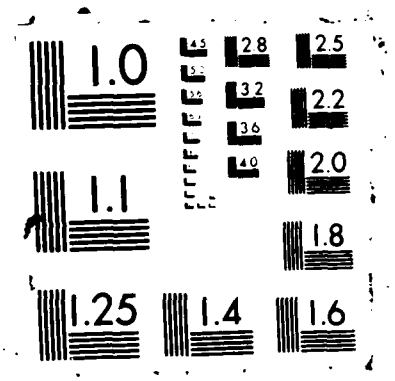
AD-A183 774 MODIFICATION OF POLYSILANES(U) CARNEGIE-MELLON UNIV 1/1
PITTSBURGH PA DEPT OF CHEMISTRY K MATYJASZEWSKI ET AL.
25 JUL 87 TR-3 N00014-87-K-0116

UNCLASSIFIED F/G 7/6 NL


1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.5
2.8
3.2
3.6
4.0

OFFICE OF NAVAL RESEARCH

Contract N00014-87-K-0116

R&T Code _____

Technical Report No. 3

MODIFICATION OF POLYSILANES

by

K. Matyjaszewski, Y. L. Chen and F. Yenca

To Be Published

in the

"Polymer Preprints"

Carnegie-Mellon University
Department of Chemistry
4400 Fifth Avenue
Pittsburgh, PA 15213

July 20, 1987

SECURITY CLASSIFICATION OF THIS PAGE

AD-A183 774

REPORT DOCUMENTATION PAGE

Form Approved OMB No 0704-0188

1a. REPORT SECURITY CLASSIFICATION	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION / AVAILABILITY OF REPORT
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) 3	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION Carnegie-Mellon University	6b. OFFICE SYMBOL (If applicable)
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry 4400 Fifth Avenue Pgh., PA 15213	7a. NAME OF MONITORING ORGANIZATION 7b. ADDRESS (City, State, and ZIP Code)
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (If applicable)
8c. ADDRESS (City, State, and ZIP Code) Department of the Navy Office of the Chief of Naval Research Arlington, Virginia 22217-5000	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER 10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO	PROJECT NO	TASK NO	WORK UNIT ACCESSION NO

11. TITLE (Include Security Classification)
MODIFICATION OF POLYSILANES

12. PERSONAL AUTHOR(S)
Matyjaszewski, Krzysztof - Chen, Y. L. - Yenca, F.

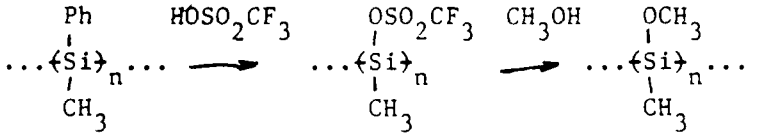
13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Technical Report	FROM 2/87 TO 7/87	July 25, 1987	3

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

New polysilanes bearing different alkoxy groups attached directly to silicon atoms were prepared by the displacement of the phenyl groups in the poly(phenylmethylsilylene) by trifluoromethanesulfonic acid and the subsequent reaction with alcohols in the presence of different bases.



This reaction was also studied for model compounds. Thus, different disilanes were converted to the 1,2-bis(trifluoromethanesulfonyloxy) tetramethyldisilane and subsequently to the corresponding 1,2-dialkoxydisilanes.

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION	
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS		
22a. NAME OF RESPONSIBLE INDIVIDUAL Matyjaszewski, Krzysztof	22b. TELEPHONE (Include Area Code) (412) 268-3209	22c. OFFICE SYMBOL

DD Form 1473, JUN 86 *Previous editions are obsolete* SECURITY CLASSIFICATION OF THIS PAGE

MODIFICATION OF POLYSILANES

F. Yenca, Y. L. Chen and K. Matyjaszewski
Department of Chemistry
Carnegie-Mellon University
4400 Fifth Avenue
Pittsburgh, PA 15213

