Polyphosphazenes: Thermomechanical Transitions

T. M. CONNELLY, JR.,* and J. K. GILLHAM, *Polymer Materials Program, Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08540*

Synopsis

Four linear phosphazene homopolymers with structure $[NPX_2]_n$, where X = Cl, OCH_2CF_3, $OCH_2C_3F_7$, and $OCH_2C_3F_6CHF_2$, two copolymers with mole ratios of the alkoxy substituents $OCH_2CF_3/OCH_2C_3F_7$ and $OCH_2CF_3/OCH_2C_3F_6CHF_2$ approximately 1/1, and two physical blends with overall compositions approximating those of the copolymers were examined between −180° and 250°C in an inert atmosphere using a fully automated torsional braid apparatus. Crystal/melt, crystal/crystal, glass, and glassy-state transitions are documented on the basis of the thermomechanical experiments. In addition to the assignment of transition temperatures, the noteworthy findings include the narrow range of values of the glass transition temperatures of the four homopolymers, the increasing negative slope of the modulus versus temperature in the glassy state with increasing size of the substituent, the presence of a transition immediately above T_g for the copolymers, and the incompatibility of the blends. A glassy-state transition in each of the fluoroalkoxypolyphosphazene materials is tentatively attributed to motion of the substituents. An additional glassy-state transition occurs in the heptafluorobutoxy- and octafluoropentoxy-substituted materials. The transition temperatures of specimens preheated to 250°C were essentially the same as those preheated to 150°C.

INTRODUCTION

This report presents low-frequency (~1 Hz) dynamic mechanical data on linear fluoroalkoxy-substituted polyphosphazenes and on the parent completely inorganic polymer $[NPCl_2]_n$. The fluoroalkoxy polymers have been developed as precursors to low-temperature elastomers. The particular fluoroalkoxy groups chosen as substituents were selected partly because of the necessity for using relatively inexpensive fluoroalcohols in the production of commercially viable materials.

Synthetic and molecular characterization efforts have been underway at The Pennsylvania State University, University Park, Pennsylvania[1]; Horizons Research, Inc., Cleveland, Ohio[2]; the Army Materials and Mechanics Research Center, Watertown, Massachusetts[3]; the University of Manchester, Manchester, United Kingdom[4,5]; The Firestone Tire and Rubber Company, Akron, Ohio[6]; and Princeton University, Princeton, New Jersey.[7,8] The efforts at Princeton University are part of an ongoing program to characterize the transitions, thermal stability, and thermomechanical behavior of high-technology polymeric materials. Semiinorganic systems which have been studied in this laboratory have included poly(carboranesiloxane)s[9] and bis/tris metal phosphinate polymers.[10]

* Present address: Churchill College, Cambridge University, Cambridge, England.

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TABLE I

Intrinsic Viscosities and Elemental Analyses

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	Intrinsic viscosity,[a] dl/g 25° C (solvent)	Elemental analysis[a] % actual (calculated)			
		C	H	N	Cl
Homopolymers					
$[NPCl_2]$	—		—		
$[NP(OCH_2CF_3)_2]$	1.1 (acetone)	19.90 (19.75)	1.65 (1.64)	5.55 (5.77)	0.03 (0.00)
$[NP(OCH_2C_3F_7)_2]$	2.1 (Freon E-1[b])	21.85 (21.67)	0.90 (0.90)	3.10 (3.16)	0.05 (0.00)
$[NP(OCH_2C_3F_6CHF_2)_2]$	4.9 (acetone)	23.71 (23.70)	1.20 (1.18)	2.85 (2.76)	0.03 (0.00)
Copolymers					
$(OCH_2CF_3)_{0.537}/$ $(OCH_2C_3F_7)_{0.463}$	0.95 (Freon E-2[c])	21.00 (20.99)	1.35 (1.16)	4.15 (4.08)	0.07 (0.00)
$(OCH_2CF_3)_{0.494}/$ $(OCH_2C_3F_6CHF_2)_{0.506}$	2.90 (acetone)	22.35 (22.42)	1.30 (1.33)	3.62 (3.73)	0.04 (0.00)

[a] Data provided by Dr. K. Reynard, Horizons, Inc.
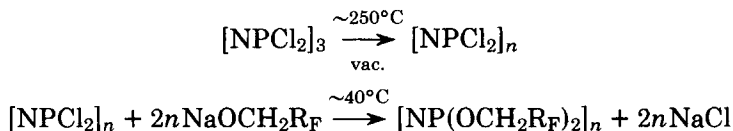
[b] $F(CFCF_3CF_2O)CHFCF_3$.

[c] $F(CFCF_3CF_2O)_2CHFCF_3$.

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SYNTHESIS

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The polymers used in this study were provided by Dr. K. A. Reynard, Horizons Research, Inc., who also provided molecular characteristics (Table I).

