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MODIFICATION OF POLYSILANES: PREPARATION OF COMB-LIKE GRAFT COPOLYMERS+

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ABSTRACT

Poly(methylphenylsilylene) has been functionalized by protodearylation with trifluoromethanesulfonic acid. Comb-like graft copolymers have been prepared by polymerizing tetrahydrofuran, 2-methyl-2-oxazoline, and isobutylvinyl ether from a partially triflated poly(methylphenylsilylene) backbone. Model studies using trimethylsilyl trifluoromethanesulfonate to initiate the cationic polymerization of these organic monomers indicated that a promoter was required to achieve more efficient initiation.

Key words: Polysilanes, polysilylenes, graft copolymers, functional polysilanes

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+ Dedicated to the memory of late Professor Zygmunt Lasocki, an outstanding organosilicon and polymer chemist

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INTRODUCTION

Polymers with inorganic elements (e.g. polysilanes, polysilazanes, polysiloxanes, polyphosphazenes) comprise an important and growing field of macromolecules due to their novel and exciting properties and applications [1,2]. Polysilanes (also called polysilylenes) are used commercially as precursors to ceramics, and can be applied as high quality photoresists, photoconductors and nonlinear optical materials [3-5]. They form an interesting class of polymers with a Si-Si sigma conjugated backbone. The most common method used to prepare polysilanes is the reductive coupling of disubstituted dichlorosilanes with molten sodium. Because of the severe reaction conditions involved with the reductive coupling, the selection of dichlorosilanes has mostly been limited to those with alkyl and aryl substituents. The incorporation of electron donating and/or withdrawing substituents, however, could significantly affect the electronic properties of polysilanes. In addition, the preparation of well-defined comb-like graft copolymers with a polysilane backbone and organic polymer side chains could lead to new and interesting morphologies based upon microphase separation due to the incompatibility of the inorganic and organic chains.

In this paper, we will present work done in our laboratories on the functionalization of polysilanes. We will focus on the modification of poly(methylphenylsilylene) with trifluoromethanesulfonic (triflic) acid to create polysilyl triflate moieties, the use of these triflate sites to initiate the polymerization of THF, 2-methyl-2-oxazoline, and isobutylvinyl ether to prepare comb-like graft copolymers, and the model studies conducted to optimize the grafting conditions.

SYNTHESIS OF POLYSILANES

As stated in the introduction, polysilanes are typically prepared by the reductive coupling of disubstituted dichlorosilanes with molten sodium in hydrocarbon solvents [3-5]. In addition to high polymer (molecular weight may exceed $M_n \approx 10^6$), lower molecular weight polymer ($M_n < 10^4$) and cyclics (Si_4 to Si_6) are formed. Some improvement in the selectivity of the formation of high polymer is possible by manipulation of the solvent, temperature, or reducing agent, and by the use of additives or sonication.

We have previously employed the use of sonication for the polymerization of methylphenyldichlorosilane [6]. Reductive coupling at ambient temperatures in the presence of ultrasound leads to monomodal polymers with relatively narrow molecular weight distributions (M_w/M_n from 1.2 to 1.5) and relatively high molecular weights (M_n from 50,000 to 100,000). The greater selectivity in this system can be explained by two phenomena. First, low molecular weight polymer (M_n from 2,000 - 10,000) which may be formed by transfer or termination side reactions is suppressed at the lower polymerization temperature. Second, ultrasound mechanically degrades higher molecular weight polysilanes, which can be involved in chain entanglement, but does not degrade lower molecular weight polymers. It should be noted that dialkyldichlorosilanes are not reactive enough to be polymerized at temperatures below 60^{o}C in non-polar solvents, but can be copolymerized with methylphenyldichlorosilane.

Aryl/alkyl substituted polysilanes can also be prepared by the ring opening polymerization of strained cyclotetrasilanes [7] as well as by the anionic polymerization of masked disilenes (adducts of disilenes to biphenyl) [8]. These routes are potentially more tolerant toward the nature of substituents, and polymers with cyano and alkoxy groups have been prepared by the ring opening process [9].

