Dependency of Thermal and Mechanical Properties on the Composition of Mixed-Substituent Poly(fluoroalkoxyphosphazenes)

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ABSTRACT: A series of poly(fluoroalkoxyphosphazenes) containing a mixture of 2,2,3,3,4,4,5,5-octafluoropentoxy and 2,2,2-trifluoroethoxy substituents was synthesized. The series included polymers with 25–94% incorporation of the trifluoroethoxy substituent, as well as single-substituent polymers with 100% octafluoropentoxy or trifluoroethoxy side groups. Polymers were analyzed by multinuclear NMR spectroscopy, gel permeation chromatography, differential scanning calorimetry, and thermogravimetric analysis, and were subjected to limiting oxygen index and microtensile testing. It was found that the T_g and T_d values among the cosubstituted polymers varied little with changes in composition, but the mechanical properties varied over a wide range. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 2569–2576, 2004

Key words: polyphosphazenes; fluoropolymers; thermal properties; elastomers; NMR

INTRODUCTION

Few materials have had a greater impact on modern technology than that of elastomers. An elastomer is defined as a polymer that returns substantially to its original shape and size after removal of the force responsible for its deformation.[1] In 1839 Goodyear's discovery of the vulcanization of natural rubber revolutionized technology.[2] About 60 years later, synthetic materials were developed with properties similar to those of vulcanized natural rubber. Over the years many technologies from automobiles to aerospace vehicles have taken advantage of the unique physical and chemical properties characteristic of both natural and synthetic elastomers.[3,4]

Most commodity elastomers have serious limitations, such as poor chemical resistance and a limited temperature range of operation resulting from poor flexibility at low temperatures and limited thermal stability.[5,6] Fluoroelastomers overcome many of these disadvantages.[5–8] The synthesis, properties, and fabrication of fluoroelastomers is discussed in detail in a recent review article.[8] Most fluoroelastomers are either fluorocarbon polymers (based on copolymers of vinylidine fluoride or tetrafluoroethylene) or fluorosilicone elastomers (Fig. 1). Fluorocarbon elastomers possess good chemical resistance and high thermal stability attributed to the nature of carbon–fluorine bonds.[8–11] Fluorosilicone elastomers are polymers with a silicon–oxygen backbone and with fluoroalkyl side groups. These polymers generally have poorer thermal stability and mechanical properties than those of fluorocarbon elastomers, but have better low-temperature flexibility.[10]

Mixed-substituent poly(fluoroalkoxyphosphazenes) are an alternative type of fluoroelastomer (Fig. 1). These polymers have a backbone of alternating phosphorus and nitrogen atoms, with two fluoroalkoxy side groups linked to each phosphorus atom. Typically, each polymer chain bears two different types of side group, such as trifluoroethoxy and octafluoropentoxy, to prevent crystallization. These materials have better low-temperature mechanical properties and lower glass-transition temperatures than those of fluorosilicone elastomers,[12] and also possess good thermal and oxidative stability.[13] Initial development of poly(fluoroalkoxyphosphazene) elastomers was carried out by Horizons, Inc.[14–16] and by the U.S. Army Laboratories.[17,18] Commercially, PN-F (Firestone)[19,20] and Eypel™-F (Ethyl Corp.)[21,22] are examples of fluoroalkoxy phosphazene elastomers that have been used as materials for O-ring seals,[12,13,23] air plenum seals,[23] and in dental applications.[13,24–26] As with most polymeric elastomers, the mechanical properties can be improved through crosslinking and compounding of the raw polymer gum with materials such as fumed silica or various types of carbon black.[8,12,27] The aim of the current work was to examine the influence of

a

$$\left(CH_2CF_2\right)_x \left(\begin{array}{c} CF_3 \\ | \\ CF_2CF \end{array}\right)_y$$

b

$$\left(\begin{array}{c} CH_3 \\ | \\ Si-O \\ | \\ (CH_2)_xCF_3 \end{array}\right)_n$$

c

$$\left(\begin{array}{c} OCH_2CF_3 \\ | \\ P=N \\ | \\ OCH_2(CF_2)_xCF_2H \end{array}\right)_n$$
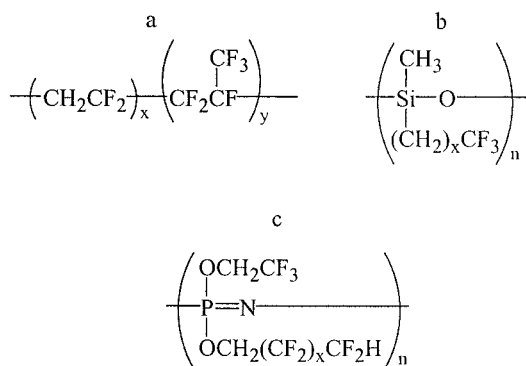
Figure 1 Examples of fluoroelastomers: (a) poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF–HFP) fluorocarbon elastomer; (b) fluorosilicone elastomer; (c) poly(fluoroalkoxyphosphazene) elastomer.

different ratios of two different fluoroalkoxy side groups on the polymer properties. Polyphosphazenes with varying ratios of 2,2,3,3,4,4,5,5-octafluoropentoxy and 2,2,2-trifluoroethoxy side groups were used for this purpose.