The synthetic route to poly(fluoroalkoxyphosphazenes) has been via the preparation of the soluble intermediate poly(dichlorophosphazene) which is subsequently reacted to form the completely substituted product:

$$[NPCl_2]_3 \xrightarrow[\text{vac.}]{\sim 250°C} [NPCl_2]_n$$

$$[NPCl_2]_n + 2n \, NaOCH_2R_F \xrightarrow{\sim 40°C} [NP(OCH_2R_F)_2]_n + 2n \, NaCl$$

When a mixture of fluoroalkoxides is employed, copolymers are obtained which are either elastomeric or plastic depending on the choice of substituents.

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Homopolymers[2]

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Fluoroalkoxy homopolymers were synthesized in a similar manner to that outlined below for copolymers using the appropriate fluoroalcohol.

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Copolymers[2]

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Synthesis of the polymeric precursor poly(dichlorophosphazene) was effected by heating distilled hexachlorophosphazene in a vacuum tube at 270°C (24 hr) and then at 250°C (150 hr). After extraction of low molecular weight material with hexane, the linear polymer was dissolved in dry benzene. The polymer solution was added slowly to a molar excess of an equimolar mixture

of the two fluoroalkoxides in tetrahydrofuran which was maintained at 40–45°C overnight. The mixture of fluoroalkoxides had been prepared at 40°C in dry tetrahydrofuran from sodium metal and an excess of the two fluoroalcohols. Copolymer was precipitated by addition of more benzene and was washed with water to remove salts. Further purification was accomplished by dissolving the polymer in the azeotropic mixture of CCl_2FCClF_2 and acetone and washing with water until the aqueous layer contained no chloride ion. After removal of the aqueous phase, the polymer was isolated by addition of benzene.

The polymers were dried in vacuo at 25°C and then characterized with respect to elemental analyses and intrinsic viscosities (Table I).

Blends

Solutions (10%, g polymer/ml solvent) of the homopolymers were mixed to form an equimolar (on the basis of repeat units) homogeneous solution. Solvent was removed in the thermal cycle which is described below.

EXPERIMENTAL PROCEDURE

Torsional Braid Analysis[11,12]

A fully automated torsional braid apparatus interfaced with a dedicated hard-wired data analyzer[13] was used to obtain the thermomechanical spectra at about 1 Hz. A repetitive sequence consisting of alignment of the optical transducer; initiation of free oscillations; and printout of temperature (mV), logarithmic decrement (Δ), and period (P, sec) for each damped wave operated automatically throughout the experiment.

Specimens for the thermomechanical studies were prepared from 10% (g polymer/ml solvent) solutions by impregnating a 2-in. heat-cleaned glass braid. After mounting in the apparatus, solvent was removed in flowing helium in the prehistory 25° → 150°C ($\Delta T/\Delta t$ = 2°C/min). The solvents used were benzene for poly(dichlorophosphazene); acetone for the OCH_2CF_3- and $OCH_2C_3F_6CHF_2$-substituted homopolymers and the corresponding copolymer; and Freon E-1 (bp 41°C) for the $OCH_2C_3F_7$-substituted homopolymer and the $OCH_2CF_3/OCH_2C_3F_7$-substituted copolymer. Thermogravimetric analyses (TGA) of the polymer solutions showed that solvent was removed during the prehistory and that the dry fluoroalkoxy polyphosphazene materials did not lose significant weight below 250°C ($\Delta T/\Delta t$ = 2.0°C/min) (Figs. 1 and 2). Immediately after the drying procedure, thermomechanical spectra were obtained for the temperature sequence 150° → −180° → 250° → −180° → 250°C ($\Delta T/\Delta t$ = ∓1.5°C/min, T <0°C; $\Delta T/\Delta t$ = ∓2°C/min, T >0°C), unless noted to the contrary in the figure captions. The maximum temperature of 250°C was chosen on the basis of being above most of the encountered physical phase transition temperatures and below the onset of severe degradation (by TGA). Mechanical experiments were performed in dried helium (flow rate ≈3 ml/min).

Two parameters were plotted versus temperature for each thermomechanical experiment.[12] The relative rigidity $1/P^2$ is a proportional measure of the
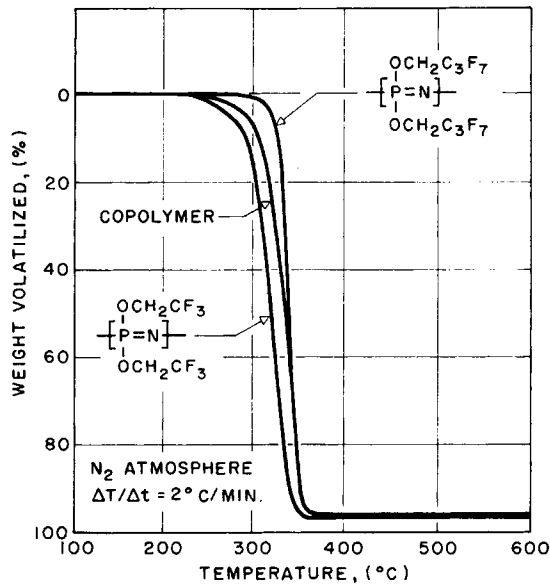
Fig. 1. Thermogravimetric analyses: $[NP(OCH_2CF_3)_2]_n$, $[NP(OCH_2C_3F_7)_2]_n$, and copolymer.