Another preparative method for polysilanes is based on the dehydrogenative coupling of primary silanes with organosubstituted derivatives of transition metals, e.g. Cp_2ZrX_2 [10]. In this reaction a polysilane with hydrido side groups is formed. An Si-H bond, in contrast to a C-H bond is quite reactive and various insertion, oxidation, and substitution reactions are possible.

Finally, polysilanes may be prepared by modification reactions. Severe conditions of the reductive coupling process can tolerate alkyl and aryl substituents. In some cases, dichlorosilanes with alkenyl [11-14] and ether groups have been successfully polymerized [15-22]. Polysilane homopolymers and copolymers of relatively high molecular weights (M_n>10,000) were prepared from compounds with vinyl [11], allyl [12], hexenyl [12], and cyclohexenyl substituents [13,14]. In some cases consumption of double bonds was noted, indicating that some of the double bonds were polymerized on the polysilane template. The soluble polymers, on standing, are converted to crosslinked materials even in the solid state and in the apparent absence of light. Although these reactions do not seem to be easily controlled, alkenyl groups could be used in addition and oxidation processes.

Polymers with ether side groups are hydrophilic and can be used for the preparation of orinted films by Langmuir-Blodgett technique [18]. Similar films can be prepared from polymers containing phenol groups, initially protected by tert-butyldimethylsilyl ether functionality [19-22]. Some of the simple aryl and alkyl substituents on polysilanes can be modified to allow the introduction of various functional groups to the polysilane backbone. The scope of this method is expanding and a few examples will be presented.

Aromatic rings can be used for electrophilic substitution reactions. For example, the phenyl groups of poly(β-phenethylmethylsilylene) has been chloromethylated with chloromethylmethyl ether catalyzed by $SnCl_4$ [23]. The chloromethyl groups has been subsequently converted to quaternary ammonium derivatives [24]. Electrophilic aromatic substitution is not highly chemoselective and is accompanied by the cleavage of Si-Si bonds which results in a decrease of molecular weights.

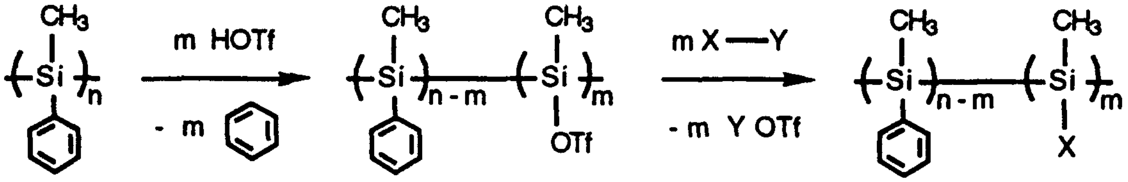
Halides cleave polysilane chains and form ...-SiR_2-SiR_2-X end-functionalized chains. The reaction of iodine and bromine with a high molecular weight polysilane produces lower molecular weight polymers with silyl iodide and bromide groups at the chain ends. These silyl halides can then be utilized to initiate the polymerization of organic monomers such as vinyl ethers and N-vinyl carbazole to produce ABA triblock copolymers. These reactions are currently being investigated in our laboratory.

PROTODEARYLATION OF POLYSILANES

Si-C bonds may be cleaved by strong acids and bases. The reaction between protonic acids and aryl substituted silanes is quite favorable [25]. It is well known in organosilicon chemistry as protodesilylation, although in macromolecular chemistry it is better defined as protodearylation (since the Si-Si skeleton usually stays intact). We have utilized the reaction of triflic acid with poly(methylphenylsilylene) to cleave various ratios of the phenyl groups from the polysilane backbone and produce electrophilic polysilyl triflate moieties.