EXPERIMENTAL

Materials

2,2,2-Trifluoroethanol and 2,2,3,3,4,4,5,5-octafluoropentanol were used as received from Aldrich (Milwaukee, WI) and VWR (Chicago, IL), respectively. Sodium hydride (95% in mineral oil) was obtained from Aldrich and was weighed into Schlenk flasks in an argon-filled glove box. Tetrahydrofuran (THF) was distilled into the reaction flask from sodium benzophenone under a dry argon atmosphere.

All reactions were carried out using standard Schlenk techniques under an atmosphere of dry argon.

Equipment

^{1}H, ^{13}C, and ^{31}P spectra were recorded on a Bruker AMX-360 NMR spectrometer (Bruker Instruments, Billerica, MA) operated at 360, 90.56, and 90.27 MHz, respectively. ^{1}H- and ^{13}C-NMR were referenced to external tetramethylsilane. ^{31}P- and ^{19}F-NMR (Bruker DPX-300, 282 MHz) proton-decoupled chemical shifts were relative to external 85% phosphoric acid and trichlorofluoromethane, respectively. Molecular weights and polydispersities were estimated using an HP 1090 gel permeation chromatograph (Hewlett–Packard, Palo Alto, CA) equipped with an HP-1047A refractive index detector, Phenomenex Phenogel 10 μm linear and mixed-bed analytical columns, and calibrated versus polystyrene standards. Sample elution was carried out at 40°C with a 0.1 wt % solution of tetra-*n*-butylammonium nitrate (Aldrich) in THF (OmniSolv).

Thermal transitions such as T_g, T_m, and crystalline transitions were determined through analysis by a TA Q10 differential scanning calorimeter (TA Instruments, New Castle, DE). Calibration was accomplished with indium, water, and cyclohexane standards. All analyses were conducted over a temperature range of -120 to 320°C at a heating rate of 10°C/min. The purge gas was nitrogen, flowing at 50 mL/min. Thermal decomposition traces were obtained from a Perkin–Elmer TGA 7 thermogravimetric analyzer (Perkin Elmer Cetus Instruments, Norwalk, CT), equipped with a standard oven and calibrated with nickel, perkalloy, and alumel. Heating occurred at a rate of 10°C/min from 50 to 800°C under a nitrogen atmosphere and a flow rate of 20 mL/min.

Limiting oxygen indices (LOIs) were determined through the use of a device constructed in accordance with ASTM-D-2863-91, and modified for testing bulk polymer samples as described previously.[28] The apparatus consists of a flame chamber and purge gas regulators; tests were run in an oxygen/nitrogen environment. LOI was taken as the oxygen concentration at which the material sustained burning for 30 s and self-extinguished. A Carver laboratory press was operated for 2 h at 85°C followed by 16 h at ambient temperature to fabricate thin sheets of the polymers. Thicknesses were controlled using stainless-steel stops with a thickness of 0.8 mm according to ASTM method D 1708-96 specifications. A microtensile die, also conforming to ASTM method D 1708-96 specifications, was used to prepare samples for microtensile testing. Microtensile tests were performed on an Instron 4201 (Instron, Canton, MA) in accordance with ASTM method D 1708-96 with a 100 N static load cell and at a rate of 100 mm/min.

Synthesis of poly[bis(fluoroalkoxyphosphazene)s] 2–9

Poly(dichlorophosphazene) (**1**) was prepared by thermal ring-opening polymerization of hexachlorocyclotriphosphazene at 250°C in an evacuated sealed tube. Polymer **1** was dissolved in 1 L THF in a 3-L round-bottom flask equipped with a mechanical stirrer. Sodium fluoroalkoxide solutions were prepared by the slow addition of varying ratios of 2,2,2-trifluoroethanol and 2,2,3,3,4,4,5,5-octafluoropentanol to slurries of NaH (95%) in 400 mL THF. The mixed sodium fluoroalkoxide solutions were then added to the solution of **1**, and the reaction mixture was stirred for 18 h at ambient temperature. The mixture was concentrated by removal of THF by a rotary evaporator and the solids were precipitated into acidic water (pH ~ 4). The polymers were rinsed with triply deionized water, air-dried overnight, dissolved in THF, and again precipitated into triply deionized water. This was followed by two precipitations into hexane and one into

dichloromethane from THF. The product was dried for 2 days in a vacuum oven at 65°C.

The amounts of polymer **1** (15.0 g, 129 mmol) and 95% NaH (7.74 g, 305 mmol) used for the synthesis of polymers **2** through **9** were kept constant.