in-phase shear modulus G' of the composite specimen. The presented loss modulus $K''G''$ is a proportional measure of the out-of-phase shear modulus G'' of the composite specimen and is computed as the product of the logarithmic decrement Δ and $1/P^2$ (note: $G'' \approx G'\Delta/\pi$). The digitized printout (Δ and P) from the data analyzer was converted to $K''G''$ and $1/P^2$ which were plotted versus temperature using a computer-driven plotter (Calcomp 565)
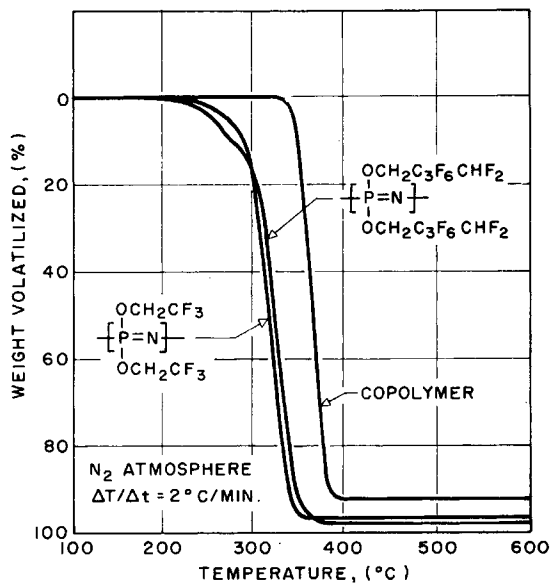
Fig. 2. Thermogravimetric analyses: $[NP(OCH_2CF_3)_2]_n$, $[NP(OCH_2C_3F_6CHF_2)_2]_n$, and copolymer.
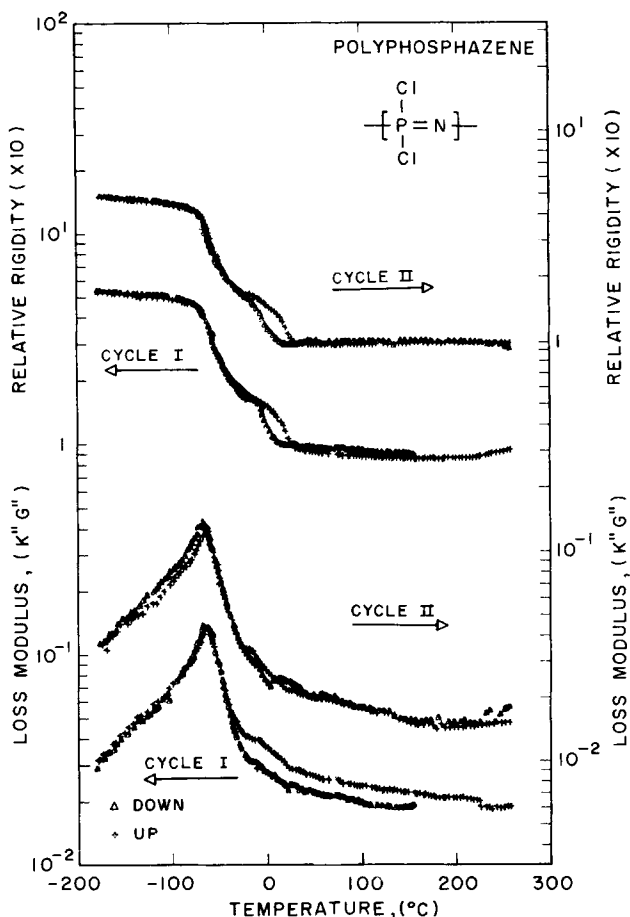
Fig. 3. Thermomechanical spectra: $[NPCl_2]_n$, He atmosphere. Prehistory: dry, 25° → 150°C. Experiment: 150° → −180° → 250° → −180° → 250°C. $\Delta T/\Delta t = 2.0°C/min$, $T > 0°C$; $\Delta T/\Delta t = 1.5°C/min$, $T < 0°C$.

(Figs. 3–12). Two sets of data appear for each of the polymers studied which correspond to the sequence 150° → −180° → 250°C (cycle I) and 250° → −180° → 250°C (cycle II), respectively (Figs. 3–10). The sequence was continuous; the curves and scale for cycle II are displaced by $\log_{10} 3$ for the purposes of presentation.