In order to estimate chemoselectivities and regioselectivities in the protodearylation process we have studied the reaction between triflic acid and various permethylated α,ω-diphenyloligosilanes [26]. It was established that the presence of a triflate group at one chain end strongly reduces the reactivity of the second phenyl group at the other end. Seven-fold rate reduction was found even in the case of pentasilane. Thus, the protodearylation of poly(methylphenylsilylene) with triflic acid should produce silyl triflate sites that are spread along the chain, instead of being grouped close together. This arrangement should be helpful in the grafting of polymers from the polysilane backbone, since the side chains will be separated and the growth of the chain should not be hindered sterically or by side reactions between chains.

Silyl triflates are very reactive compounds in nucleophilic substitution reactions and has been used in our laboratories for the preparation of various alkoxy, amino, alkyl and aryl derivatives in the reaction with alcohols, amines, and organometallic derivatives, respectively [11,27]:



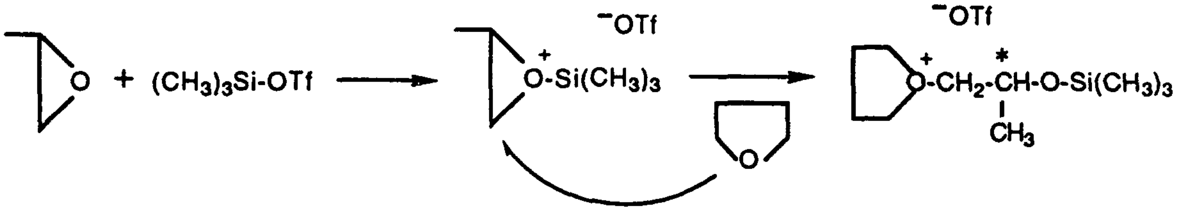
(1)

Similar reactions have been reported later for linear oligosilanes [28], polysilanes [29], as well as for branched "polysilynes" [30].

MODEL STUDIES AND GRAFTING

Silyl triflates can initiate the cationic polymerization of alkenes and heterocycles. They have been used in the polymerization of tetrahydrofuran (THF) [31,32], lactones [33], 2-methyl-2-oxazoline (MeOXZ) [34], and vinyl ethers [35-38].

We have studied the cationic ring opening polymerization of THF initiated by trimethylsilyl triflate (TMSOTf) as a model for the grafting of THF from the triflated sites of poly(methylphenylsilylene). The model polymerizations showed that TMSOTf is not an efficient initiator due to poor charge distribution in the trimethylsilyl-tetrahydrofuranium cation. Most of the positive charge is located on the exocyclic trimethylsilyl group. Therefore, subsequent THF molecules attack the silicon atom in a bimolecular exchange reaction instead of attacking the α-endocyclic carbon atom which would lead to ring opening. As a result, initiation is slow and results in broad polydispersities and polymers with molecular weights that are higher than expected from the ($[THF]_0$ - $[THF]_e$)/[TMSOTf] ratio. The use of 1,2-propylene oxide (PRO-OX) as a promoter along with TMSOTf for the polymerization of THF strongly accelerates initiation and, as can be seen in Table 1, leads to more narrow polydispersities and molecular weights that are much closer to the ($[THF]_0$ - $[THF]_e$)/[TMSOTf] ratio [39]. PRO-OX is not as nucleophilic as THF, so it should be used in excess of TMSOTf to facilitate its reaction with TMSOTf. The best [PRO-OX]/[TMSOTf] ratio found in these studies is 10:1 (see Table 1). The trimethylsilyl oxiranium ion formed by the reaction of PRO-OX and TMSOTf is much more reactive than the trimethylsilyltetrahydro-furanium cation, so attack by THF is much faster:



(2)

It is possible that the trimethylsilyl oxiranium ion is attacked by the triflate counterion to form the corresponding alkyl ester which is also capable of initiating the polymerization of THF.

