Macromolecules 1990, *23*, 4042-4046

Cationic Polymerization of Tetrahydrofuran Initiated by Trimethylsilyl Trifluoromethanesulfonate

Jeffrey S. Hrkach and Krzysztof Matyjaszewski*

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Ave., Pittsburgh, Pennsylvania 15213

Received December 5, 1989; Revised Manuscript Received February 21, 1990

ABSTRACT: The initiation of the cationic ring-opening polymerization of tetrahydrofuran by trimethylsilyl trifluoromethanesulfonate has been investigated by ^{1}H NMR and ^{19}F NMR. These studies indicate that the formation of the 1-(trimethylsilyl)tetrahydrofuranium cation is reversible due to a fast exchange process. Equilibrium constants K = 1.5 L/mol in CD_2Cl_2 at 25 °C for this reaction have been calculated from the NMR data. A series of MNDO calculations for various tetrahydrofuranium cations indicate that charge is mostly located on the silyl moiety. Grafting of poly(tetrahydrofuran) side chains from poly(phenylmethylsilylene) containing a few trifluoromethanesulfonate groups has been studied. Grafting has been confirmed by a strong change of molecular weight of a copolymer before and after photochemical degradation of a polysilane backbone.

Introduction

The cationic ring-opening polymerization of tetrahydrofuran (THF, **1**) can be initiated by strong protonic acids such as trifluoromethanesulfonic, perchloric, chlorosulfonic, and fuming sulfuric acid and heteropolyacids.[1-3] It can also be initiated by various Lewis acids such as phosphorous pentafluoride, antimony pentafluoride, or boron trifluoride (coinitiators are required for the last system), by esters of strong acids, by carbenium salts, by onium salts, etc.[1,2]

Recently, various alkenes and heterocyclics were cationically polymerized in the presence of trimethylsilyl trifluoromethanesulfonate (TMSOTf, **2**).[4] This initiator has not been, however, very successful in the cationic polymerization of lactones.[5] We also found that the polymerization of styrenes is, in fact, initiated not by silyl triflate but by triflic acid, which is a product of hydrolysis of silyl triflate.[6] Nevertheless, there are a number of reports which describe effective cleavage of esters and ethers by silyl esters and halides.[7,8] We are interested in the formation of graft copolymers from polysilanes, and the initiation of THF polymerization by TMSOTf can be considered the model study of the grafting process.[9] Polymerization of THF in the presence of triflate anions proceeds as a process without termination and transfer and can potentially lead to well-defined graft copolymers.

Below we describe the results of the polymerization of THF initiated by TMSOTf and discuss the possible application of this system to the preparation of graft copolymers.

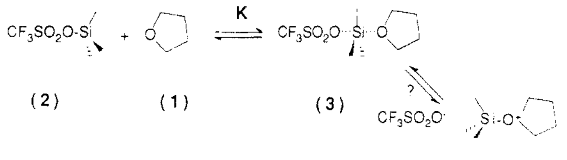
Experimental Section

Tetrahydrofuran was distilled and dried over calcium hydride prior to use. Trimethylsilyl triflate and 2,6-di-*tert*-butylpyridine were stored over calcium hydride. NMR tubes were prepared in a drybox (Model HE-493, Vacuum Atmospheres Co.) under inert atmosphere, capped with rubber septa, and sealed with Teflon tape. Subsequent additions to the tubes were made via syringe. NMR data were obtained from an IBM NR/300 300-MHz FTNMR spectrometer or a GE-300 300-MHz FTNMR spectrometer. Poly(phenylmethylsilylene) was synthesized from phenylmethyldichlorosilane and a sodium dispersion by using an immersion-type ultrasonic probe (W-140, Heat Systems-Ultrasonics, Inc.).[10] Grafting experiments were carried out on a high-vacuum line equipped with a mercury diffusion pump. Molecular weights and polydispersities for all polymers were calculated by using a Waters 510 gel permeation chromatograph equipped with a 450 variable-wavelength detector and a 410 differential refractometer. The columns used were Ultrastyragel Linear, 10^3 and 10^2 Å, arranged in series. Calibration was based on polystyrene standards. The solvent used was THF.