INTRODUCTION

High molecular weight polymers containing Si-Si bonds in the main chain are known for more than 30 years but due to the insolubility of the initially prepared polysilanes they were not studied in detail until recently. The successful conversion of poly(dimethylsilylene) to silicon carbide fibers and the subsequent preparation of soluble polysilanes gave rise to new studies of these materials[1]. Polysilanes may find application in microlithography as imageable etch barriers[2], mid - UV solvent developed photoresists[3], self-developing deep UV photoresists[4], or contrast enhancement layers[5]. They were successfully used as catalysts for polymerization of vinyl monomers[6]. Polysilanes, after doping with strong electrophiles, showed strong increase of conductivity (10 orders of magnitude) to the level of semiconductors[7]. Polysilanes were also used to reinforce ceramics[8] and, as mentioned before, they found application as precursors to silicon carbide fibers[1].

The synthesis of polysilanes is based on the coupling reaction (Wurtz type) between alkali metals (Na, K, Li) and different dichlorodisubstituted silanes. In addition to the mixture of the relatively high molecular weight polymers (M_n > 100,000), low molecular weight polymer (M_n < 5,000), and some cyclic oligomers are formed[7,9-14]. The yield of the high polymer is usually low. Some improvement was recently reported by varying the solvent and by inverse addition procedure.

In exploring new synthetic routes to linear well-defined polysilanes we used low temperature coupling reaction with ultrasonic activation of the sodium surface[15]. We have also been studying the ring-opening polymerization of the strained cyclic polysilanes[15]. The second route allows some variation in the structure of substituents at the silicon atom but the severe reaction conditions of a classical reductive coupling process limit the substituents structure to alkyl and aryl groups.

Polysilanes with functional side groups have not yet been prepared although they might have very interesting properties. For example, solubility of polymers could be varied in a controlled way, the physical, spectral, chemical, and conductive properties of polysilanes could also be influenced. Some substituents may increase stability of intermediate silylenes and facilitate photodegradation, some others may increase photostability of polymers.

We report below on some modifications of polysilanes and the relative studies with model compounds.

EXPERIMENTAL

^{1}H NMR spectra were recorded on either IBM model NR/80 spectrometer (at 80 MHz) or GE model 300 spectrometer (at 300 MHz). All chemical shifts are reported as parts-per-million (δ scale) from tetramethylsilane (TMS) using either TMS, methylene chloride or nitromethane as internal standards.

All experiments were carried out under dry nitrogen or argon atmosphere. Organic solvents and silicon halides were dried and distilled from calcium hydride prior to use. Preparation of 1,2-bis(trifluoromethanesulfonyloxy) tetramethyldisilane, (1) was described in detail in Ref. 16. The high molecular weight monomodal poly(phenylmethylsilylene) was prepared by reductive coupling reaction using ultrasonic bath[15].

RESULTS AND DISCUSSION

Model studies.

We have used two disilanes as models of polysilanes: hexamethyldisilane and 1,2-diphenyltetramethyldisilane. These disilanes are known to be converted to the corresponding chlorides. However, reactivities of chlorosilanes are quite often insufficient for the complete modification of the polymer backbone, which requires rapid reaction at concentrations lower than 10^{-3} mol/L. Therefore, we have chosen conversion to silyl trifluoromethanesulfonates, groups a few orders of magnitude more reactive than silyl chlorides in nucleophilic substitution.

We have recently reported on the different methods of preparation of 1,2-bis(trifluoromethanesulfonyloxy)-tetramethyldisilane (1)[16]. This compound can be prepared in high yield from hexamethyldisilane, 1,2-diphenyltetramethyldisilane, or 1,2-dichlorotetramethyldisilane and triflic acid:

$$2\ HOSO_2CF_3 + R\text{-}Si(CH_3)_2\text{-}Si(CH_3)_2\text{-}R \longrightarrow$$

$$\longrightarrow CF_3SO_3\text{-}Si(CH_3)_2\text{-}Si(CH_3)_2\text{-}OSO_2CF_3 + 2\ HR$$

where R = Cl, CH_3, C_6H_5

Ditriflate is stable at room temperature in the absence of moisture and can be easily distilled (bp = 87°C/5 mm Hg).