Table 1

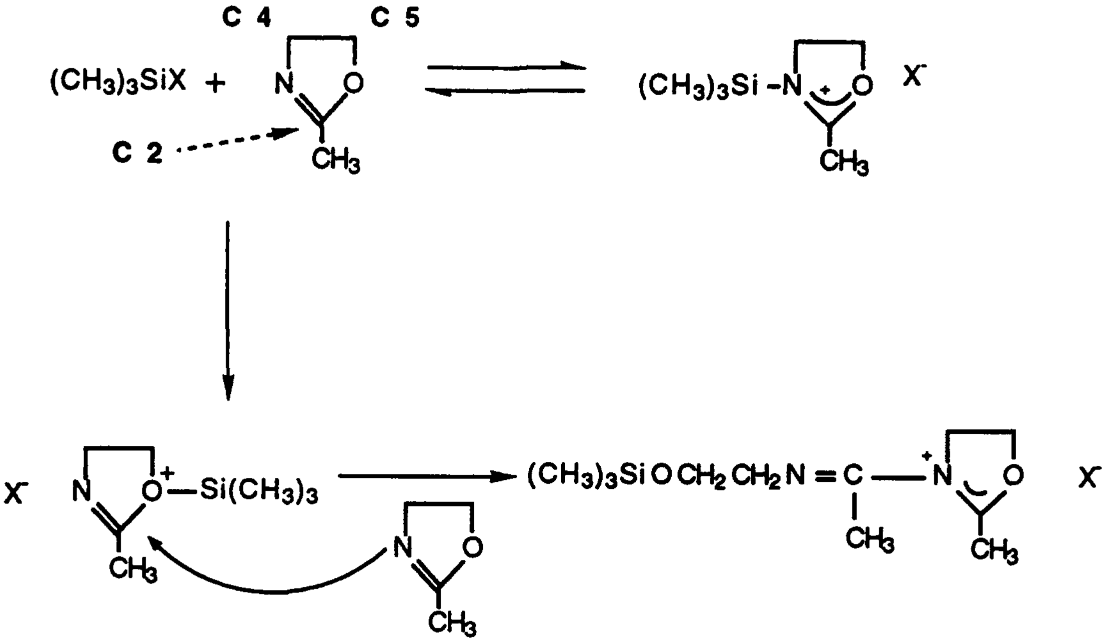
The use of 1,2-propylene oxide as a promoter has also been applied to the grafting of THF from the triflated sites of modified low molecular weight poly(methylphenylsilylene) [40]. Low molecular weight poly(methylphenylsilylene) (M_n=4300, DP=36) was reacted with HOTf in order to displace 20% of the phenyl groups. This should produce an average of 7 triflate moieties per PSI chain. After allowing sufficient time for this reaction to take place, 2,6-di-*tert*-butylpyridine (PYR) was added to the reaction mixture to quench any remaining HOTf. PYR is a very efficient and selective proton trap [39]. It does not react with silyl triflates or growing tetrahydrofuranium cations. This is important, because free HOTf can initiate the polymerization of THF leading to homo-polyTHF impurities. Fourteen hours after the addition of PRO-OX and THF, the solution was very viscous and the reaction was terminated with methanol and PYR. The resulting graft copolymer was precipitated from excess methanol and analyzed by GPC. Table 2 contains molecular weight data for the polymers involved in the grafting process. A small, high molecular weight shoulder was present in the original poly(methylphenylsilylene). The M_n of the triflated (actually methoxylated since it is treated with methanol before GPC analysis) poly(methylphenylsilylene) is smaller than that for the original poly(methylphenylsilylene) and the polydispersity is more narrow due to a small extent of cleavage of Si-Si bonds in the poly(methylphenylsilylene) backbone by HOTf. A comparison of the methoxylated poly(methylphenylsilylene) with the graft copolymer shows that the molecular weight of the graft copolymer is much higher. The M_n value of 47,900 is less than the expected theoretical value of approximately 64,000. The polydispersity of the graft copolymer is 3.28.