The maxima of the out-of-phase shear modulus curves were used for assigning phase transition temperatures. A distinction between transitions was made on the basis of examination of thermohysteresis in the temperature cycle: glass transition (T_g) and glassy-state transitions (T_{sec}) occurred at essentially the same temperature on both cooling and heating, whereas crystallization (T_{crys}) occurred at lower temperatures than subsequent melting (T_m). In one polymer, $[NP(OCH_2CF_3)_2]_n$, distinct changes in rigidity and loss occurred with thermohysteresis at a phase change below the crystal/melt transition. This was attributed to a crystal/crystal transition. The temperature of the transition is designated T_{cC} on cooling, T_{Cc} on heating. Multiple transitions involving the crystalline regions have been noted for
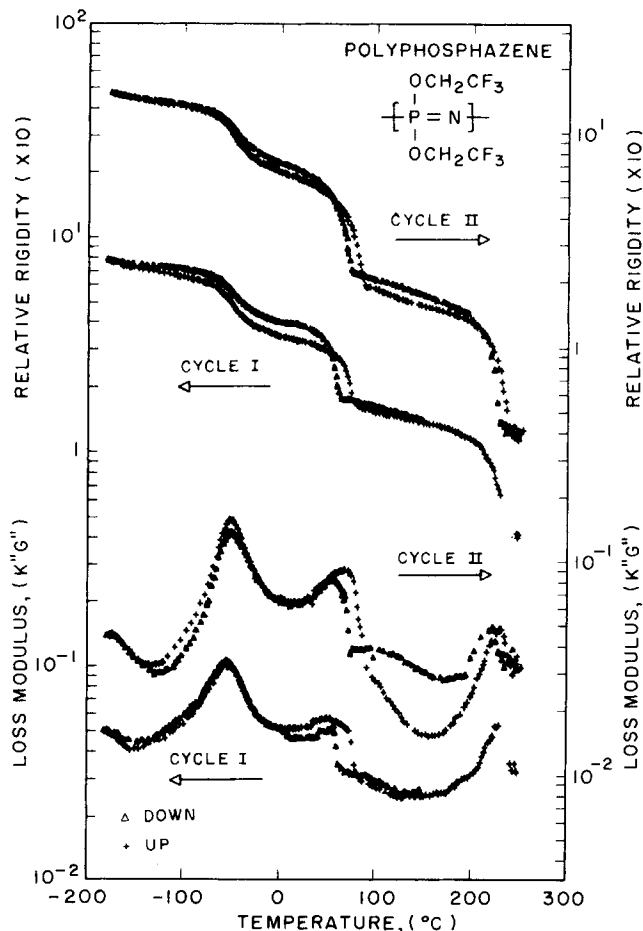
Fig. 4. Thermomechanical spectra: $[NP(OCH_2CF_3)_2]_n$, He atmosphere. Prehistory: dry, $25° \to 150°C$. Experiment: $150° \to -180° \to 250° \to -180° \to 250°C$. $\Delta T/\Delta t = 2.0°C/min$, $T > 0°C$; $\Delta T/\Delta t = 1.5°C/min$, $T < 0°C$.

$[NP(OCH_2CF_3)_2]_n$[14,15] and for some aryloxy polyphosphazenes.[3] The results of dynamic mechanical experiments using a torsional pendulum ($\sim$1 Hz) and vibrating reed ($\sim$300 Hz) have been reported[4] for the trifluoroethoxy- and some aryloxy-substituted polyphosphazenes.

The out-of-phase shear modulus G'', rather than the logarithmic decrement Δ, is used as a measure of loss for assigning transition temperatures because of internal consistency between G'' and dG'/dT.[12] Use of Δ in place of G'' increases the intensity of higher-temperature loss peaks relative to lower-temperature loss peaks (because $K''G'' \approx \Delta/P^2$ and P generally increases with temperature). This mode provides better resolution in some cases and is illustrated in Figures 11 and 12.

RESULTS AND DISCUSSION

The data of the thermomechanical experiments are shown in Figures 3 to 12. Assignments of the transition temperatures are summarized in Table II.

