independently synthesized GTP oligomer P_3* (dp = 3) demonstrated that termination is much slower than propagation. As chain length of the living GTP oligomer increases, the rate of cyclization decreases by more than an order of magnitude. Detailed product analysis for the oligomer mixture prepared from 3:1 MMA:P_1* revealed that, for oligomers whose dp = 4–9, depolymerization of MMA can occur. Termination was more rapid for tris(piperidino)sulfonium bifluoride ($TPSHF_2$) than tetrabutylammonium bibenzoate (TBABB) catalyzed reactions, in accord with previously reported catalyst reactivity in GTP propagation.

Group transfer polymerization (GTP) of methacrylates affords polymers whose degree of polymerization is dictated by the stoichiometry of initiator and monomer.[1-3] GTP proceeds by transferring a reactive group to the incoming monomer, yielding a so-called "living end". GTP proceeds smoothly at room temperature and yields polymers with a narrow molecular weight distribution. We have now identified and characterized the major mode of termination in GTP. This paper details the study of oligomer mixtures by in situ FT-IR and product analysis of quenched aliquots. We have also studied the termination reaction as a single event by the independent synthesis of an intermediate oligomer.

Experimental Section

Materials. Tetrahydrofuran (THF) and pentane were distilled from sodium and benzophenone. Solvents were stored and handled in a drybox. Commercially available methyl methacrylate was passed through a short column of neutral alumina in the drybox to remove inhibitors and acidic impurities. [(1-Methoxy-2-methyl-1-propenyl)oxy]trimethylsilane (P_1*) was prepared according to a literature procedure[4] and was slowly distilled twice through a 24-in. spinning band column before use. Tris(piperidino)sulfonium bifluoride ($TPSHF_2$) was prepared according to a previously published procedure.[5] The synthesis of tetrabutylammonium bibenzoate has been described elsewhere.[6] The synthesis of dimethyl 2,4,4-trimethyl-2-[3-methoxy-2-methyl-3-(trimethylsiloxy)prop-2-en-1-yl]glutarate, P_3*, was described in a previous publication.[5] By that method, P_3* is obtained as a 87:13 mixture of *Z*:*E* geoisomers.

Methods. ^{1}H NMR spectra were recorded with either a Nicolet NT300/WB or GE QE300 spectrometer. ^{29}Si and ^{13}C NMR spectra were recorded with a Nicolet NT300/WB spectrometer. The stopped-flow apparatus has been described in a previous publication.[5] FT-IR spectra were recorded with either a Nicolet 170SX or 20SXB spectrometer.

Oligomer Characterization. For the 3:1 MMA:P_1* oligomer mixture, detailed product compositions were determined as a function of time. Aliquots were quenched in methanol, and the amounts of linear and cyclic oligomers were analyzed by gas and gel permeation chromatographies. Calibrated product distributions for oligomers up to dp = 6 were determined by using an internal standard (*n*-decane) in GC analysis. GC analyses were performed on a Hewlett-Packard 5890A chromatograph with a FID detector using a Macrobore DB1-30M (1.5-μm film) column. The identity of components was ascertained by comparison to elution times of authentic samples and by GC/MS identifications. Calibration of detector response was possible for MMA, P_1, P_2, P_3^c, P_3, P_4^c, and P_4; it was assumed that higher oligomers had a response similar to that of P_4^c and P_4. GC/MS data were obtained