For polymer **2**, 72.02 g (310 mmol) 2,2,3,3,4,4,5,5-octafluoropentanol was used for the synthesis of the fluoroalkoxide solution. The product was isolated as a white fibrous/waxy material. Yield = 46.0 g (70%).
^{1}H-NMR (d_6-acetone): δ = 6.5 (t of t, J = 52.5, 25.2 Hz, OCH$_2$CF$_2$CF$_2$CF$_2$CF_2H), 4.3 (t, J = 13.7 Hz, OCH_2CF$_2$CF$_2$CF$_2$CF$_2$H). ^{13}C-NMR (d_6-acetone): δ = 108–120 (overlapping multiplets, OCH$_2$CF$_2$CF$_2$CF$_2$CF$_2$H), 64.5 (t, OCH$_2$CF$_2$CF$_2$CF$_2$CF$_2$H). ^{31}P-NMR (d_6-acetone): δ = −5.8 (s). ^{19}F-NMR (d_6-acetone): −120.6 (s), −124.7 (s), −129.5 (s), −138.0 (s) (OCH$_2$CF$_2$CF$_2$CF$_2$CF$_2$H).

For polymer **3**, 7.63 g (76 mmol) 2,2,2-trifluoroethanol and 54.31 g (234 mmol) 2,2,3,3,4,4,5,5-octafluoropentanol were used for the synthesis of the fluoroalkoxide solution. The product was isolated as a white fibrous/waxy material. Yield = 38.2 g (67%).
^{1}H-NMR (d_6-acetone): δ = 6.6 (t, OCH$_2$CF$_2$CF$_2$CF$_2$CF_2H), 4.6 (mlt, OCH_2CF$_2$CF$_2$CF$_2$CF$_2$H), 4.6 (mlt, OCH_2CF$_3$). ^{13}C-NMR (d_6-acetone): δ = 108–120 (overlapping multiplets, OCH$_2$CF$_2$CF$_2$CF$_2$CF$_2$H), 64.5 (t, OCH$_2$CF$_2$CF$_2$CF$_2$CF$_2$H), 124 (qt, OCH$_2$CF$_3$), 65 (t, OCH$_2$CF$_3$). ^{31}P-NMR (d_6-acetone): δ = −6.1 (s). ^{19}F-NMR (d_6-acetone): δ = −120.6 (s), −124.7 (s), −129.5 (s), −138.0 (s) (OCH$_2$CF_2CF_2CF$_2$CF$_2$H), −74.7 (s, OCH$_2$CF_3).

For polymer **4**, 11.90 g (119 mmol) 2,2,2-trifluoroethanol and 44.42 g (191 mmol) 2,2,3,3,4,4,5,5-octafluoropentanol were used for the synthesis of the fluoroalkoxide solution. The product was isolated as a tan gum. Yield = 36.0 g (71%).
^{1}H-NMR (d_6-acetone): δ = 6.6 (t, OCH$_2$CF$_2$CF$_2$CF$_2$CF_2H), 4.6 (mlt, OCH_2CF$_2$CF$_2$CF$_2$CF$_2$H), 4.6 (mlt, 2H, OCH_2CF$_3$). ^{13}C-NMR (d_6-acetone): δ = 108–120 (overlapping multiplets, OCH$_2$CF_2CF$_2$CF$_2$CF$_2$H), 64.5 (t, OCH$_2$CF$_2$CF$_2$CF$_2$CF$_2$H), 124 (qt, OCH$_2$CF$_3$), 65 (t, OCH$_2$CF$_3$). ^{31}P-NMR (d_6-acetone): δ = −6.1 (s). ^{19}F-NMR (d_6-acetone): δ = −120.6 (s), −124.7 (s), −129.5 (s), −138.0 (s) (OCH$_2$CF_2CF_2CF$_2$CF$_2$H), −74.7 (s, OCH$_2$CF_3).

For polymer **5**, 16.84 g (168 mmol) 2,2,2-trifluoroethanol and 32.97 g (142 mmol) 2,2,3,3,4,4,5,5-octafluoropentanol were used for the synthesis of the fluoroalkoxide solution. The product was isolated as a tan gum. Yield = 26.2 g (57%).
^{1}H-NMR (d_6-acetone): δ = 6.6 (t, OCH$_2$CF$_2$CF$_2$CF$_2$CF_2H), 4.6 (mlt, OCH_2CF$_2$CF$_2$CF$_2$CF$_2$H), 4.6 (mlt, 2H, OCH_2CF$_3$). ^{13}C-NMR (d_6-acetone): δ = 108–120 (overlapping multiplets, OCH$_2$CF$_2$CF$_2$CF$_2$CF$_2$H), 64.5 (t, OCH$_2$CF$_2$CF$_2$CF$_2$CF$_2$H), 124 (qt, OCH$_2$CF$_3$), 65 (t, OCH$_2$CF$_3$). ^{31}P-NMR (d_6-acetone): δ = −6.1 (s). ^{19}F-NMR (d_6-acetone): δ = −120.6 (s), −124.7 (s), −129.5 (s), −138.0 (s) (OCH$_2$CF_2CF_2CF$_2$CF$_2$H), −74.7 (s, OCH$_2$CF_3).