Results and Discussion

Initiation Step. Electrophilic species interact with a THF molecule to form complexes (e.g., BF_3) or corresponding tetrahydrofuranium ions (ethyl triflate, triethyloxonium salts, carbenium ions).[2] Silyl esters do not, however, interact strongly enough with esters and ethers to form oxonium ions. They form rather loose complexes, although it has been reported that trimethylsilyl and triphenylsilyl perchlorate are ionized in sulfolane and acetonitrile solution.[11,12] This could suggest that sulfolane or acetonitrile is silylated, because silylenium ions are extremely reactive, and silicon prefers to expand its valence to a penta- or hexacoordinated state rather than to reduce it to a trivalent silylenium species.[13]

^{1}H NMR studies have shown that the signals of the α- and β-methylene protons of THF shift upfield upon addition of TMSOTf. At the same time, the signal of TMSOTf is slightly broadened without significant shift. The gradual increase of the THF signals allows estimation of the equilibrium constant between THF and TMSOTf.



(1)

Independent of the state of ionization of the complex between THF (**1**) and TMSOTf (**2**), the following equation is valid for large excess of TMSOTf over complex **3**:

$$K = [\mathbf{3}]/([\mathbf{1}][\mathbf{2}]) = [\mathbf{3}]/(([\mathbf{1}]_0 - [\mathbf{3}])([\mathbf{2}]_0 - [\mathbf{3}])) \cong [\mathbf{3}]/(([\mathbf{1}]_0 - [\mathbf{3}])[\mathbf{2}]_0) \quad (2)$$

Therefore, the concentration of the complex equals

$$[\mathbf{3}] = (K[\mathbf{1}]_0[\mathbf{2}]_0)/(1 + K[\mathbf{2}]_0) \quad (3)$$

The chemical shift of the rapidly exchanging THF and complex molecules is the weighted average of both species:

0024-9297/90/2223-4042$02.50/0

Table I
Charge Distributions and Bond Lengths for a Series of Tetrahydrofuranium Cationic Species (R–THF$^+$) by MNDO Calculations

	charge distribution, %				bond length, Å	
R	O	C_{endo}	C_{exo}	ring	O–C_{endo}	O–C_{exo}
	−32.2	15.1		0	1.409	
H	−15.7	16.5		68.3	1.4714	0.962
Me	−24.0	18.5	22.8	58.8	1.4722	1.460
t-Bu	−23.5	17.8	11.9	54.5	1.4721	1.509
MeOC[a]	−27.6	18.0	39.3	50.7	1.467	1.512
TMS	−34.3	15.7	81.7[c]	34.3	1.446	1.854
TSiS[b]	−31.8	15.4	20.9[c]	36.5	1.445	1.828

[a] Methoxymethyl (CH_3OCH_2). [b] Trisilylsilyl ($(SiH_3)_3Si$). [c] Charge on the α-Si atom.

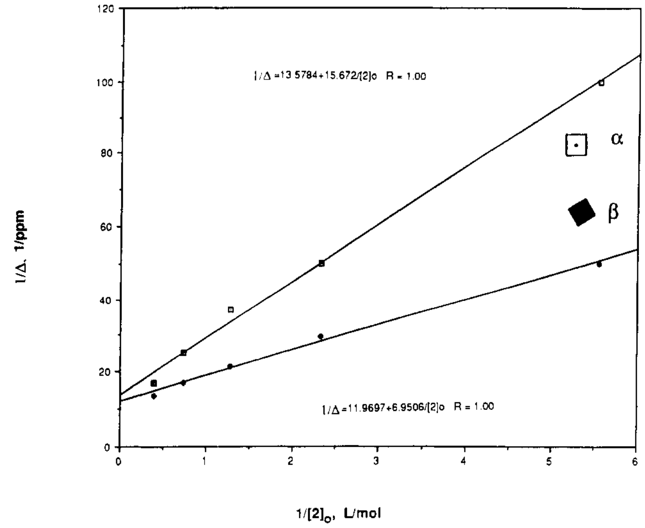


Figure 1. Dependence of THF chemical shifts on [TMSOTf]: $[TMSOTf]_0$ = from 0.1 to 2.5 M; $[THF]_0$ = 0.02 M; [2,6-di-*tert*-butylpyridine]$_0$ = 0.45 M in CD_3NO_2 at 22 °C.

$$\delta^{av}[1]_0 = \delta_1([1]_0 - [3]) + \delta_3[3] \qquad (4)$$

Remembering that $\Delta^{max} = \delta_3 - \delta_1$, the observed downfield shift (Δ) equals

$$\Delta = \delta^{av} - \delta_1 = (\delta_3 - \delta_1)[3]/[1]_0 = \Delta^{max}[3]/[1]_0 \qquad (5)$$

Combination of eqs 3 and 5 leads to

$$1/\Delta = 1/(K\Delta^{max}[2]_0) + 1/\Delta^{max} \qquad (6)$$

Figure 1 shows the plot of $1/\Delta$ versus $1/[2]_0$. The slope and intercept give both unknown values K = 1.5 L/mol and Δ^{max} = 0.084 and 0.074 ppm for α- and β-methylene protons, respectively. The larger shift for the α-methylene group is due to a larger increase of the positive charge. Observation of only one average signal for complexed and free species at room temperature as well as at low temperature indicates a very rapid exchange process.