TABLE II
Transition Data (°C)ᵃ

	T_{crys}	T_m	T_{cC}	T_{Cc}	T_g	T_g'	T_{sec}	$T_{sec'}$	$T_{sec}/T_g{}^b$	$T_{sec'}/T_g{}^b$	$T_g/T_m{}^b$	$T_g/T_{Cc}{}^b$
Homopolymers												
[NPCl₂]	−10	13	A	A	−66 (0.73)ᶜ	A	A	A	A	A	0.72	A
[NP(OCH₂CF₃)₂]	223	238	58	68	−53 (0.72)	A	A	~−180 (0.87)	A	0.4	0.43	0.65
[NP(OCH₂C₃F₇)₂]	89	100	A	A	−65 (0.82)	A	−155 (1.12)	−174 (1.26)	0.57	0.48	0.56	A
[NP(OCH₂C₃F₆CHF₂)₂]	A	A	A	A	−64 (0.59)	A	−143 (0.80)	−167 (0.90)	0.62	0.51	A	A
Copolymers												
(OCH₂CF₃)₀.₅₃₇/ (OCH₂C₃F₇)₀.₄₆₃	A	A	A	A	−63 (0.99)	−49 (0.48)	−161 (1.63)	−173 (1.79)	0.53	0.48	A	A
(OCH₂CF₃)₀.₄₉₄/ (OCH₂C₃F₆CHF₂)₀.₅₀₆	A	A	A	A	−64 (0.67)	−49 (0.41)	−160 (1.30)	−172 (1.39)	0.54	0.48	A	A
Blends												
[NP(OCH₂CF₃)₂]₀.₅₀/ [NP(OCH₂C₃F₇)₂]₀.₅₀	218, 95	238, 102	46	62	−61 (0.61)	A	−160 (0.79)	−176 (0.86)	0.54	0.46	0.42, 0.56	0.66
[NP(OCH₂CF₃)₂]₀.₅₀/ [NP(OCH₂C₃F₆CHF₂)₂]₀.₅₀	228	246ᵈ	70	75	−61 (0.69)	A	−144 (0.85)	−166 (0.94)	0.60	0.51	0.41	0.60

ᵃ From maxima of loss moduli; A ≡ absent.
ᵇ °K/°K.
ᶜ Hz.
ᵈ Data not shown.
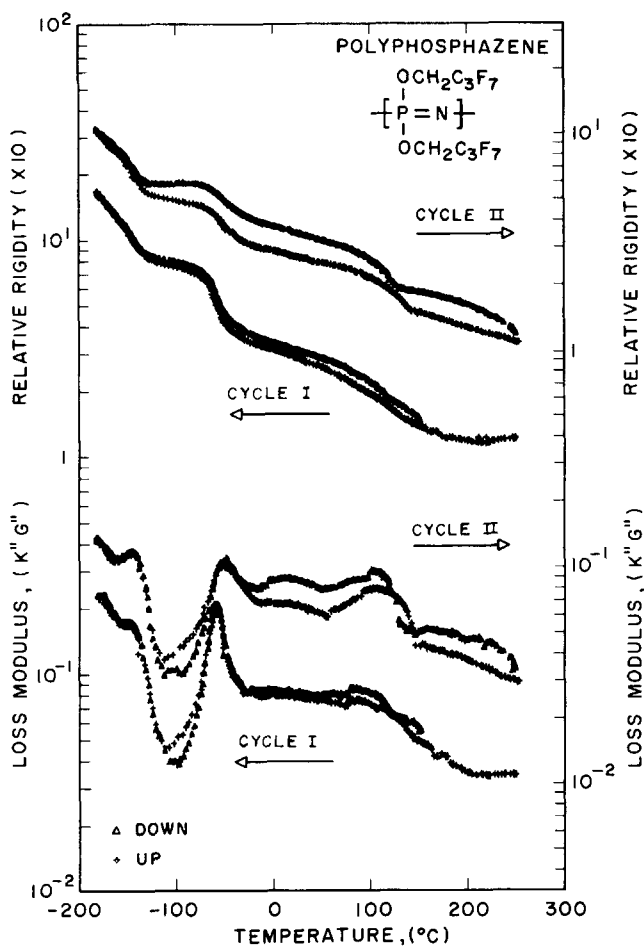
Fig. 5. Thermomechanical spectra: $[NP(OCH_2C_3F_7)_2]_n$, He atmosphere. Prehistory: dry, $25° \rightarrow 150°C$. Experiment: $150° \rightarrow -180° \rightarrow 250° \rightarrow -180° \rightarrow 250°C$. $\Delta T/\Delta t = 2.0°C/min$, $T > 0°C$; $\Delta T/\Delta t = 1.5°C/min$, $T < 0°C$.