For polymer **6,** 22.76 g (228 mmol) 2,2,2-trifluoroethanol and 19.30 g (83 mmol) 2,2,3,3,4,4,5,5-octafluoropentanol were used for the synthesis of the flu-

oroalkoxide solution. The product was isolated as a tan gum. Yield = 25.9 g (65%).
^{1}H-NMR (d_6-acetone): δ = 6.6 (t, OCH$_2$CF$_2$CF$_2$CF$_2$CF_2H), 4.6 (mlt, OCH_2CF$_2$CF$_2$CF$_2$CF$_2$H), 4.6 (mlt, 2H, OCH_2CF$_3$). ^{13}C-NMR (d_6-acetone): δ = 108–120 (overlapping multiplets, OCH$_2$CF$_2$CF$_2$CF$_2$CF$_2$H), 64.5 (t, OCH$_2$CF$_2$CF$_2$CF$_2$CF$_2$H), 124 (qt, OCH$_2$CF$_3$), 65 (t, OCH$_2$CF$_3$). ^{31}P-NMR (d_6-acetone): δ = −6.1 (s). ^{19}F-NMR (d_6-acetone): δ = −120.6 (s), −124.7 (s), −129.5 (s), −138.0 (s) (OCH$_2$CF_2CF_2CF$_2$CF$_2$H), −74.7 (s, OCH$_2$CF_3).

For polymer **7**, 24.85 g (248 mmol) 2,2,2-trifluoroethanol and 14.40 g (62 mmol) 2,2,3,3,4,4,5,5-octafluoropentanol were used for the synthesis of the fluoroalkoxide solution. The product was isolated as a tan gum. Yield = 24.1 g (67%).
^{1}H-NMR (d_6-acetone): δ = 6.6 (t, OCH$_2$CF$_2$CF$_2$CF$_2$CF_2H), 4.6 (mlt, OCH_2CF$_2$CF$_2$CF$_2$CF$_2$H), 4.6 (mlt, 2H, OCH_2CF$_3$). ^{13}C-NMR (d_6-acetone): δ = 108–120 (overlapping multiplets, OCH$_2$CF$_2$CF$_2$CF$_2$CF$_2$H), 64.5 (t, OCH$_2$CF$_2$CF$_2$CF$_2$CF$_2$H), 124 (qt, OCH$_2$CF$_3$), 65 (t, OCH$_2$CF$_3$). ^{31}P-NMR (d_6-acetone): δ = −6.1 (s). ^{19}F-NMR (d_6-acetone): δ = −120.6 (s), −124.7 (s), −129.5 (s), −138.0 (s) (OCH$_2$CF_2CF_2CF$_2$CF$_2$H), −74.7 (s, OCH$_2$CF_3).

For polymer **8**, 28.60 g (286 mmol) 2,2,2-trifluoroethanol and 6.00 g (26 mmol) 2,2,3,3,4,4,5,5-octafluoropentanol were used for the synthesis of the fluoroalkoxide solution. The product was isolated as a white semicrystalline material. Yield = 22.0 g (66%).
^{1}H-NMR (d_6-acetone): δ = 6.6 (t, OCH$_2$CF$_2$CF$_2$CF$_2$CF_2H), 4.6 (mlt, OCH_2CF$_2$CF$_2$CF$_2$CF$_2$H), 4.6 (mlt, 2H, OCH_2CF$_3$). ^{13}C-NMR (d_6-acetone): δ = 108–120 (overlapping multiplets, OCH$_2$CF$_2$CF$_2$CF$_2$CF$_2$H), 64.5 (t, OCH$_2$CF$_2$CF$_2$CF$_2$CF$_2$H), 124 (qt, OCH$_2$CF$_3$), 65 (t, OCH$_2$CF$_3$). ^{31}P-NMR (d_6-acetone): δ = −6.1 (s). ^{19}F-NMR (d_6-acetone): δ = −120.6 (s), −124.7 (s), −129.5 (s), −138.0 (s) (OCH$_2$CF_2CF_2CF$_2$CF$_2$H), −74.7 (s, OCH$_2$CF_3).

For polymer **9,** 31.04 g (310 mmol) 2,2,2-trifluoroethanol was used for the synthesis of the fluoroalkoxide solution. The product was isolated as a white semicrystalline material. Yield = 23.5 g (75%).
^{1}H-NMR (d_6-acetone): δ = 4.6 (q, J = 7.9 Hz, 4H, OCH$_2$CF$_3$). ^{13}C-NMR (d_6-acetone): δ = 124 (qt, OCH$_2$CF$_3$), 65 (t, OCH$_2$CF$_3$). ^{31}P NMR (d_6-acetone): δ = −6.3 (s). ^{19}F-NMR (d_6-acetone): −74.7 (s).