At this point, a comparison can be made to the polymerization of THF initiated by methyl trifluoromethanesulfonate (methyl triflate, MeOTf). The Δ values for the α- and β-methylene protons in this system are 1.29 and 0.65 ppm, respectively.[15] The larger Δ values indicate that the amount of positive charge on the endocyclic carbon atoms is much greater than in the TMSOTf system (see Table I). This is reflected in the faster initiation rates for this system relative to the TMSOTf system.

Another method of investigating the nature of the interactions between THF and TMSOTf is ^{19}F NMR. Triflate anion absorbs at −78.1 ppm whereas covalent alkyl triflates absorb at −74.3 ppm in CD_3NO_2. As seen in parts a and b of Figure 2, the chemical shift of TMSOTf increases slightly in the presence of THF from −77.8 to −78.1 ppm. This would indicate very strong polarization of the Si–O bond in the silyl ester. On the other hand, ^{29}Si NMR spectroscopy of TMSOTf indicates that this compound is tetracoordinated and not tricoordinated like the silylenium cations. Figure 2c shows the ^{19}F NMR spectrum of the reaction mixture after the addition of methyl triflate. After 5 min, unreacted methyl triflate was still observed along with the 1-methyltetrahydrofuranium cation. The anion in this species and 2 could not be distinguished although the signal at −78.1 ppm became broader. Thus, the conclusion from the initiation studies is that silyl triflate interacts with THF molecules weakly but exchanges very rapidly, since only one average signal of THF in ^1H NMR is observed at 2:1 and higher $[THF]_0/[TMSOTf]_0$ ratios. Similar results were obtained in less polar solvents such as methylene dichloride and chloroform. The signal of TMSOTf could not be distinguished from the signal of triflate anion. This also indicates that TMSOTf must be very rapidly attacked by any triflate anion, since it is not itself ionized. Thus, the

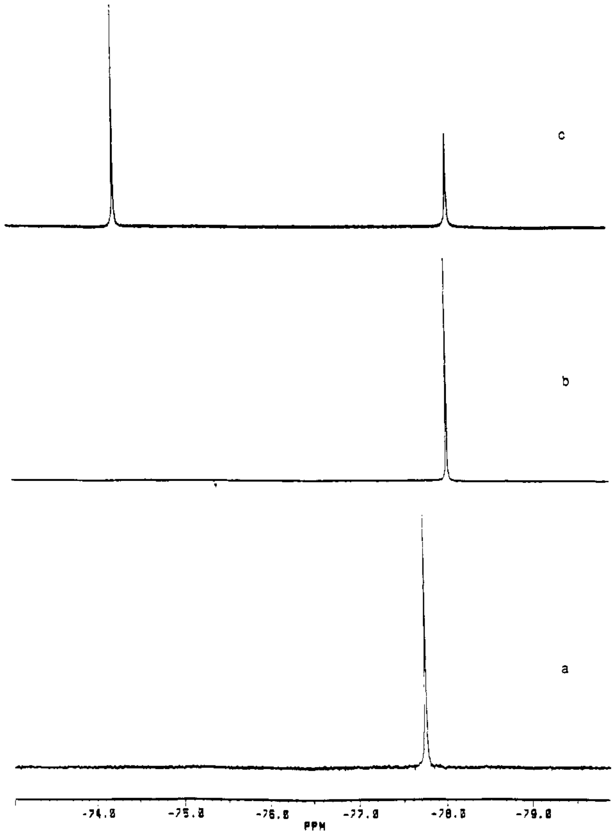
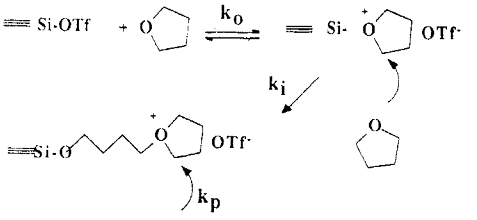