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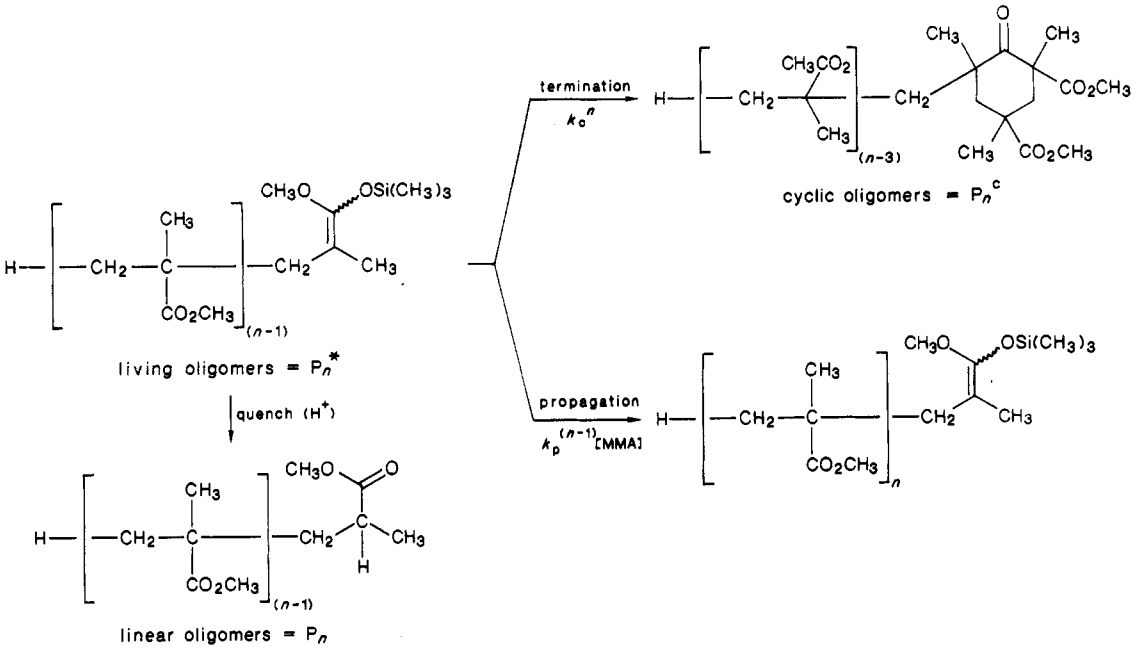
Scheme I



with a Varian 3700 GC with a V. G. Micromass 16-F mass spectrometer or a Du Pont 21-491 mass spectrometer. Peak areas of the compounds in the GPC analyses were cross-referenced to GC data using the cyclic trimer (P_3^c) as common standard. The cyclic oligomers elute just before the corresponding linear oligomers in the GPC. It was possible to confirm identity of each type of structural form by use of simultaneous UV detection. At 300 nm, it was possible to selectively detect the ring carbonyl of cyclic oligomers. The method of GPC analysis is described in ref 7.

Results

Scheme I outlines the two major reaction pathways available to a GTP living oligomer. In the presence of a monomer such as methyl methacrylate (MMA), propagation can occur. We have found that for oligomers with dp ≥ 3 ($n \geq 3$ according to Scheme I), self-termination by cyclization is also possible. This cyclization is an intramolecular nucleophilic attack by the silyl ketene acetal end group on a backbone ester with a resultant displacement of methoxide (in the form of (trimethylsilyl)methoxide) to form a substituted cyclohexanone (P_n^c). The propensity of a GTP oligomer to self-terminate is demonstrated by the 85% isolated yield of 2,4-(dicarbomethoxy)-2,4,6,6-tetramethylcyclohexanone (P_3^c) from the overnight reaction of 0.050 mol of MMA and 0.025 mol of [(1-methoxy-2-methyl-1-propenyl)oxy]trimethylsilane, P_1*, in THF using 0.00125 mol of tetrabutylammonium bibenzoate (TBABB) as catalyst. This process is analogous to the major termination pathway in anionic polymerization of methacrylates, commonly referred to as backbiting.[7-9] Scheme I does not depict the necessary involvement of catalyst in the GTP reaction process. As with MMA addition,[1] we have found that catalyst must be present in order for termination of a GTP oligomer to occur. We have performed a detailed analysis of the kinetic and mechanistic features of this termination pathway in GTP. All rates reported for cyclization in this paper are based on the following reaction model:

$$\text{cat} + P_n^* \underset{}{\overset{k_c}{\rightleftharpoons}} (\text{cat}\cdot P_n^*) \xrightarrow{k_c^n} P_n^c$$

The rate of reaction is given by

$$R = -d[P_n^*]/dt = k_c^n[(\text{cat}\cdot P_n^*)] = k_c^n K_c[P_n^*][\text{cat}]$$

The integrated rate equation can be simplified by assuming [cat] remains constant, leading to the following equation:

$$\ln ([P_n^*]_o/[P_n^*]) = k_{app}t$$

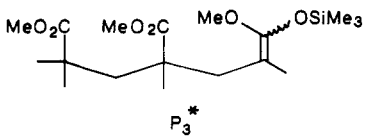
where

$$k_{app} = k_c^n K_c[\text{cat}]$$

The second-order rate term $k_c^n K_c$ has been determined by measuring $k_{app}/[\text{cat}]$ using FT-IR and product analysis.