RESULTS AND DISCUSSION

Synthesis and structural characterization of polymers

Poly(dichlorophosphazene) (**1**) was prepared by thermal ring-opening polymerization of hexachlorocyclotriphosphazene. Polymer **1** readily underwent replacement of the labile chlorine atoms, by the fluoroalkoxide nucleophiles, sodium 2,2,3,3,4,4,5,5-octafluoropentoxide and 2,2,2-trifluoroethoxide in THF, to yield poly(fluoroalkoxyphosphazene)s as shown in Table I. Thus, the mixed-substituent polymers **3** through **8** were synthesized by the simultaneous addition of the sodium fluoroalkoxide solutions

TABLE I
Side Group Ratios and Molecular Weight Characterization (Polymers 2–9)

$[NP(OCH_2(CF_2)_4H)_x(OCH_2CF_3)_y]_n$	%x	%y	%Yield	M_n ($\times 10^5$)	M_w ($\times 10^5$)	PDI
2	100	0	70	1.78	15.09	8.5
3	75	25	67	2.38	7.06	3.0
4	58	42	71	4.43	20.75	4.7
5	42	58	57	5.20	14.80	2.8
6	23	77	65	4.17	12.71	3.0
7	13	87	67	5.55	18.25	3.3
8	6	94	66	4.40	14.58	3.3
9	0	100	75	1.29	4.53	3.5

to **1** to yield polymers with 25 to 94% trifluoroethoxy substituents (Scheme 1). Simultaneous addition of the nucleophiles was used because of the higher reactivity of the sodium trifluoroethoxide and the ability of the nucleophiles to undergo side-group exchange reactions with each other. ^{31}P-NMR spectroscopy was used to monitor the reactions to ensure complete replacement of the chlorine atoms. The single-substituent control polymers poly[bis(octafluoropentoxyphosphazene)] and poly[bis(trifluoroethoxyphosphazene)] (**2** and **9**) were synthesized by the addition of a slight excess of the sodium 2,2,3,3,4,4,5,5-octafluoropentoxide or sodium 2,2,2-trifluoroethoxide in THF to a solution of **1** in THF.

Polymers **2**– **9** were characterized using [1]H-, ^{31}P-, ^{13}C-, and ^{19}F-NMR spectroscopy. Quantitative information about the ratios of side groups was obtained from the ^{1}H-NMR spectra. Although the peaks of the CH_2 protons of trifluoroethoxy and octafluoropentoxy groups overlap at 4.6 ppm, the ratios of side groups could still be determined by integration of the terminal proton in the octafluoropentoxy group at 6.6 ppm (Fig. 2). Twice the integration of the octafluoropentoxy terminal hydrogen is the amount of octafluoropentoxy CH_2 proton contribution to the overlapping peak at 4.6 ppm. ^{31}P-NMR spectra of the mixed-substituent polymers gave overlapping peaks from phosphorus atoms that bear two trifluoroethoxy groups, two octafluoropentoxy groups, or one of each fluoroalkoxy group, and they appeared as a singlet at −6.1 ppm and could be used only for qualitative characterization. Fluorine–fluorine coupling was not detectable in the ^{19}F-NMR spectra attributed to the small coupling constants (<1 ppm) within the fluoroalkyl chains of the octafluoropentoxy side groups. This usually oc-

curs only in symmetrically substituted fluoroalkanes.[29,30]

The molecular weights of the poly(fluoroalkoxyphosphazene)s **2**– **9**, as determined by gel permeation chromatography (GPC) versus polystyrene standards, are shown in Table I. The broad polydispersities obtained (2.8–8.5) are typical of polymers prepared by the thermal ring-opening polymerization route to polymer **1**.[13] As a consequence, the molecular weights of the fluoroalkoxy-substituted polymers also varied considerably at a range of 1.29–5.55 $\times 10^5$ for M_n. The range of the M_w values obtained (4.53 $\times$ 10[5]–2.075 $\times$ 10[6]) was considerably larger. In addition, factors such as hydrodynamic radius and molecular weight differences in the substituents probably influence the apparent molecular weight distributions.

Fire resistance and thermal stability

Limiting oxygen index tests and thermogravimetric analyses were performed on each of the polymers (Table II). Overall, the poly(fluoroalkoxyphosphazene)s possess excellent fire resistance and thermal stability. Incorporation of only 6% of octafluoropentoxy substituents was sufficient to increase the oxygen
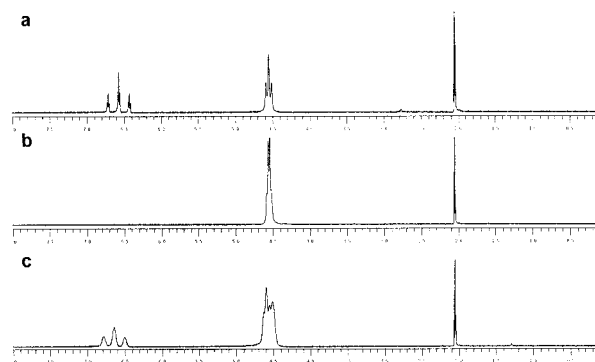
Figure 2 Substituent ratio determination by ^{1}H-NMR: (a) poly[bis(octafluoropentoxyphosphazene)] (**2**); (b) poly-[bis(trifluoroethoxyphosphazene)] (**9**); (c) mixed-substituent poly(fluoroalkoxyphosphazene) (**5**).

Scheme 1 Synthesis of poly(fluoroalkoxyphosphazene)s.