Figure 2. ^{19}F NMR spectra: (a) TMSOTf in CD_3NO_2; (b) 5 min after addition of THF (2 equiv); (c) 5 min after addition of MeOTf. $[TMSOTf]_0$ = 0.55 M, $[THF]_0$ = 1.1 M, and $[MeOTf]_0$ = 0.55 M in CD_3NO_2 at 22 °C.

equilibrium between different species is established very fast, similar to protonic acids. This is another example of the similarity between protons and trimethylsilyl species, which are called "bulky protons".[14]

MNDO Calculations for Various Tetrahydrofuranium Cations. The MNDO method was used to calculate structures of tetrahydrofuranium cations with various alkyl and silyl moieties. Semiempirical calculations refer to molecules in the gas phase; therefore, no solvation is taken into account. Solvation does play a very important role, however, especially for ionic species. Nevertheless, the MNDO method may give an approximate idea of the structure, charge distribution, and bond orders in the molecule of interest, especially when compounds in a homologous series are investigated.

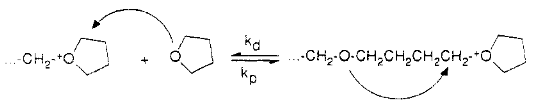
The calculations (cf. Table I) show that in all cations there is considerable loosening in the C_{endo}–O bond which is broken in the ring-opening process. However, the increase of the bond length is much smaller for silyl cations, 0.046 Å, than for alkylated or protonated species, approximately 0.07 Å. Charge distributions also indicate that attack of a monomer on the endocyclic carbon atom should be less likely for silyl cations than for alkyl cations. The percent positive charge on C_{endo} for methylated and protonated species is 18.5% and 16.5%, respectively. For the trimethylsilylated species, however, the percent positive charge is only 15.7%. This explains why initiation is so slow for TMSOTf. The rate-limiting step in the initiation process is not the transfer of the TMS group from TMSOTf to THF (which is very fast and reversible, k_0) but the ring opening of the first silyltetrahydrofuranium cation. The subsequent opening of the 1-alkyltetrahydrofuranium cation should not be affected by the remote silyl end group and should occur with the rate constant close to the propagation rate constant.



(7)

Polymerization Studies. Polymerization of THF is a reversible process which is controlled by temperature and monomer concentration. This is due to the small strain in the five-membered ring. At 25 °C, the monomer equilibrium concentration in bulk equals $[M]_e = 3.1$ mol/L, but it increases in CH_2Cl_2 or $CHCl_3$ solutions up to $[M]_e = 5.1$ mol/L at $[M]_0 = 8.0$ mol/L.[15] This big change originates in the strong interactions between nucleophilic THF and electrophilic chlorinated solvents. Thus, at THF concentrations of $[M]_0 < 2$ mol/L polymerization is not possible, and initiation can be studied alone. Polymerization requires at least 50 vol % THF at room temperature.

Typically, polymerization proceeds by the attack of a monomer on the endocyclic carbon atom in the growing tetrahydrofuranium ion with a rate constant of propagation k_p:



(8)

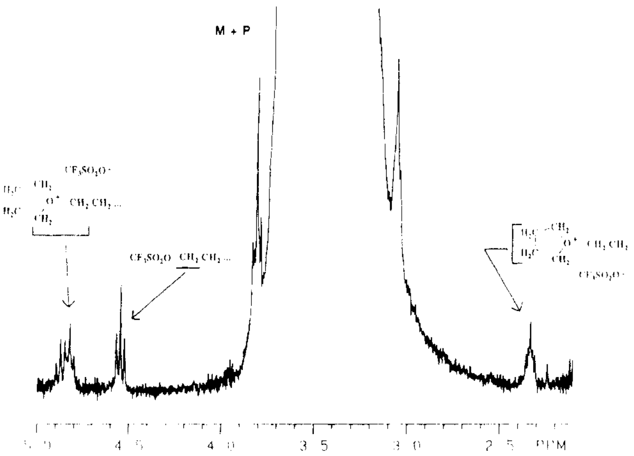
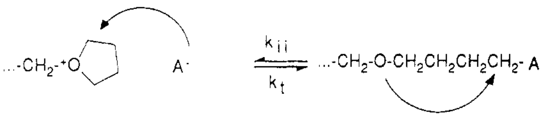


Figure 3. ^{1}H NMR spectrum of the active species in the polymerization of THF by TMSOTf: $[TMSOTf]_0 = 0.1$ M; $[THF]_0 = 8.0$ M in CD_2Cl_2 at 22 °C, sealed tube.