1,2-Dialkoxytetramethyldisilanes were prepared in the reaction of 1 with different alcohols:

$$CF_3SO_3\text{-}Si(CH_3)_2\text{-}Si(CH_3)_2\text{-}OSO_2CF_3 + 2\ ROH \longrightarrow$$

$$\longrightarrow RO\text{-}Si(CH_3)_2\text{-}Si(CH_3)_2\text{-}OR + 2\ HOSO_2CF_3$$

1 reacts also with amines. It forms disilylamines with secondary amines:

$$CF_3SO_3\text{-}Si(CH_3)_2\text{-}Si(CH_3)_2\text{-}OSO_2CF_3 + 4R_2NH \longrightarrow$$

$$\longrightarrow R_2N\text{-}Si(CH_3)_2\text{-}Si(CH_3)_2\text{-}NR_2 + 2\ R_2NH_2^+,\ CF_3SO_3^-$$

and pyridinium salts with pyridine.

Reactions on polymers.

Our model studies have shown that phenyl groups are cleaved much faster and much more efficiently than alkyl groups. Therefore, we have chosen poly(phenylmethylsilylene) as the starting material. Conversion of this polymer to the triflate derivative was followed by ^{1}H NMR. The broad signal of the phenyl groups in the initial polymer at the aromatic region was being replaced by the sharp singlet of benzene formed in this reaction:

$$\cdots\text{-}\underset{\text{Me}}{\overset{\text{Ph}}{\underset{|}{\overset{|}{Si}}}}\text{-}\cdots + n HOSO_2CF_3 \longrightarrow \cdots\text{-}\underset{\text{Me}}{\overset{OSO_2CF_3}{\underset{|}{\overset{|}{Si}}}}\text{-}\cdots + n C_6H_6$$

Methyl groups even after replacement of the phenyl groups by triflate show a broad signal due to the tacticity of the polymer chain (Fig. 1a and 1b).

Displacement proceeds rapidly for the first 80% of the phenyl groups. No acidic protons at 9.3 ppm can be observed up to this conversion. Later displacement becomes more difficult, and small amount of the phenyl groups (less than 10%) remain even with the excess acid. This can be ascribed to the isotactic triads or pentads where bimolecular reaction of the acid can be hindered by the neighboring triflate groups.

Nearly completely substituted polymer is stable in chlorinated solvents (CH_2Cl_2, $CHCl_3$) and in aromatic solvents (C_6H_6, $C_6H_5CH_3$) in the absence of moisture. It reacts rapidly with moisture forming insoluble crosslinked polymer with siloxane linkages between chains. This reaction proceeds via formation of the silanol intermediates which rapidly condense with silyl triflates from the same or from different chains.

Modification of triflate substituted polysilane was carried out in the presence of amines using different alcohols as nucleophiles.

Reaction of triflate substituted polymer with pyridine led to the rapid precipitation of the polysalt. Later upon addition of the methanol or butanol this precipitate was slowly being dissolved. NMR of the reation mixture showed the presence of the protonated pyridine and poly(methylalkoxysilylene). Apparently the effect of the tacticity on the more remote alkoxy group is much smaller since a broad singlet of the methoxy group was found in the ^1H NMR spectra (cf. Fig. 1c). Similar effect was observed for vinyl ethers.

Reaction carried out in the presence of pyridine yielded some insoluble polymer probably due to the electrophilic attack of a polymeric silyl triflate on the p-C atom in the pyridine. Better results were obtained using triethylamine as a base trapping triflic acid. Molecular weight of polysilanes after modification decreases indicating some degradation of polymer.

Polysilane bearing several triflate groups in the backbone was used as initiators for the cationic polymerization of THF. This led to the graft copolymer with very high density of grafting. Molecular weight of this copolymer was equal to $\overline{M}_w = 6.10^5$ and GPC analysis using RI and UV detectors showed no homopolymer of THF in this system.