TABLE II
Thermal Analysis of Polymers 2–9 by LOI, TGA, and DSC

Polymer	Trifluoroethoxy substituent (%)	Oxygen index	Onset T (°C)	T_{50} (°C)	T_g (°C)	Mesophase (°C)	T_m (°C)
2	0	>40	520	630	−72	—	—
3	25	>40	380	580	−69	—	—
4	42	>40	380	595	−72	—	—
5	58	>40	380	575	−73	—	—
6	77	>40	380	575	−73	—	—
7	87	>40	380	577	−73	—	—
8	94	>40	380	580	−73	16	139
9	100	26	380	580	−73	66	234

index (OI) values from a value of 26 for poly[bis(trifluoroethoxyphosphazene)] (**9**) to more than 40 for polymers **2**– **8**.[31] Incorporation of the octafluoropentoxy group increases the ratio of carbon to hydrogen, which generally results in better fire resistance (higher OI values).[32] However, this alone is not enough to account for the magnitude of the observed increase. Other contributing factors include the increased fluorine content[33] of the polymers that contain octafluoropentoxy substituents and possible thermal crosslinking reactions through the terminal hydrogen of the octafluoropentoxy side group. In addition, different pyrolysis residues were obtained from the trifluoroethoxy single-substituent polymer (**9**) than from the other polymers. Polymer **9** gave only a small amount of black char after the polymer melted and self-extinguished. Polymers **2**– **8** also melted and self-extinguished, but left a small amount of adhesive gum that could not be ignited.

Fire resistance was dominated by the presence of the octafluoropentoxy side group, although the thermal decomposition was controlled by the trifluoroethoxy side groups, as can be seen from the TGA results (Table II and Fig. 3). The onset temperatures of decomposition for the polymers with trifluoroethoxy substituents were all near 380°C and T_{50} values ranged from 575 to 595°C. By contrast, the octafluoropentoxy single-substituent polymer showed no weight loss until 520°C and had a faster rate of decomposition (T_{50} of ~ 620°C) than that of polymers **3**– **9**. The thermal stability is also influenced by depolymerization reac-

tions of the polymers probably to small-molecule cyclic species. It should be noted that depolymerization of some poly(fluoroalkoxyphosphazenes), over long periods of time at temperatures above 150°C, can occur below the onset temperatures observed in the TGA experiments.[34]

Glass-transition temperatures

The glass-transition temperatures of polymers **2**– **9** were found to be between −69 and −73°C (−92 to −99°F) by DSC (Table II). This indicates excellent low-temperature flexibility, a property that is important for elastomers to be used in low-temperature environments such as high-altitude aerospace applications. Polymers that contain up to 87% trifluoroethoxy substituents (**2**– **7**) are amorphous polymers with no additional transitions detected above the T_g. However, polymers **8** and **9**, with 94 and 100% trifluoroethoxy substituents, respectively, were semicrystalline materials. Mesophase transitions[12] at 16 and 66°C and crystalline melting transitions of 139 and 234°C, respectively, were detected for **8** and **9**, as shown in Figure 4. With just 6% incorporation of the octafluoropentoxy substituent, polymer **8** showed significantly decreased crystallinity and lower temperature transitions (mesophase and T_m) than those of the trifluoroethoxy single-substituent polymer (**9**). Thus, incorporation of the octafluoropentoxy side group disrupts crystalline domains in the poly(fluoroalkoxyphosphazene)s because of the size, flexibility, and mobility of the longer fluoroalkoxy side group. Figure 4 illustrates the absence of mesophase and crystalline melting transitions in the polymers that have more than 6% octafluoropentoxy substituents (**2**– **7**).

Mechanical properties

Qualitatively, the polymers can be divided into three groups. The mixed-substituent poly(fluoroalkoxyphosphazenes) **4**– **7** (25–87% trifluoroethoxy substituent) were elastomeric gums that, when crosslinked, are applicable elastomers. Only polymer **4** had a tendency
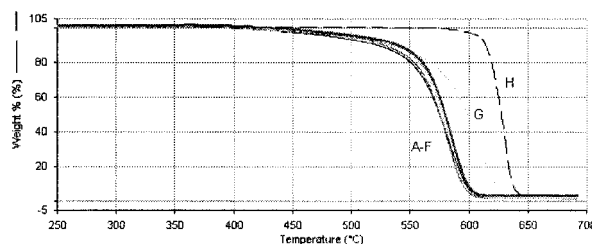

Figure 3 TGA traces of polymers **2**– **9**: (A)–(F) polymers **3** and **5**– **9**; (G) polymer **4**; (H) polymer **2**.
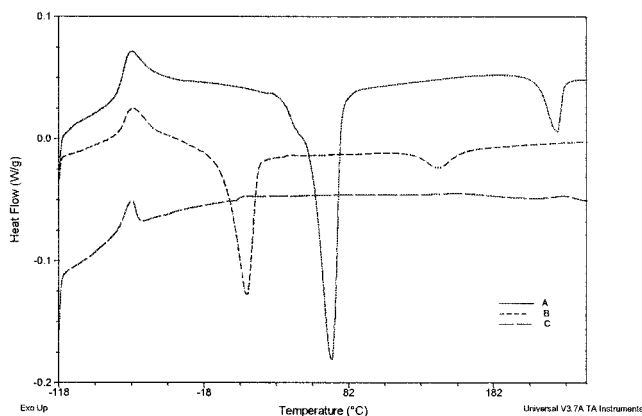
Figure 4 DSC traces showing loss of crystallinity: (A) poly[bis(trifluoroethoxyphosphazene)] (**9**); (B) mixed-substituent poly(fluoroalkoxyphosphazene) (**8**) with 94% trifluroethoxy substituents; (C) mixed-substituent poly(fluoroalkoxyphosphazene) (**6**) with 58% trifluroethoxy substituents.