The reversible depropagation reaction proceeds with a rate constant k_d. The ratio of these rate constants is equal to the reciprocal of the monomer equilibrium concentration $k_p/k_\alpha = 1/[M]_e$. The reaction in eq 8 is the only reaction with complex counterions. When the counterion is capable of forming covalent bonds, the ionic active species are in equilibrium with covalent species. This is the case for trifluoromethanesulfonate anions. The equilibrium position depends strongly on the polarity of the reaction medium and on temperature. Ionization is exothermic and favored in more polar solvents. In methylene dichloride, nearly equal proportions of ions and esters are present. In nitromethane, practically only ions (95%) are present[15]



(9)

At the initiation stage, the equilibrium position is strongly influenced by the exocyclic groups, but after initiation is completed the initiator residue will have a minor influence on the equilibrium. Propagating ions and esters were directly observed by NMR at the later stages of polymerization. The proportions of both species were calculated from the integration of signals at 4.85 ppm (six α-endocyclic and α-exocyclic protons in the oxonium ion) and at 4.56 ppm (two α-methylene protons in the ester) (cf. Figure 3). The integration of the signals of the unreacted TMSOTf (0.5 ppm) to the trimethylsilylalkoxy end groups gave the proportion of the reacted initiator. There are four signals in the end group region (cf. Figure 4). The most shielded one is due to hexamethyldisiloxane, which is formed by hydrolysis of TMSOTf. It was identified by the addition of a pure sample of hexamethyldisiloxane. This signal is quite small in the experiments run in NMR tubes sealed under vacuum, but it gradually increases in tubes sealed with rubber septa. Trifluoromethanesulfonic acid is the additional product of hydrolysis. It alone can initiate polymerization of THF. Hindered pyridine (2,6-di-*tert*-butylpyridine) was added to prevent initiation with the acid. The pyridine reacts only with protons and does not react with either silyl triflate or the growing tetrahydrofuranium ions. Polymerization proceeds smoothly in the presence of the hindered pyridine. The origin of the other three singlets is not precisely known. The intensity of the middle singlet increases with conversion, and therefore it can be assigned to the terminal end group of chains with a degree of polymerization higher than three. The other signals may correspond to oligomers with a degree of polymerization of three, two, or one (open chain ester).

The signal of TMSOTf is very broad, because it exchanges with oxygen atoms in monomer and polymer molecules. Initiation with TMSOTf is very slow. Rate constants of initiation were calculated from the change of the NMR spectra and confirmed by the kinetics of the monomer consumption. The slope of the curve describing monomer conversion in semilogarithmic coordinates is equal to the product of the apparent rate constant, k_p^{app}, and concentration of active sites ([AC], i.e., reacted initiator). One must remember that covalent species are much less active than oxonium ions; therefore the slope equals the product of the rate constant of ionic propagation, k_p^{i}, and concentration of oxonium ions, [Ox]:

$$-\mathrm{d}\ln[\mathrm{M}]/\mathrm{d}t = k_p^{obs}[\mathrm{I}]_0 = k_p^{app}[\mathrm{AC}] \approx k_p^{i}[\mathrm{Ox}] \qquad (10)$$

Because rate constants of ionic propagation as well as apparent rate constants of propagation with triflate anions are known for various solvents,[2,15] it is very easy to calculate the proportion of the consumed initiator:

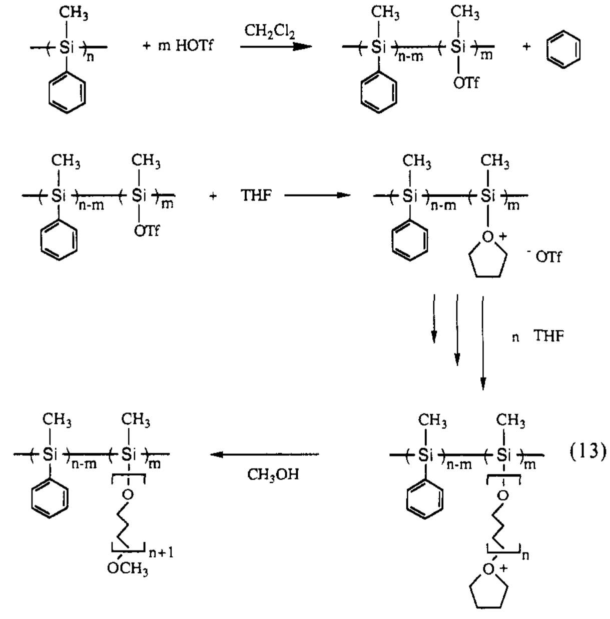
$$([\mathrm{I}]_0 - [\mathrm{I}])/[\mathrm{I}]_0 = k_p^{obs}/k_p^{app} \qquad (11)$$