The GPC analysis employs the use of two detectors; a photodiode array detector (UV) and a differential refractive index detector (RI). The RI response of poly(methylphenylsilylene) is much weaker compared to the UV response. In addition, polyTHF has no UV response. As a result, the presence of a strong RI response that corresponds to the UV response is a very good indicator that polyTHF is indeed grafted onto poly(methylphenylsilylene). Such a condition is met for this system. We also employed the photo-instability of poly(methylphenylsilylene) to further determine the composition of the graft copolymer. Poly(methylphenylsilylene) can be degraded by UV light, whereas polyTHF cannot. The graft product (in THF) was exposed to UV light and re-analyzed by GPC. No UV response was detected after exposure. An RI response was seen at a molecular weight lower than the graft copolymer, since the polyTHF chains are no longer held together by the poly(methylphenylsilylene) backbone. The M_n of the free polyTHF was 10,600, which is higher than the expected theoretical value of 8,300. This indicates that the concentration of grafting sites was lower than expected. The polydispersity of the free polyTHF was 2.14.

These results indicate that poly(methylphenylsilylene)-*g*-poly(tetrahydrofuran) has been prepared by cationically polymerizing THF from active silyl triflate moieties on low molecular weight poly(methylphenylsilylene) in the presence of 1,2-propylene oxide. Although PRO-OX has been shown to provide a faster, more efficient initiation for the polymerization of THF, the molecular weight of the polyTHF isolated from the graft copolymer was still higher than expected and the polydispersity was fairly broad. In addition, the number of polyTHF chains per poly(methylphenylsilylene) was less than the calculated number. Therefore, this method of preparing comblike graft copolymers has some limitations and does not produce very well-defined products.

Table 2

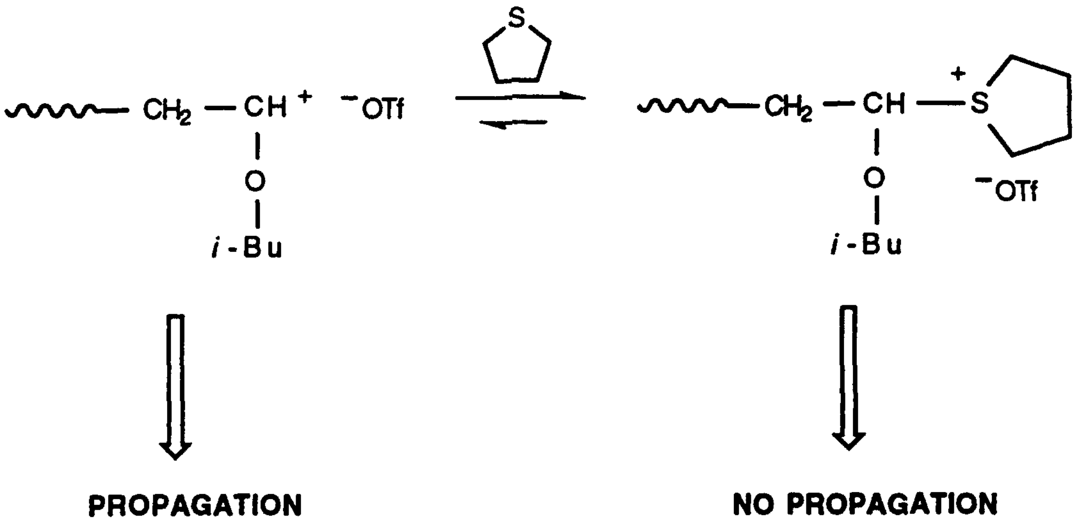
As with the THF system, the use of TMSOTf for the polymerization of 2-methyl-2-oxazoline (MeOXZ) leads to inefficient initiation [34]. The positive charge in the N-trimethylsilyl-2-methyl-2-oxonium ion is distributed mostly onto the trimethylsilyl group. As a result, propagation does not take place. Instead, TMSOTf is eventually attacked by the oxygen atom of MeOXZ, producing an O-trimethylsilyl-2-methyl-2-oxonium ion. This cation is attacked at C2, instead of the typical attack at C5, yielding an unusual imine dimeric cation:



(3)

This imine dimeric cation is unreactive, because the charge is drawn away from the ring toward the imine functionality. Only after a very long time in the presence of a large excess of MeOXZ does propagation take place. The use of 1,2-propylene oxide as a promoter in a 2:1 PRO-OX/TMSOTf ratio overcomes this problem and provides a more efficient initiation process that leads to propagation without the formation of the imine dimeric cation. MeOXZ has been successfully grafted from triflated poly(methylphenylsilylene) using PRO-OX as a promoter.