Figure 5 Mechanical properties of polymers **2**– **9**.

to undergo viscous flow over a period of several weeks. Poly[bis(octafluoropentoxyphosphazene)] (**2**) and the mixed-substituent polymers with 25 and 94% trifluoroethoxy substituents (**3** and **8**) had tough waxlike properties, whereas poly[bis(trifluoroethoxyphosphazene)] (**9**) is a tough, fibrous, microcrystalline material. The properties of polymers **8** and **9** are attributed to the crystallinity present in the samples, but an explanation for the similar properties seen in polymers **2** and **3** is less clear. The nonelastomeric character of polymers with ≥75% octafluoropentoxy substituents might be a consequence of the ability of the terminal hydrogen of the octafluoropentoxy side group to participate in dipole–dipole hydrogen bonding–like interactions. These types of interactions have been used to explain the higher boiling points of molecules with the CF_2H unit compared to similar molecules with the CF_3 moiety.[35–37] In addition, Künzler and Ozark[38] noticed that copolymers of dimethylacrylamide with methacrylate end-capped polydimeth-
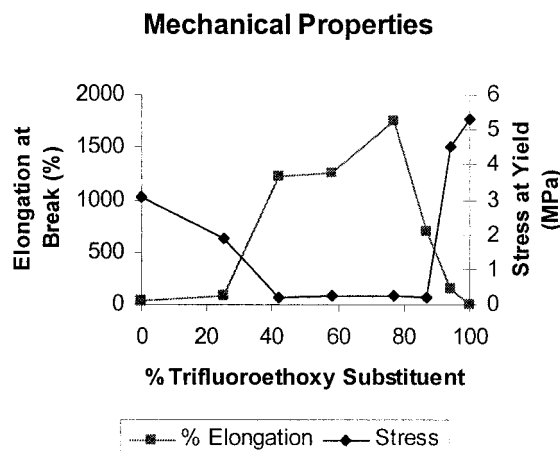
ylsiloxanes that had octafluoropentoxy side chains did not phase separate. They attributed this to hydrogen-bond interactions between the terminal hydrogen and the amide linkage.[38] Thus, it is possible that the high octafluoropentoxy content of polymers **2** and **3** could induce sufficient inter- and intrachain bond–dipole interactions to account for the tough, waxlike properties that are characteristic of these polymers.

Variations in the ratios of side groups had a marked effect on the mechanical properties, as summarized in Table III. The stress at yield was greater than 1.8 MPa for polymers **2** and **3** (0–25% trifluoroethoxy side group) but decreased with higher incorporation of the trifluoroethoxy substituent to about 0.2 MPa for polymers **4** through **7** (42–87% trifluoroethoxy content) (Fig. 5) until it reached more than 4.5 MPa for polymers **8** and **9** (94–100% trifluoroethoxy substitutent). This behavior can be explained in terms of the bond–dipole interactions proposed for the octafluoropentoxy side group and the crystalline properties of polymers **8** and **9**. The bond–dipole interactions decrease in number with increased incorporation of the trifluoroethoxy group. These interactions can also account

TABLE III
Mechanical Properties of Polymers 2–9

| Polymer	Trifluoroethoxy substituent (%)	Stress at yield (MPa)	Stress SD	%Strain (MPa)	Strain SD	Young's modulus (MPa)	Modulus SD
2	0	3.06	0.61	26.9	9.6	35.97	3.34
3	25	1.86	0.71	90.6	30.4	17.81	2.10
4	42	0.21	0.01	1217.5	251.0	0.46	0.05
5	58	0.24	0.04	1258.0	49.9	0.64	0.08
6	77	0.24	0.02	1753.6	100.7	0.65	0.03
7	87	0.20	0.01	686.3	39.2	0.68	0.09
8	94	4.53	1.08	147.8	40.0	16.39	9.44
9	100	5.33[a]	2.65[a]	4.8	2.6	158.30	54.99