Then, rate constants of initiation are calculated graphically from the equation

$$-\mathrm{d}\ln[\mathrm{I}]/\mathrm{d}t = k_i\int[\mathrm{M}]\,\mathrm{d}t \qquad (12)$$

In solvents of medium polarity, CH_2Cl_2 and $CHCl_3$, at 20 °C the rate constants of initiation with TMSOTf ($k_i \approx 10^{-6}$ mol^{-1}·L·s^{-1}) are much lower than with alkyl triflates ($k_i \approx 10^{-4}$ mol^{-1}·L·s^{-1}). This is in agreement with the observed small downfield shift in the silylated tetrahydrofuranium species and semiempirical calculations of charge distribution and calculated bond loosening in cations.

Grafting from Polysilanes. As stated previously, our main interest is in the grafting of THF from poly(phenylmethylsilylene) (PSI). The calculations showed that the charge distribution and bond lengths in the tetrahydrofuranium cation based on the trimethylsilyl and polysilyl species are similar and that the initiation rate constants could be similar in both cases. The general scheme for the grafting process is as follows:



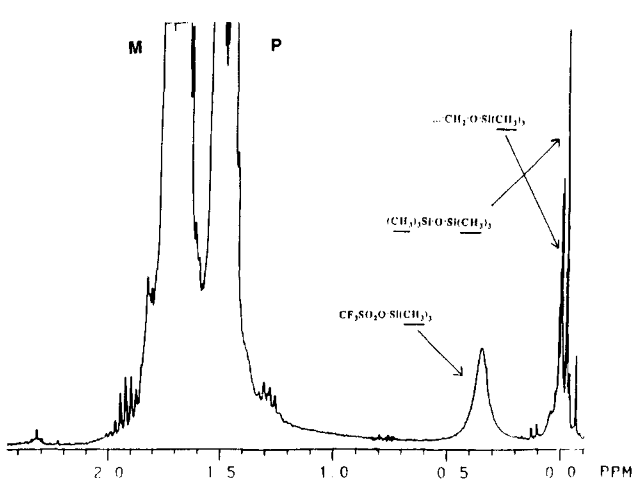


Figure 4. ^{1}H NMR spectrum of the silyl species in the polymerization of THF by TMSOTf: $[\mathrm{TMSOTf}]_0$ = 0.1 M; $[\mathrm{THF}]_0$ = 8.0 M in CD_2Cl_2 at 22 °C, sealed tube.

In a typical experiment, trifluoromethanesulfonic acid (HOTf) is added to a solution of low molecular weight (approximately 2000, DP = 17) poly(phenylmethylsilylene) in methylene chloride on a high vacuum line. The mole ratio of silylene units of PSI to HOTf is 5:1. Low molecular weight poly(phenylmethylsilylene) is used so that the change in molecular weight upon grafting can be easily detected by GPC. The purpose of the HOTf is to displace a portion, theoretically 20% or 3.4 per PSI chain, of the phenyl groups from poly(phenylmethylsilylene) yielding partially triflated poly(phenylmethylsilylene) and benzene as the side product. This reaction is fast and quantitative.[16] Next, THF is distilled into the reaction mixture. The theoretical mole ratio of THF to activated triflate sites on the polymer chain is 180:1. Due to the equilibrium monomer concentration of THF under these conditions, however, the actual polymerization ratio is 80:1. From the above mole ratios, the graft product should contain 3.4 polyTHF chains with DP = 80 per PSI chain, yielding a molecular weight of 22 000. The first step of this reaction involves the attack of THF on the triflated silicon atoms of the polymer chain forming poly(silyltetrahydrofuranium) cations. Further attack by THF leads to the propagation of the poly(tetrahydrofuran) chain. As with the TMSOTf system, the attack of the second THF molecule on the poly(silyltetrahydrofuranium) species is expected to be slow due to the distribution of the positive charge. The reaction is terminated after the required time with an excess of methanol.