Fourier Transform Infrared Spectroscopy

FT-IR spectroscopy is a useful tool for studying the termination of MMA oligomers. The silyl ketene acetal functionality of the living oligomers has a $\nu_{C=C}$ stretching absorption at 1687 cm^{-1} and a backbone ester $\nu_{C=O}$ absorption at 1740 cm^{-1}. The cyclohexanone termination product has a characteristic ring $\nu_{C=O}$ absorption at 1716 cm^{-1} (for P_3^c, $\epsilon = 608$). Infrared spectroscopy was used to characterize changes in oligomer solutions prepared from 2:1 and 3:1 ratios of MMA:P_1*, respectively. The oligomerization of P_1* and MMA was performed in THF at room temperature with TBABB catalysis. Upon addition of MMA to the stirred solution of P_1* and TBABB, an aliquot was transferred to an IR optical cell. For both 2:1 and 3:1 reactions, MMA was consumed within 2 min. In addition to studying oligomer mixtures, we also examined the discrete cyclization reaction of P_3*. In the absence



of catalyst, P_3* is stable. A stopped-flow FT-IR apparatus was used to mix P_3* and TBABB and to follow cyclization of P_3* to cyclohexanone P_3^c. Figure 1 shows a series of FT-IR spectra versus time for the cyclization of P_3*. Frequency of the living end absorption is invariant with oligomer molecular weight so that absorption intensity reflects the sum concentration of all living oligomers. Kinetic information on GTP termination was typically obtained by following the decrease in the silyl ketene acetal peak because it had the least overlap with adjacent peaks. Table I contains rates obtained from linear regression of

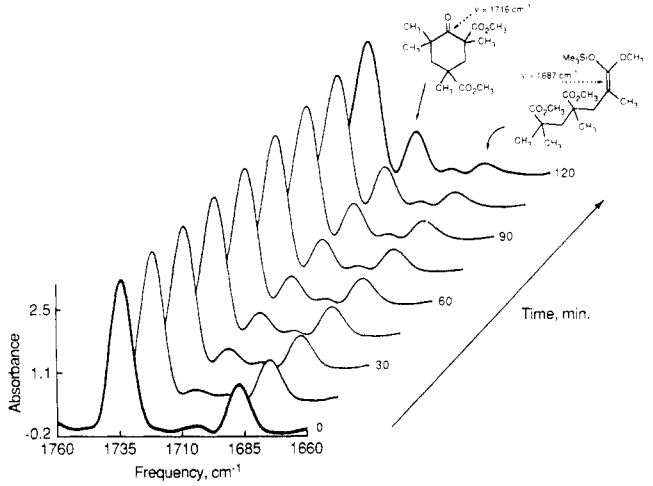


Figure 1. FT-IR spectrum versus time for cyclization of P_3* catalyzed by tetrabutylammonium bibenzoate.

Table I
Termination Kinetics of Group Transfer Oligomers Based on FT-IR Spectroscopy[a]

reaction conditions	rate of cyclic ketone formation,[b] L mol^{-1} s^{-1}	rate of living end loss,[c] L mol^{-1} s^{-1}
2:1 MMA:P_1*[d]	0.008	0.011
3:1 MMA:P_1*[d]	0.009	0.010
0.25 M P_3*		0.062

[a] THF, 25 °C, 0.0125 M TBABB. [b] Based on growth of $\nu_{C=O}$ at 1716 cm^{-1}. [c] Based on decrease of $\nu_{C=C}$ at 1687 cm^{-1}. [d] $[P_1^*]_0$ = 0.25 M.

concentration–time profiles. The agreement between rate determinations based on living end disappearance (column 3 in Table I) and cyclic ketone formation (column 2) indicates that the primary mode of termination in GTP is cyclization.

Catalyst Effect

Using stopped-flow FT-IR, relative rates of cyclization for an oligomer mixture prepared from 10:1, MMA:P_1* were determined using two different catalysts. The MMA and P_1* were mixed and allowed to age in the IR cell until the MMA had been completely consumed. Then, spectra were taken to monitor the decrease in the area of the $\nu_{C=C}$ peak at 1687 cm^{-1}; from this, the cyclization rate for the mixture of living oligomers could be determined. Based on this method and using the same reaction conditions for each catalyst, TBABB catalysis was compared with tris(piperidino)sulfonium bifluoride ($TPSHF_2$) catalysis. From the data in Table II, it is clear that bifluoride is a more effective catalyst for termination relative to bibenzoate. This relative effectiveness of these two catalysts parallels their ability to promote MMA addition in GTP.[5,6]