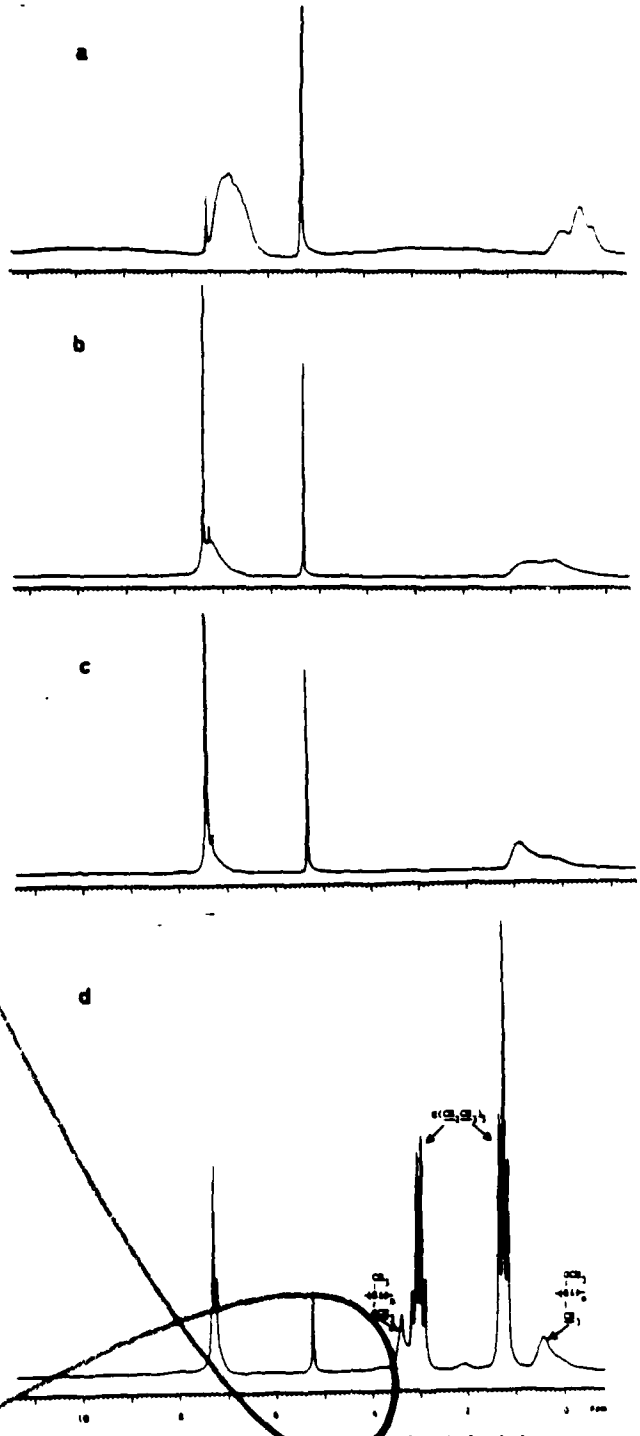


Fig. 1 ^1H-NMR spectra of poly(phenylmethylsilylene) ($\{SiPhMe\}_0 = 0.42M$) (a), after reaction with triflic acid ($[HOSO_2CF_3]_0 = 0.17M$) (b), $[HOSO_2CF_3]_0 = 0.34M$) (c), and poly(methyl methoxy silylene) ($\{SiOMeMe\} = 0.42M$) in $CDCl_3$ solvent using CH_2Cl_2 as internal standard.