Successful grafting has been confirmed by GPC analysis. A comparison of the UV response of the original low molecular weight poly(phenylmethylsilylene) (Figure 5a) to that of the graft product (Figure 5b) indicates a large increase in molecular weight. The M_n for the original low molecular weight poly(phenylmethylsilylene) is 2000, whereas the M_n for the high molecular weight peak in Figure 5b is 81 000. The high molecular weight peak represents only 40% of the total peak area in Figure 5b. This, along with the presence of a low molecular weight peak of approximate M_n = 2000, indicates that a major portion of the original low molecular weight poly(phenylmethylsilylene) remains unreacted. A corresponding high molecular weight peak with M_n = 81 000 detected by the differential refratometer (RI) indicates the incorporation of poly(tetrahydrofuran) in the graft product. Further evidence of grafting is seen in Figure 5c, which shows the RI response of homopoly(tetrahydrofuran) obtained after the degradation of the poly(phenylmethylsilylene) backbone by UV irradiation. The decrease in molecular weight to approximately 40 000 indicates the loss of the poly(phenylmethylsilylene) backbone and the presence of independent poly(tetrahydrofuran) chains. The decrease shows that the average

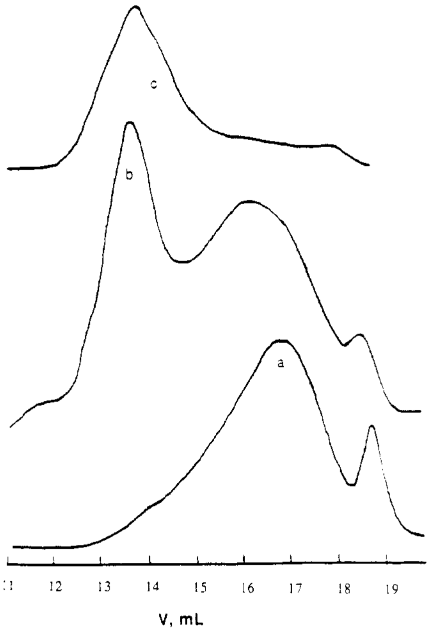


Figure 5. Gel permeation chromatograms: (a) low molecular weight poly(phenylmethylsilylene) (UV response); (b) poly(phenylmethylsilylene)-*graft*-poly(tetrahydrofuran) (UV response); (c) homopoly(tetrahydrofuran) after UV degradation of poly(phenylmethylsilylene) backbone (RI response). Grafting conditions: $[PSI]_0 = 0.25$ M; $[HOTf]_0 = 0.05$ M; $[THF]_0 = 9.0$ M in CH_2Cl_2 at 25 °C. See text for details.

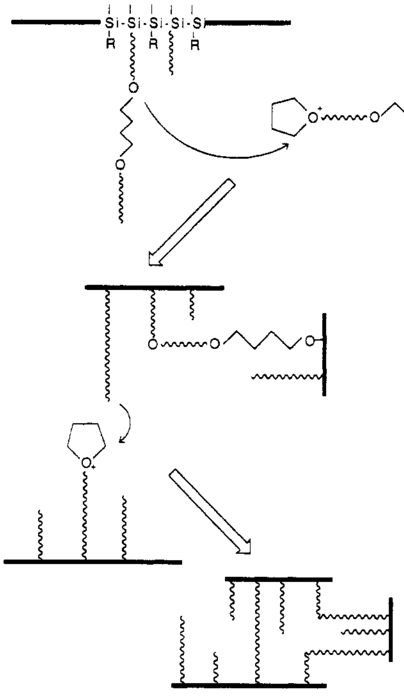
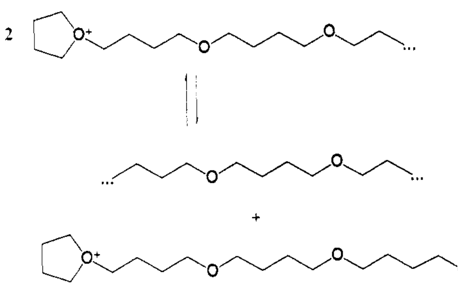


Figure 6. Simplified gelation scheme for the grafting of THF from poly(phenylmethylsilylene).

number of poly(tetrahydrofuran) chains per poly(phenylmethylsilylene) chain is 2, not 3.4 as calculated from the experimental mole ratios. Molecular weights of the graft product were higher than expected, and the molecular weight distributions were very broad. This can be explained by incomplete triflation of PSI along with slow initiation in THF polymerization.