Oligomer Distributions

At 2 min after addition of MMA, GPC analysis revealed the presence of linear oligomers up to dp = 12, and a small amount of the cyclic oligomer, P_3^c, was also present. The final composition (24 h) consisted of only cyclic oligomers (see Figure 2). It is evident from Figure 2 that the ultimate fate of all oligomers is cyclization. However, based on mass balance, the product composition for aliquots removed over a 24-h period also revealed disproportionate formation of P_3^c. The initial distribution of linear oligomers is in equilibrium because the mass of some oligomers is not preserved with respect to conversion to their corresponding cyclic forms. The data in Table III show the composition profiles at two times for the same oligomer mixture. In column 2 is the initial linear oligomer distribution, and in column 3 is the final distribution of cyclic oligomers (the same aliquots whose GPC analyses are shown in Figure 2). For linear oligomers with dp = 4–9, there is a net loss of mass balance. Mass balance can be largely accounted for by the mass increase observed for P_3^c. This shift is best explained by *depropagation of living*

Table II
Termination Rates for an Oligomer Mixture Prepared from 10:1 MMA:P_1*[a]

catalyst (concn, M)	rate,[b] L mol^{-1} s^{-1}
TBABB (0.0053)	0.0018
$TPSHF_2$ (0.001)	13.0

[a] $[MMA]_0$ = 1.0 M, $[P_1^*]_0$ = 0.1 M, THF, 25 °C. [b] Rate = k_{app}/[cat].

Table III
Composition of 3:1 MMA:P_1* Reaction Mixture[a]

n	mol of P_n at 2 min[b]	mol of P_n^c at 1300 min[c]	Δ mol (P_n^c – P_n)
2	0.03		−0.03
3	0.064	0.161	+0.101
4	0.041	0.012	−0.029
5	0.028	0.013	−0.011
6	0.023	0.012	−0.011
7	0.018	0.011	−0.007
8	0.012	0.009	−0.003
9	0.008	0.007	−0.001
10	0.005	0.005	0.00
11	0.003	0.003	0.00
12	0.002	0.002	0.00

[a] 25 °C. [b] At 2 min, only one cyclic product is present; 0.018 mol of P_3^c. [c] At 1300 min, there are no linear oligomers remaining.

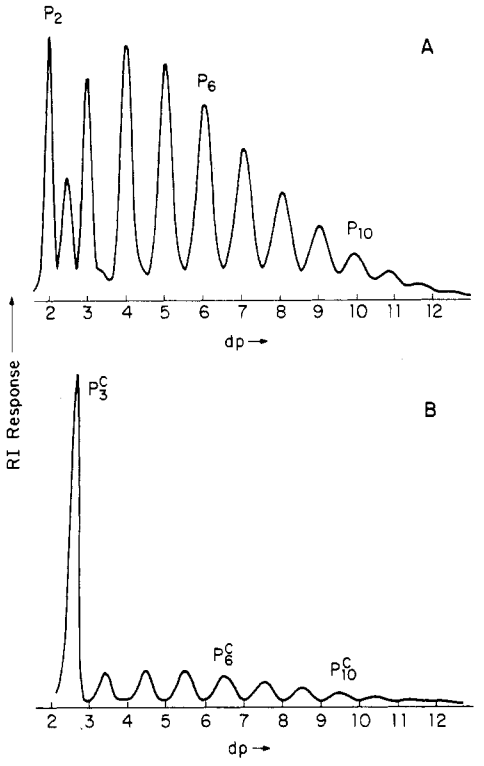


Figure 2. Gel permeation chromatographs of quenched aliquots from 3:1 MMA:P_1* reaction: (A) reaction time = 2 min, (B) reaction time = 1300 min.

Table IV
Comparison of Group Transfer to Anionic Polymerization at 25 °C in THF

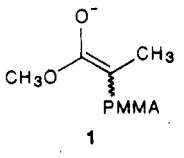
end group	k_p^2/k_c^3, mol L^{-1}
lithium ester enolate[a]	8
silyl ketene acetal[b]	250[c]

[a] $[MMA]_0$ = 0.1 M, $[MIB–Li]_0$ = 0.05 M; see ref 7. [b] [TBABB] = 0.0125 M, $[P_3*]_0$ = 0.25 M, $[MMA]_0$ = 0.125 M. [c] k_p^2 taken from ref 5.