Homopolymers

$[NPCl_2]_n$ **(Fig. 3; Table II).** A region of crystallizing/melting is observed. A distinct glass transition but no distinct glassy-state transitions are observed.[8] The high value of 0.72 for the ratio T_g/T_m (°K/°K) of this symmetrical polymer is noteworthy since this ratio ranges from 0.5 to 0.67 for many linear polymers, the former value corresponding to symmetric and the latter to asymmetric polymers.[16]

$[NP(OCH_2CF_3)_2]_n$ **(Fig. 4, Fig. 11; Table II).** A region of crystallizing/ melting and, at lower temperatures, a crystal/crystal transition are observed. A glass transition and a single glassy-state transition are evident. The present thermomechanical data complement torsional pendulum ($-150°$ to $100°C$), vibrating reed ($-150°$ to $60°C$), and dielectric ($-150°$ to $60°C$) data on other samples of the polymer.[4] The activation energy for the glass transition process is reported to be 47 kcal/mole on the basis of dielectric measure-
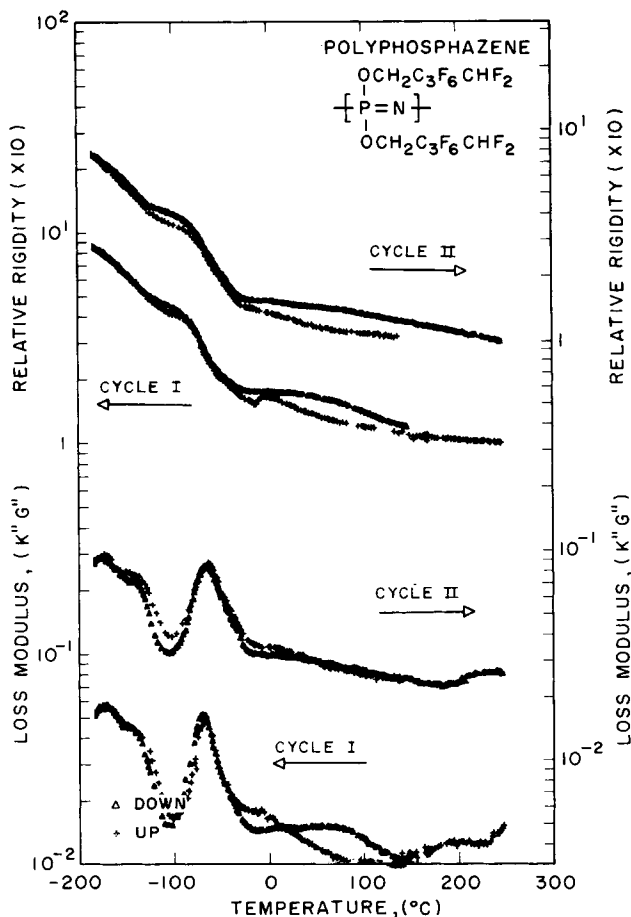
Fig. 6. Thermomechanical spectra: $[NP(OCH_2C_3F_6CHF_2)_2]_n$, He atmosphere. Prehistory: dry, $25° \rightarrow 150°C$. Experiment: $150° \rightarrow -180° \rightarrow 250° \rightarrow -180° \rightarrow 150°C$. $\Delta T/\Delta t = 2.0°C/min$, $T > 0°C$; $\Delta T/\Delta t = 1.5°C/min$, $T < 0°C$.

ments and somewhat lower on the basis of dynamic mechanical experiments at two frequencies.[4] The crystal/crystal transition (58° to 68°C) for the trifluoroethoxy-substituted polymer has been investigated by calorimetric[15] and x-ray techniques.[14] The T_g/T_m (°K/°K) and T_g/T_{Cc} (°K/°K) ratios are 0.43 and 0.65, respectively.

$[NP(OCH_2C_3F_7)_2]_n$ (Fig. 5, Fig. 11; Table II). A region of crystallizing/melting is displayed. A glass transition and two glassy-state transitions are evident. The ratio for T_g/T_m (°K/°K) is 0.56.

$[NP(OCH_2C_3F_6CHF_2)_2]_n$ (Fig. 6, Fig. 11; Table II). No crystal/melt transition is observed. A glass transition and two glassy-state transitions are evident. (A loss shoulder with a peak in the rigidity curve, observed with increasing temperature in the vicinity of 0°C in cycle I, is probably the result of small amounts of water; it is also observed in the behavior of a blend containing this polymer, Fig. 10, cycle I.)