Polymerization of THF is accompanied by very slow transfer to polymer (etheral oxygen atoms) by the formation of acyclic oxonium ions. These ions disproportionate by cleavage in either direction to give a mixture of ungrafted chains with two living ends and temporarily dead polyether segments which are grafted at both ends to polysilylene chains. For chains growing in one direction, this reaction leads to the additional formation of a mixture of chains growing in two directions and inactive chains:



(14)

For polysilanes having more than one poly(tetrahydrofuran) branch, a gelation is expected (cf. Figure 6). The initiation step from polysilanes must have been also very slow since no gelation was observed. This indicates that although up to five poly(tetrahydrofuran) chains could grow from one polysilane backbone, no more than two sites were activated during the time required for the completion of the polymerization. However, after a few days some precipitate was found. It should correspond to the discussed cross-linked copolymer.

It can be concluded from our studies that TMSOTf can initiate the polymerization of THF, although this system is limited by the exchange process at the early stages of initiation. We have also demonstrated the successful grafting of THF from poly(phenylmethylsilylene). At present, the influence of several additives on the activation and acceleration of the initiation process is being studied.

Acknowledgment. The support of the National Science Foundation (DMR-8803774) is gratefully acknowledged. K.M. acknowledges support from a Presidential Young Investigator Award and matching funds from ARCO Chemicals, Eastman Kodak, Hoechst Celanese, PPG Industries, and Xerox Corp.

References and Notes

(1) Dreyfuss, P.; Dreyfuss, M. P. *Adv. Polym. Sci.* **1967**, *4*, 528.
(2) Penczek, S.; Kubisa, P.; Matyjaszewski, K. *Adv. Polym. Sci.* **1980**, *37*, 1.
(3) Bednarek, M.; Brzezinska, K.; Stasinski, J.; Kubisa, P.; Penczek, S. *Makromol. Chem.* **1989**, *190*, 929.
(4) (a) Gong, M. S., Hall, H. K., Jr. *Macromolecules* **1986**, *19*, 3011. (b) Hall, H. K., Jr.; Buyle Padias, A.; Atsumi, M.; Way, T. F. *Macromolecules* **1990**, *23*, 678.
(5) Dunsing, R.; Kricheldorf, H. R. *Eur. Polym. J.* **1988**, *24* (2), 145.
(6) Lin, C. H.; Matyjaszewski, K. *J. Polym. Sci., Polym. Chem. Ed.* **1990**, *28*, 1771.
(7) Emde, H.; Domsch, D.; Feger, H.; Frick, U.; Gotz, A.; Hergott, H. H.; Hofmann, K.; Kober, W.; Krageloh, K.; Oesterle, T.; Steppan, W.; West, W.; Simchen, G. *Synthesis* **1982**, 1.
(8) Ho, T. L.; Olah, G. A. *Angew. Chem.* **1976**, *88*, 847.
(9) Hrkach, J. S.; Ruehl, K. E.; Matyjaszewski, K. *Polymer Prepr.* **1988**, *29* (2), 112.
(10) Kim, H. K.; Matyjaszewski, K. *Polymer Prepr.* **1988**, *29* (1), 168.
(11) Lambert, J. B.; Schilf, W. *J. Am. Chem. Soc.* **1988**, *110*, 2201.
(12) Lambert, J. B.; Schilf, W. *J. Am. Chem. Soc.* **1988**, *110*, 6364.
(13) Bassindale, A. R.; Stout, T. *Tetrahedron Lett.* **1985**, *26*, 3403.
(14) Hwu, J. R.; Wetzel, J. M. *J. Org. Chem.* **1985**, *50*, 3946.
(15) Penczek, S.; Matyjaszewski, K. *J. Polym. Sci.* **1976**, *56*, 255.
(16) Matyjaszewski, K.; Chen, Y. L. *J. Organomet. Chem.* **1988**, *340*, 7.

Registry No. 1, 109-99-9; 1 (homopolymer), 24979-97-3; (1)-(phenylmethylsilylene) (graft copolymer), 128302-38-5; (2), 27607-77-8; HOTf, 1493-13-6; 1-(trimethylsilyl)tetrahydrofuranium, 128302-37-4; phenylmethylsilylene (homopolymer), 76188-55-1; dichloromethylphenylsilane (homopolymer), 31324-77-3.