The polymerization of isobutylvinyl ether (IBVE) intiated by TMSOTf in the presence of various carbonyl compounds as promoters and dimethyl sulfide as an agent to control the rate of polymerization has been reported [36]. The direct reaction between alkenes and trimethylsilyl compounds is not favored, and TMSOTf cannot initiate the polymerization of styrene [41]. Polymerization is often initiated by triflic acid which is formed by hydrolysis of TMSOTf; however, no polymerization happens in the presence of proton traps such as hindered pyridine [42]. In addition, the polymerization of IBVE cannot be initiated by trimethylsilyl iodide without the presence of acetone as a promoter [43]. On the other hand, experiments conducted in our laboratory indicate that N-vinyl carbazole, a much more reactive alkene, can be polymerized by trimethylsilyl iodide without the use of a promoter. We studied the polymerization of IBVE with TMSOTf using acetone as the promoter and tetrahydrothiophene as the controlling agent. Tetrahydrothiophene reacts with the propagating cationic centers to produce an unreactive sulfonium ion [44,45]. An exchange reaction takes place between the inactive sulfonium ion and the active carbenium ion. Thus, the lifetime of the carbenium ion is reduced and the rate of propagation is slowed creating less opportunity for side reactions:



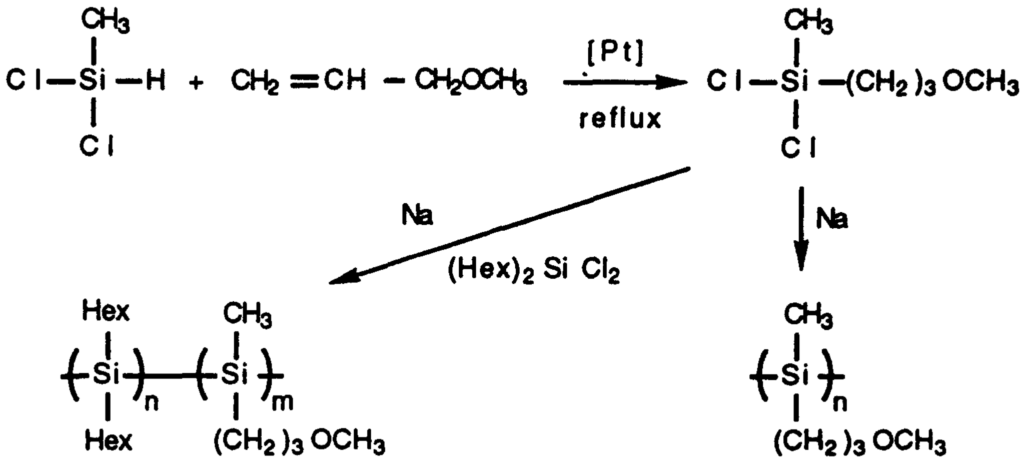
(4)

The polymerization of IBVE using acetone as the promoter at -25°C produced polymer with a number average molecular weight of 13,600, which is nearly twice that expected from the [IBVE]/[TMSOTf] feed ratio. The polydispersity was 2.5. IBVE was also grafted from triflated poly(methylphenylsilylene) at -30°C. The number average molecular weight of the precipitated copolymer was 105,000 (theoretical M_n = 119,000) and its polydispersity was 2.5. The improvements in the initiating system may allow the preparation of well-defined graft copolymers by this method.

