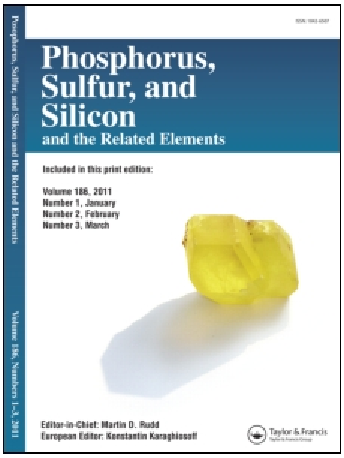
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

New Phosphorus-Fluorocarbon Hybrid Polymer Systems

Robert H. Neilson; Junmin Ji; Sridevi Narayan-Sarathy; Dennis W. Smith; David A. Babb

To cite this Article Neilson, Robert H. , Ji, Junmin , Narayan-Sarathy, Sridevi , Smith, Dennis W. and Babb, David A.(1999) 'New Phosphorus-Fluorocarbon Hybrid Polymer Systems', Phosphorus, Sulfur, and Silicon and the Related Elements, 144: 1, 221 — 224

To link to this Article: DOI: 10.1080/10426509908546222

URL: http://dx.doi.org/10.1080/10426509908546222

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus, Sulfur and Silicon, 1999, Vol. 144-146, pp. 221-224
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

New Phosphorus-Fluorocarbon Hybrid Polymer Systems

ROBERT H. NEILSON[a], JUNMIN JI[a],
SRIDEVI NARAYAN-SARATHY[a], DENNIS W. SMITH[b] and
DAVID A. BABB[b]

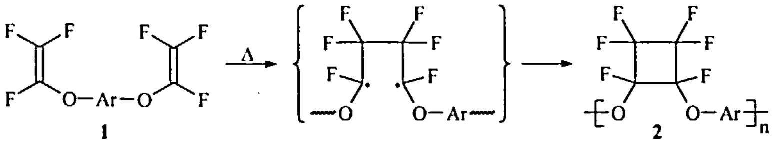
[a]*Department of Chemistry, Texas Christian University, Fort Worth, TX 76129 and* [b]*Central & New Businesses Research and Development, The Dow Chemical Company, Freeport, TX 77541*

The thermally-induced cyclodimerization of aryl-trifluorovinyl ethers (TFVE, **1**) readily affords highly stable and processible perfluorocyclobutane (PFCB, **2**) polymers, many of which have useful optical, mechanical, and/or surface properties. We report here on the synthesis and characterization of some novel TFVE and PFCB functionalized phosphorus-based polymers systems. These new polymers have been prepared by three general methods: (1) condensation polymerization of appropriate TFVE-substituted Si-N-P precursors, (2) deprotonation-substitution reactions of preformed poly(methylphenyl-phosphazene), and (3) cyclodimerization-polymerization of various TFVE-substituted phosphorus derivatives.

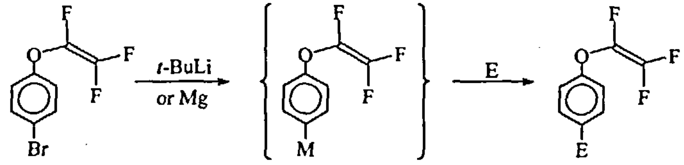
Keywords: phosphazene; fluorocarbon; polymer; trifluorovinyl; phosphoranimine

INTRODUCTION

Perfluorocyclobutane (PFCB) polyarylethers represent a unique class of fluoropolymers which combine the processibility and durability of engineering thermoplastics with the optical, electrical, thermal stability, and chemically resistant properties of fluoropolymers. Such polymers (**2**) are prepared by the step growth, radical mediated [2π + 2π] thermal cyclopolymerization of trifluorovinyl ethers (**1**). They comprise a variety of thermoplastic and thermosetting materials with a tunable range of performance.[1-5] In addition, PFCB chemistry offers a single component condensate- and catalyst-free cure option in contrast to most other inorganic/organic hybrid materials.