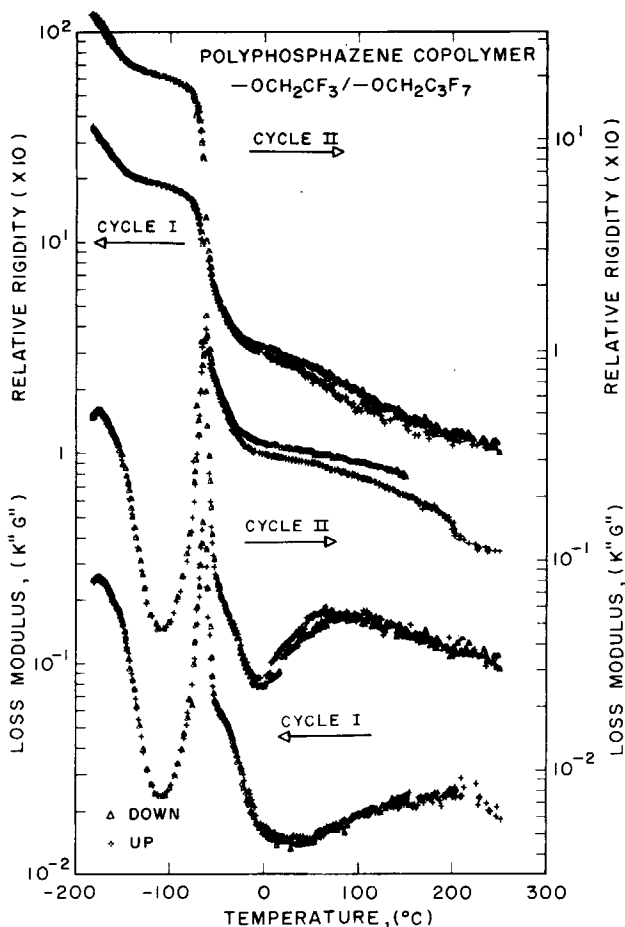The following observations are noteworthy in comparing the homopolymers:

Fig. 7. Thermomechanical spectra: $(OCH_2CF_3)/(OCH_2C_3F_7)$ copolymer, He atmosphere. Prehistory: dry, $25° \rightarrow 150°C$. Experiment: $150° \rightarrow -180° \rightarrow 250° \rightarrow -180° \rightarrow 250°C$. $\Delta T/\Delta t = 2.0°C/min$, $T > 0°C$; $\Delta T/\Delta t = 1.5°C/min$, $T < 0°C$.

1. The range of the glass transition temperatures is narrow ($-53°$ to $-66°C$) and precludes definitive analysis of the effects of substituents on intra- and intermolecular factors. However, it appears that the value of the glass transition temperature decreases slightly with increasing substituent length in the fluoroalkoxy polymers. The influence appears to be greater in the aryloxy-substituted polymers, $[(p\text{-}CH_3C_6H_4O)_2PN]_n$ and $[(p\text{-}CH_3CH_2C_6H_4O)_2PN]_n$, for which the glass transition of the latter is more than 30°C lower than that of the former.[3]

2. The slope of rigidity versus temperature in the glassy state increases markedly with increasing size of the substituent alkoxide, and, corresponding to this observation, the intensity of the glassy-state loss peaks is greater for the butoxy- and pentoxy-substituted polymers than for the ethoxy-substituted polymer.

3. On the basis of assignments of transition temperatures for cycles I and II, preheating to 250°C produced little degradation. However, the thermohysteresis displayed above the glass transition is indicative of physical
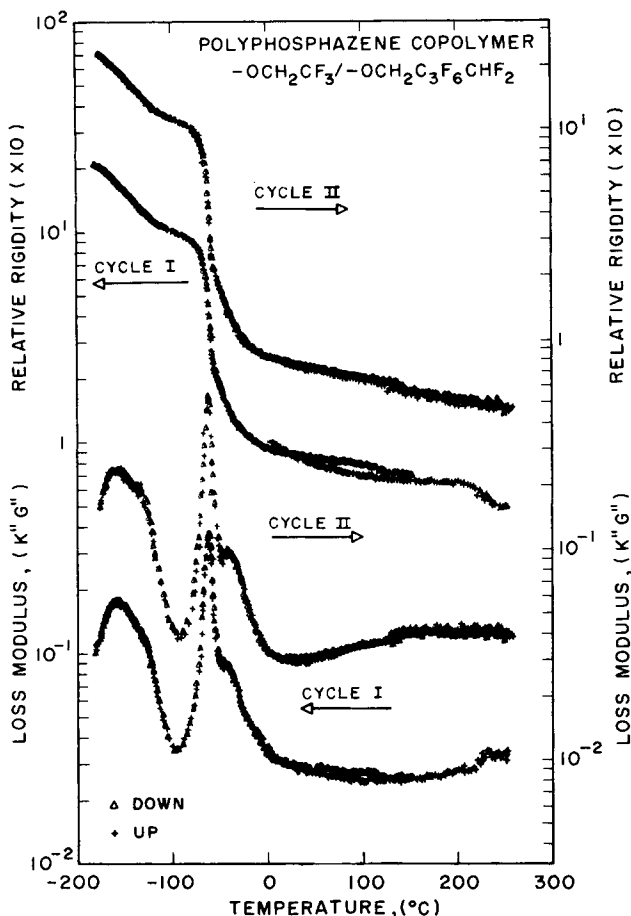
Fig. 8. Thermomechanical spectra: $(OCH_2CF_3)/(OCH_2C_3F_6CHF_2)$ copolymer, He atmosphere. Prehistory: dry, $25° \rightarrow 150°C$. Experiment: $150° \rightarrow -180° \rightarrow 250° \rightarrow -180° \rightarrow 250°C$. $\Delta T/\Delta t = 2.0°C/min$, $T > 0°C$; $\Delta T/\Delta t = 1.5°C/min$, $T < 0°C$.

and/or chemical changes. Depolymerization has been shown to occur[17] in the vicinity of 200°C.