[a] Polymer did not yield.
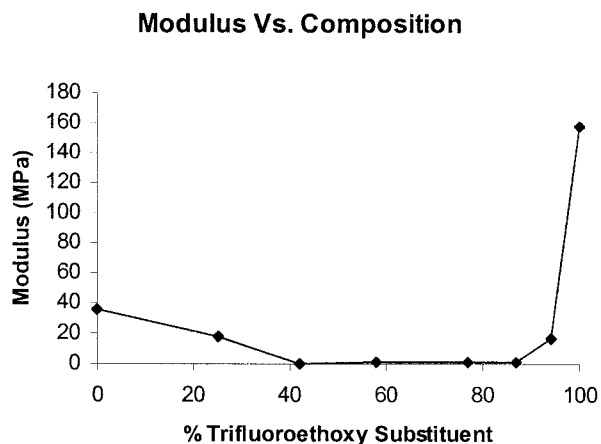
Figure 6 Young's moduli of polymers **2**– **9**.

for decreased elongation to break of the octafluoro-pentoxy single-substituent polymer (**2**) (9.6%) and polymer **3** (90.6%) relative to mixed-substituent polymers **4** through **7** that had elongation to break values > 600% (Fig. 5). At very high incorporations of the trifluoroethoxy side group, crystallinity becomes an important factor, as seen in the stress increases for polymers **8** and **9** compared to those of the polymers with lower trifluoroethoxy incorporation. Intermolecular interactions through crystalline "crosslinks" have this effect in other polymer systems. Increases in intermolecular forces substantially decreased the elongation to break, but increased the stress at yield (Fig. 5). However, although only a small amount of the octafluoropentoxy side group was needed to reduce the crystallinity of the trifluoroethoxy single-substituent polymer, more than 25% of the trifluoroethoxy side groups were required to induce a similar effect on the mechanical properties of the octafluoropentoxy single-substituent polymer system.

The values of the Young's modulus followed the same trend as those found for the stress results (Fig. 6). The single-substituent polymers (**2** and **9**) and the mixed-substituent polymers closest in composition (**3** and **8**) showed higher modulus values than those of the other mixed-substituent polymers, probably because of the magnitude of molecular interactions that take place in the system. The largest increase in modulus came between polymers **8** and **9**, where the greater crystallinity of the single-substituent polymer caused an increase of over 100 MPa.

The influence of molecular weight on the mechanical properties was examined by a comparison of polymers **4**– **8**. GPC analysis of the mixed-substituent polymers **4** gave a polydispersity of 4.7 and an M_w of >2 × 10^6. Polymers **5**– **8** had similar molecular weights (M_n 4.17–5.55 × 10^5, M_w 1.3–1.8 × 10^6) and similar polydispersities of 2.8–3.3. Despite these differences, polymer **4** showed mechanical properties very similar

to those of polymers **5**– **7**. However, polymer **8** showed drastically different mechanical properties, such as strength at yield and elongation to break, than those of polymers **5**– **7**. This suggests that the mechanical properties of the polymers studied here depend primarily on polymer composition and not on molecular weight.

DSC experiments were used to examine all the polymers before and after fabrication into thin sheets to ensure that no increase in crystallinity had occurred. Semicrystalline polymers (**8** and **9**) and waxy polymers (**2** and **3**) were also analyzed after microtensile testing. DSC traces showed no changes that would be indicative of increased crystallinity after fabrication, as illustrated by Figure 7, which shows the DSC traces for poly[bis(trifluoroethoxyphosphazene)] (**9**) before and after hot-press fabrication and also after microtensile testing.

CONCLUSIONS

The poly[bis(fluoroalkoxyphosphazenes)] examined showed good thermal stability, high OI values, and large variations in mechanical properties. The T_g and T_d values of the cosubstituted polymers differed very little from one another but the mechanical properties and molecular interactions were highly dependent on the ratios of the side groups. Polymers **2**, **3**, **8**, and **9** had the strongest intermolecular interactions and showed higher Young's modulus and stress at yield, but much lower elongation to break, than those of polymers **4**– **7**.

Polymers **4**– **7** have the properties needed for the fabrication of good elastomers. These polymers, which ranged in composition from 42 to 87% of the trifluoroethoxy side group, possess very similar thermal and mechanical behavior. Further improvements to these polymers through the incorporation of a crosslinking
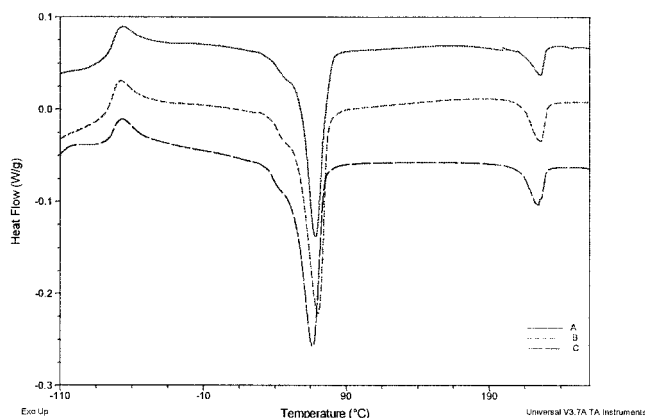

Figure 7 DSC traces of poly[bis(trifluoroethoxyphosphazene)] (**9**): (A) before hot-press; (B) after hot-press; (C) after mechanical testing.

moiety and compounding with suitable materials can yield resilient low-temperature elastomers.

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