REFERENCES

1. S. Yajima, Y. Hasegawa, J. Hayashi, M. Ijmura, J. Mater. Sci. 13, 2569 (1978).
2. H. Hiraoka, U. S. Patent 4, 464, 480 (1984).
3. D. C. Hofer, R. D. Miller, C. G. Willson, SPIE Adv. Resist. Tech. 469, 16 (1984).
4. J. M Zeigler, F. A. Harrah, A.W. Johnson, *ibid*, 539, 166 (1984).
5. D. C. Hofer, R. D. Miller, C. G. Willson, A. Neureuther, *ibid*, 469, 108 (1984).
6. R. West, in "Comprehensive Organometal. Chemistry", E. Abel Ed., Pergamon Press, Oxford 1981, Chapt. 9.4.
7. R. West, L. D. David, P. I. Djurovich, K. L. Stearley, K. S. V. Srinivasan, H. Yu, J. Amer. Chem. Soc. 103, 7352 (1981).
8. K. Mazdyasni, R. West, L. D. David, J. Amer. Cer. Soc. 61, 504 (1978).
9. J. M. Zeigler, Polym. Prepr. 27, 109 (1986).
10. C. A. Burkhard, J. Amer. Chem. Soc. 71, 963 (1949).
11. R. E. Trujillo, J. Organomet. Chem., 198, C27 (1980).
12. P. Trefonas, P. I. Djurovich, R. West, R. Miller, D. Hofer, J. Polym. Sci., Polym. Letters Ed. 21, 819 (1983).
13. J. P. Wesson, T. C. Williams, J. Polym. Sci. Polym. Chem. Ed. 18, 959 (1980).
14. R. West, J. Organomet. Chem., 300, 327 (1986).
15. K. Matyjaszewski, H. K. Kim, and Y. L. Chen, ACS Symposium Series, submitted.
16. Y. L. Chen and K. Matyjaszewski, J. Organomet. Chem., Submitted.

ACKNOWLEDGMENTS:

This work has been supported by the grant from the Office of Naval Research.

Modification of triflate substituted polysilane was carried out in the presence of amines using different alcohols as nucleophiles.

Reaction of triflate substituted polymer with pyridine led to the rapid precipitation of the polysalt. Later upon addition of the methanol or butanol this precipitate was slowly being dissolved. NMR of the reation mixture showed the presence of the protonated pyridine and poly(methylalkoxysilylene). Apparently the effect of the tacticity on the more remote alkoxy group is much smaller since a broad singlet of the methoxy group was found in the ^1H NMR spectra (cf. Fig. 1c). Similar effect was observed for vinyl ethers.

Reaction carried out in the presence of pyridine yielded some insoluble polymer probably due to the electrophilic attack of a polymeric silyl triflate on the p-C atom in the pyridine. Better results were obtained using triethylamine as a base trapping triflic acid. Molecular weight of polysilanes after modification decreases indicating some degradation of polymer.

Polysilane bearing several triflate groups in the backbone was used as initiators for the cationic polymerization of THF. This led to the graft copolymer with very high density of grafting. Molecular weight of this copolymer was equal to $\overline{M}_w = 6.10^5$ and GPC analysis using RI and UV detectors showed no homopolymer of THF in this system.

REFERENCES

1. S. Yajima, Y. Hasegawa, J. Hayashi, M. Ijmura, J. Mater. Sci. 13, 2569 (1978).
2. H. Hiraoka, U. S. Patent 4, 464, 480 (1984).
3. D. C. Hofer, R. D. Miller, C. G. Willson, SPIE Adv. Resist. Tech. 469, 16 (1984).
4. J. M Zeigler, L. A. Harrah, A.W. Johnson, *ibid*, 539, 166 (1984).
5. D. C. Hofer, R. D. Miller, C. G. Willson, A. Neureuther, *ibid*, 469, 108 (1984).
6. R. West, in "Comprehensive Organometal. Chemistry", E. Abel Ed., Pergamon Press, Oxford 1981, Chapt. 9.4.
7. R. West, L. D. David, P. I. Djurovich, K. L. Stearley, K. S. V. Srinivasan, H. Yu, J. Amer. Chem. Soc. 103, 7352 (1981).
8. K. Mazdyasni, R. West, L. D. David, J. Amer. Cer. Soc. 61, 504 (1978).
9. J. M. Zeigler, Polym. Prepr. 27, 109 (1986).
10. C. A. Burkhard, J. Amer. Chem. Soc. 71, 963 (1949).
11. R. E. Trujillo, J.Organomet. Chem., 198, C27 (1980).
12. P. Trefonas, P. I. Djurovich, R. West, R. Miller, D. Hofer, J. Polym. Sci., Polym. Letters Ed. 21, 819 (1983).
13. J. P. Wesson, T. C. Williams, J. Polym. Sci. Polym. Chem. Ed. 18, 959 (1980).
14. R. West, J. Organomet. Chem., 300, 327 (1986).
15. K. Matyjaszewski, H. K. Kim, and Y. L. Chen, ACS Symposium Series, submitted.
16. Y. L. Chen and K. Matyjaszewski, J. Organomet. Chem., Submitted.