Recently the synthesis and characterization of new siloxane-containing PFCB hybrid systems where the PFCB ring is contained within the main chain as well as other PFCB hybrid systems containing organosilane units have been prepared.[3-5] This previous work, and that reported herein, makes use of a versatile intermediate strategy of delivering the trifluorovinyl ether group, in tact, to a substrate monomer or polymer. We have found that useful Grignard (**4**) and lithium (**5**) reagents[6] can be easily obtained from the aryl bromide (**3**). The remarkable stability of the Grignard and lithium derivatives in the presence of the extremely electrophilic trifluorovinyl ether group has been rationalized by theoretical calculations from which it is predicted that the trifluorovinyl ether group stabilizes the aryl-TFVE anion by ca. 11 kcal/mol vs. the aryl-methoxy analog.[6]

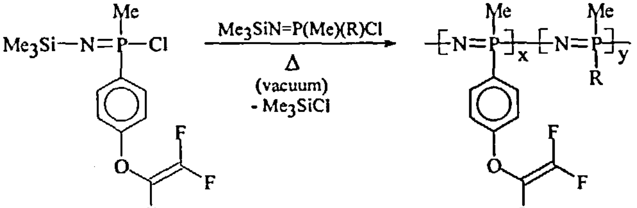


3 **4**: M = MgBr, **5**: M = Li

RESULTS and DISCUSSION

We report here on the synthesis and characterization of some novel TFVE and PFCB functionalized phosphorus-based polymers systems. These new polymers have been prepared by three general methods as described in the following sections. Full details of the synthesis and characterization of these new polymers and their precursors will be reported elsewhere.

Polymerization of TFVE-Substituted Si-N-P Precursors. The synthesis of poly(alkyl/aryl)phosphazenes, $[R_2P=N]_n$, via the condensation polymerization of suitable N-silylphosphoranimines, $Me_3SiN=PR_2X$, is now a well established procedure.[7] Typically, this process utilizes the P-trifluoroethoxy ($X = OCH_2CF_3$) or P-phenoxy ($X = OPh$) derivatives to afford high molecular weight *polymeric* phosphazene products. In contrast, the P-halo analogs ($X = Cl, Br$) generally yield *cyclic* phosphazene products. By using the organometallic reagents (i.e., **4** and **5** above) and synthetic methodology reported recently,[6] we have prepared a series of new Si-N-P compounds (e.g., **6**) containing the TFVE group (i.e., $R = p\text{-}C_6H_4\text{-}OCF=CF_2$).

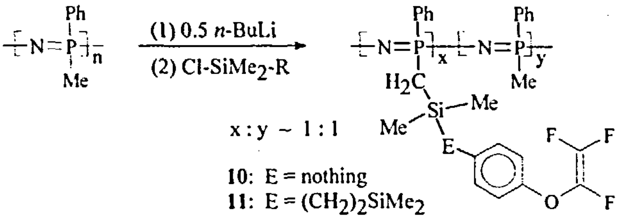


6

7: homopolymer (y = 0)
8: copolymer, R = Me (x : y = 1 : 2.3)
9: copolymer, R = Ph (x : y = 1 : 2.3)

Thermolysis studies indicated that, while the P-OCH_2CF_3 and P-OPh analogs were very thermally stable, the P-chloro compound **6** did yield a novel TFVE-functionalized polymer **7** and copolymers such as **8** and **9**. Polymers **7-9** were soluble, film-forming, thermoplastics with molecular weights in the 10^4 - 10^5 range and glass transition temperatures (T_g) between -5 and 33°C.

Derivatization of Preformed Polyphosphazenes. Work by Wisian-Neilson and coworkers[8] has shown that poly(alkyl/arylphosphazenes) such as $[Ph(Me)P{=}N]_n$ readily undergo deprotonation at the P-Me sites to afford reactive polymeric anions. Subsequent addition of electrophiles leads to a wide variety of organic and/or inorganic functionalized poly(alkyl/arylphosphazenes). We have utilized this general approach to attach the TFVE group to the phosphazene backbone through organosilicon spacer units (e.g., **10** and **11**). The TFVE-organosilicon reagents were first prepared by treating the appropriate dichlorosilanes with the lithium reagent **5**.[6]