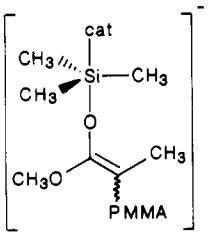
oligomers. Depropagation was also reported for the lithium ester enolate analogues (anionic polymerization).[7] Based on product compositions determined at different times, concentration time profiles were constructed for formation of several cyclic oligomers P_n[c]. From these profiles, rates of cyclization were estimated for the formation of these species. Comparison to the discrete cyclization rate for P_3* in Table I revealed that cyclization of P_3* is at least an order of magnitude faster than cyclization of higher oligomers. The higher rate of cyclization for P_3* is a reflection of greater steric hindrance to cyclization in the higher oligomers.

Discussion

The results demonstrate that cyclization is the primary mode of termination in GTP. No evidence was obtained for any other type of termination process. It is instructive to compare these results for termination in GTP to similar work on the organolithium-initiated oligomerization of MMA where the major termination pathway was also shown to be cyclization.[7] Table IV gives the ratio of k_p^2 (the rate of MMA addition to P_3*) to k_c^3 (the rate of cyclization of P_3*). The ratio of propagation to termination depends on the concentration of MMA because the overall reaction order is different for the two processes. As the MMA concentration decreases, so does the rate ratio: k_p^2/k_c^3. At sufficiently low enough MMA concentration, cyclization actually becomes faster than propagation. A comparison of relative rates of propagation and termination for the two polymerization processes shows that GTP has a markedly lower propensity to terminate versus propagate. This provides the first quantitative information supporting the qualitative observation that GTP is a more living process than anionic polymerization at room temperature. This difference in relative rates may be a reflection of different transition states for cyclization. In anionic polymerization, the cyclization is known to occur via an ionic intermediate (structure 1). However, in GTP,



1



2

it is not possible to clearly distinguish between a transition state which involves a dissociated intermediate akin to that in anionic polymerization (1) or an associated intermediate like pentavalent silicon structure 2. It is plausible that 2 retains high reactivity to monomer addition (propagation) while having a lower tendency to undergo cyclization.

The ratio of 250 for propagation/termination given in Table IV is a lower limit for GTP under the reaction conditions we used here. The rate of propagation remains constant with increasing chain length,[5] while the cyclization rate decreases slightly with chain length. For oligomers whose dp > 3, the ratio of propagation/termination will be greater than 2500.

Conclusions

By use of product analysis and in situ spectroscopic observation, cyclization has been identified as the major, if not sole, termination pathway in group transfer polymerization. The rate of cyclization decreases with the chain length of the oligomer. The ratio of propagation to termination is much higher for GTP than for anionic polymerization. The rate of termination is faster for oligomers in the presence of a bifluoride catalyst relative to bibenzoate. Detailed product analysis has revealed that depropagation of GTP oligomers occurs for an oligomer mixture prepared from 3:1 MMA:P_1* with a disproportionate formation of P_3[c].

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Registry No. MMA, 80-62-6; P_1*, 31469-15-5.

References and Notes

(1) (a) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; Rajanbabu, T. V. *J. Macromol. Sci., Chem.* **1984**, *A21*(8, 9), 943. (b) Sogah, D. Y.; Hertler, W. R.; Webster, O. W.; Cohen, G. W. *Macromolecules* **1987**, *20*, 1473–1488, references cited therein.
(2) 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) Sogah, D. Y.; Farnham, W. B. *Organosilicon and Bioorganosilicon Chemistry: Structures, Bonding, Reactivity and Synthetic Application*; Sakurai, H., Ed.; Wiley: New York, 1985; Chapter 20.
(4) Ainsworth, C.; Chen, F.; Kuo, Y. N. *J. Organomet. Chem.* **1972**, *46*, 59.
(5) Brittain, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 7440–7444.
(6) Dicker, I. B.; Cohen, G. M.; Farnham, W. B.; Hertler, W. B.; Laganis, E. D.; Sogah, D. Y., submitted for publication in *Macromolecules*.
(7) Müller, A. H. E.; Lochman, L.; Trekoval, J. *Makromol. Chem.* **1986**, *187*, 1473–1482.
(8) (a) Lochman, L.; Trekoval, J.; Müller, A. H. E. *Makromol. Chem.* **1984**, *185*, 1819–1826. (b) Adler, H. J.; Lochman, L.; Pokorny, S.; Berger, W.; Trekoval, J. *Makromol. Chem.* **1982**, *183*, 2901–2912.
(9) (a) Tsvetanov, C. B.; Müller, A. H. E.; Schulz, G. V. *Macromolecules* **1985**, *18*, 863–868. (b) Warzelhan, V.; Höcker, H.; Schulz, G. V. *Makromol. Chem.* **1978**, *179*, 2221–2240.