ACKNOWLEDGMENTS

This work has been supported by the grant from the Office of Naval Research.

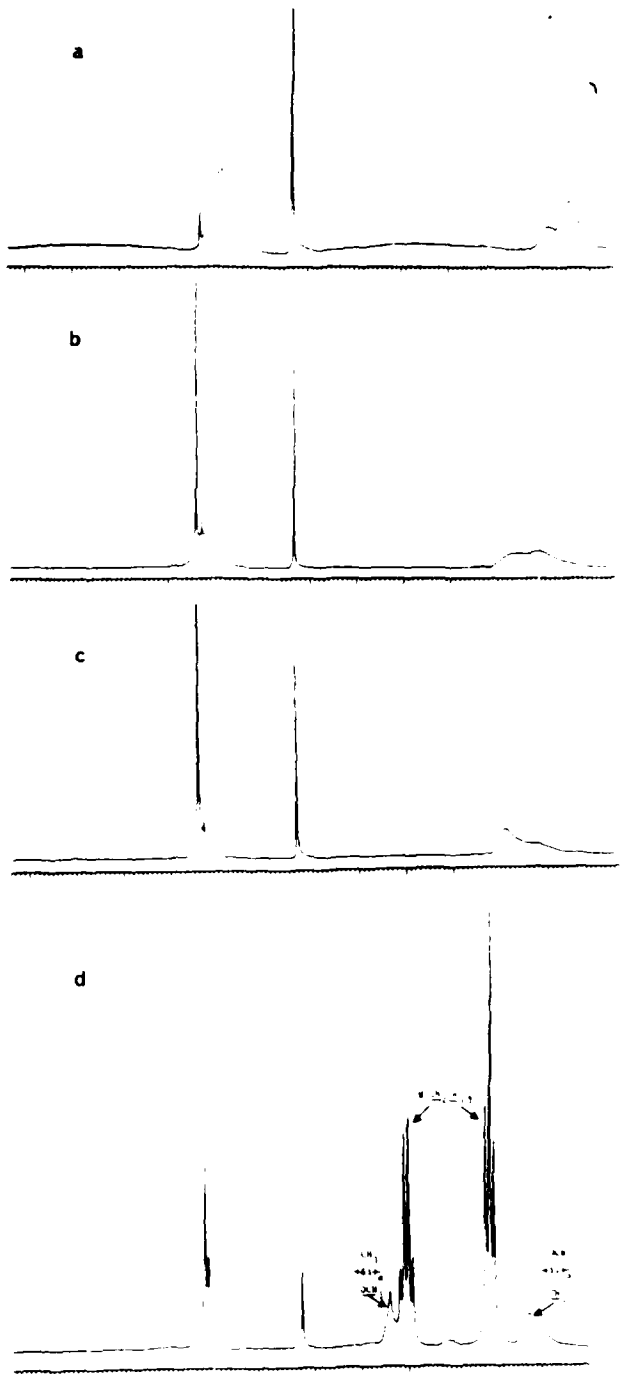


Fig. 1 ^1H NMR spectra of poly phenylmethylsilylene (-SiPhMe-)$_n$ = 0.42M (a), after reaction with triflic acid (HOSO$_2$CF$_3$)$_0$ = 0.17M (b), (HOSO$_2$CF$_3$)$_0$ = 0.34M (c), and poly methylmethoxysilylene (-SiOMeMe-) = 0.42M in CDCl$_3$, solvent using CH_2Cl_2 as internal standard.

END

9-87

DTIC