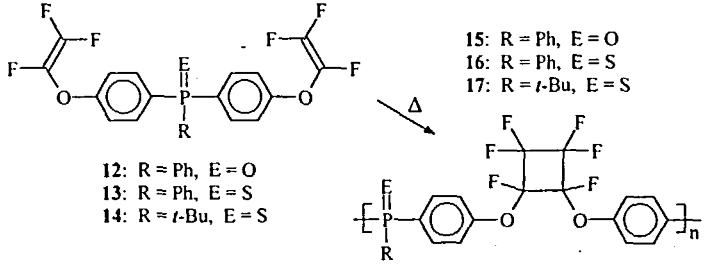


10: E = nothing
11: E = $(CH_2)_2SiMe_2$

When heated at about 160°C for 12 hrs, all of these new TFVE-substituted polyphosphazenes (**7** - **11**) are converted from soluble, flexible thermoplastics to much harder, tougher, insoluble resins. This transformation is undoubtedly due to the facile thermal cyclodimerization of the pendant TFVE groups to generate crosslinks via PFCB (perfluorocyclobutane) units. The flexibility and other physical properties of these phosphazene-fluorocarbon resins can be controlled and, to some extent, tailored by varying the degree of TFVE substitution along the backbone and/or the length of the spacer between the polymer backbone and the TFVE group.

Cyclodimerization-Polymerization of TFVE-Phosphorus Monomers. As noted earlier, when compounds of type **1** are heated, cyclodimerization of the TFVE groups results in a polymerization reaction that yields linear PFCB polymers of type **2**. In order to apply this process to the synthesis of novel phosphorus-PFCB hybrid polymers, we first prepared a series of bis-TFVE phosphorus monomers (**12** - **14**) by treatment of the appropriate dichlorophosphoryl derivatives with two equivalents of the TFVE lithium reagent **5**. The analogous phosphines (E = nothing) were similarly prepared.

Subsequent heating (180°C, 12 hrs) of these neat liquid monomers resulted in their smooth polymerization to afford the new PFCB-phosphorus copolymers **15** - **17** in high yield. These new materials were isolated as hard, glassy polymers that were soluble in common organic solvents. The molecular weights, however, were relatively low (ca. 2,000 - 20,000), possibly due to the substantial increase in viscosity as the polymerization process occurred. Polymers **15** - **17** were hard, amorphous materials with T_g values above 150°C. The analogous P-III precursors (E = nothing) also underwent cyclodimerization but, surprisingly, the products were very insoluble and thus not fully characterized.



12: R = Ph, E = O
13: R = Ph, E = S
14: R = *t*-Bu, E = S

15: R = Ph, E = O
16: R = Ph, E = S
17: R = *t*-Bu, E = S

Further studies of all of the new polymeric materials reported here and their TFVE-phosphorus precursors are continuing in our laboratory and complete results will be reported in due course.

Acknowledgment. The authors thank the Texas Higher Education Coordinating Board (Advanced Technology Program) and The Robert A. Welch Foundation for generous financial support of the work at Texas Christian University.

References

[1] Babb, D. A.; Ezzell, B. R.; Clement, K. S.; Richey, W. F.; Kennedy, A. P. *J.Polym.Sci., Part-A, Polym. Chem.* **1993**, *31*, 3465.
[2] Smith, D. W., Jr.; Babb, D. A. *Macromolecules* **1996**, *29*, 852.
[3] Neilson, R. H.; Ji, J.; Narayan-Sarathy, S.; Oxley, J. D.; Smith, D. W., Jr. *Abstract* of Papers, 30th Organosilicon Symp.: London, Ontario, **1997**.
[4] Narayan-Sarathy, S; Ji, J; Neilson, R. H.; Smith, D. W., *Jr Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1998**, *39*, 609.
[5] Narayan-Sarathy, S.; Ji, J.; Neilson, R. H.; Smith, D. W., *Jr. Polym. Prepr., (Am. Chem. Soc. Div. Polym. Chem.)* **1998**, *39*, 530.
[6] Ji, J.; Narayan-Sarathy, S.; Neilson, R. H.; Oxley, J. D.; Smith, D. W., Jr.; Babb, D. A.; Rondan, N. G. *Organometallics* **1998**, *17*, 783.
[7] See, for example, the following and references cited therein: (a) Neilson, R.H.; Wisian-Neilson, P. *Chem. Rev.* **1988**, *88*, 541. (b) Neilson, R.H.; Jinkerson, D. L.; Kucera, W. R.; Longlet, J.J.; Samuel, R.C.; Wood, C.E. *ACS Symposium Series* **1994**, *572*, 232. (c) Wisian-Neilson, P. *Encyclopedia of Inorganic Chemistry*, King, R. B., Ed.; Wiley: Chichester, England, **1994**, Vol. 7, 3371.
[8] Wisian-Neilson, P.; Koch, K. A.; Zhang, C. *Macromolecules* **1998**, *31*, 1808 and references cited therein.