ETHERS AS FUNCTIONAL GROUPS

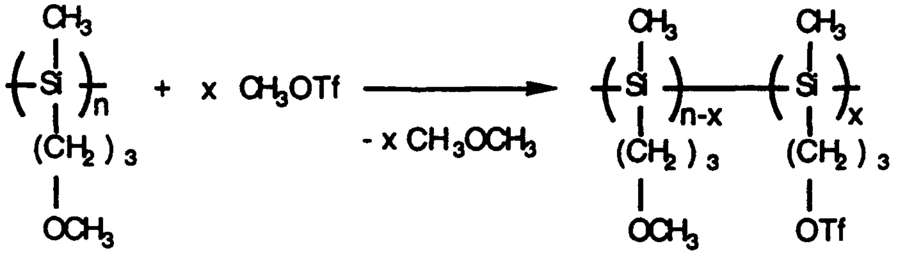
Ethers can be considered to be protective groups for phenols and alcohols and have been used for this purpose. Usually aryl-alkyl ethers are more stable than dialkyl ethers and are not cleaved before the polysilane chain. Silyl-aryl ethers can be cleaved under much milder acidic conditions yet are sufficiently stable to survive the reductive coupling conditions of polymerization. They have been incorporated onto a polysilane backbone, then cleaved to produce hydrophilic phenol moieties that can modify the surface properties of the polysilanes [19-22].

The synthesis of polysilanes with dialkyl ether side groups [15-17, 46] have been reported. Homopolymers and copolymers with di-n-hexylsilylene units of high molecular weight have been prepared:



(5)

The dialkyl ether can be modified to the corresponding alkyl triflate by the reaction with methyl triflate:



(6)

Methyl triflate does not react with Si-Si bonds and produces dimethyl ether, an inert and volatile by-product. In addition, alkyl triflates are very reactive and can easily form various esters and amines, as well as ammonium, sulfonium and phosphonium salts. This reactivity may be utilized to prepare a variety of functionalized polysilanes. Alkyl triflates are more efficient initiators for the polymerization of THF and MeOXZ than silyl triflates. There is no need for the use of promoters with these initiators. Also, graft copolymers prepared from these sites on a polysilane chain will contain only Si-CH_2 linkages and should be more stable than those previously prepared.

CONCLUSIONS

The model polymerizations of THF, MeOXZ, and IBVE, and their subsequent grafting from the silyl triflate moieties of modified poly(methylphenylsilylene) have been accomplished. The model studies showed that trimethylsilyl triflate is not an efficient initiator, however, initiation can be improved through the use of 1,2 propylene oxide as a promoter in the THF and MeOXZ systems and the use of acetone for IBVE. The improvement in these systems is not enough to be extended to the preparation of well-defined graft copolymers. Unless the graft copolymers are well-defined, good microphase separation will not be seen, therefore limiting the quality of the morphologies and the physical properties of the copolymers. In addition to this limitation, the graft copolymers prepared in the above systems contain unstable Si-X-CH_2 (X= N,O) linkages at the graft points. Therefore, a different system is being developed to overcome these limitations and allow the preparation of stable, well-defined comblike graft copolymers. We have prepared a new class of polysilanes with alkyl-methyl ether substituents capable of transformation to triflated alkyl groups.

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Table 1.
Molecular Weights and Polydispersities of PolyTHF Initiated by TMSOTf

$[THF]_0$	$[TMSOTf]_0$	$[PRO\text{-}OX]_0$	M_n	M_w/M_n
8.1	0.03	0.03	21,700	1.99
7.9	0.08	0.32	7,000	1.75
7.9	0.08	0.80	5,400	1.65

prepared in CH_2Cl_2 at 20°C in the presence of 2,6-di-*t*-butyl pyridine

Table 2.
Molecular Weights and Polydispersities for Grafting Reaction

Sample	M_w	M_n	M_w/M_n
Original PSI	17,900	4,300	4.12
Methoxylated PSI*	7,300	3,300	2.24
PSI-g-polyTHF	157,400	47,900	3.28
PolyTHF**	22,700	10,600	2.14

*Triflated PSI after treatment with methanol

**After copolymer degradation by UV light