Two glassy-state relaxations are observed for each fluoroalkoxy homopolymer (and for each copolymer and polymer blend); the exception is the $[NP(OCH_2CF_3)_2]$ homopolymer, which displays one glassy-state transition. Where two glassy-state relaxations are present, T_{sec} denotes the higher-temperature loss peak and $T_{sec'}$ denotes the lower-temperature transition.

The lower temperature, $T_{sec'}$, relaxation may result from motion of the alkoxy substituents. The intensities and $T_{sec'}/T_g$ (°K/°K) ratios, 0.48 and 0.51, for the heptafluorobutoxy and octafluoropentoxy polyphosphazenes, respectively, might reflect the relative closeness of the masses and lengths of the two alkoxy groups. The crystallinity of $[NP(OCH_2C_3F_7)_2]_n$ does not appear to exert much influence on the glassy-state relaxations of the polymer.

The semicrystalline material from poly[bis(trifluoroethoxy)phosphazene] exhibits a single glassy-state relaxation near −180°C. On the basis of the $T_{sec'}/T_g$ (°K/°K) ratio being 0.4, this relaxation is considered to correspond
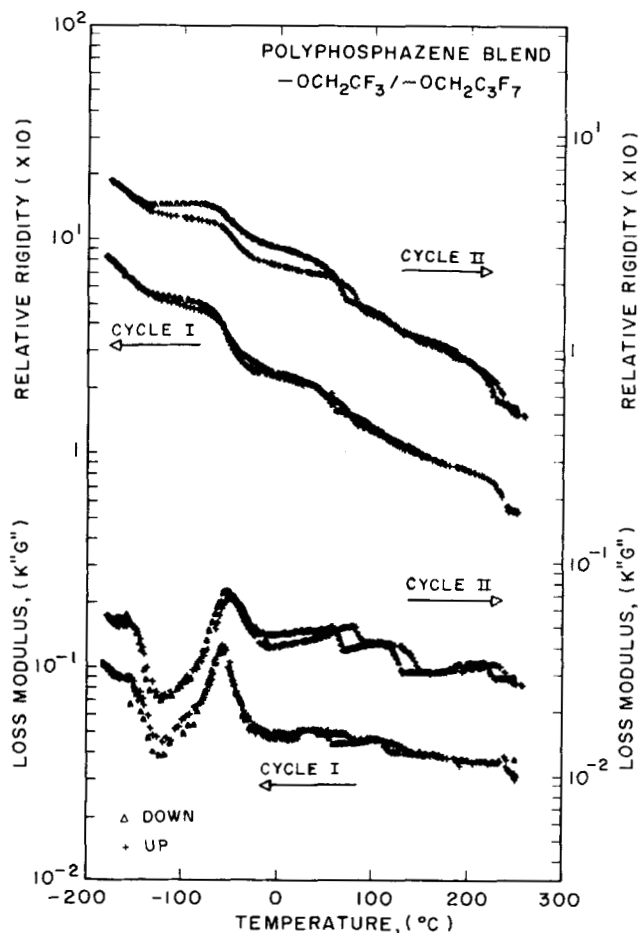
Fig. 9. Thermomechanical spectra: $[NP(OCH_2CF_3)_2]_n/[NP(OCH_2C_3F_7)_2]_n$ blend, He atmosphere. Prehistory: dry, $25° \rightarrow 150°C$. Experiment: $150° \rightarrow -180° \rightarrow 250° \rightarrow -180° \rightarrow 250°C$. $\Delta T/\Delta t = 2.0°C/min$, $T > 0°C$; $\Delta T/\Delta t = 1.5°C/min$, $T < 0°C$.

to the $T_{sec'}$ rather than the T_{sec} process. The $T_{sec'}$ mechanism, based on motion of the ethoxy side group, is consistent with the intensity of the observed loss peak in relation to that observed for the heptafluorobutoxy- and octafluoropentoxy-substituted homopolymers.

On the basis of the present data, no definitive glassy-state relaxations are observed for poly(dichlorophosphazene).[8]

Copolymers

Copolymer $OCH_2CF_3/OCH_2C_3F_7$ (Fig. 7; Table II). No crystal/melt transition region is observed. A glass transition loss peak with a high-temperature shoulder, and an intense glassy-state doublet are evident in the loss spectra. A decrease in rigidity which occurs with increasing temperature at about $180°C$ (cycle I) is presumably due to flow.

Copolymer $OCH_2CF_3/OCH_2C_3F_6CHF_2$ (Fig. 8, Fig. 12; Table II). No crystal/melt transition region is observed. A glass transition loss peak, a
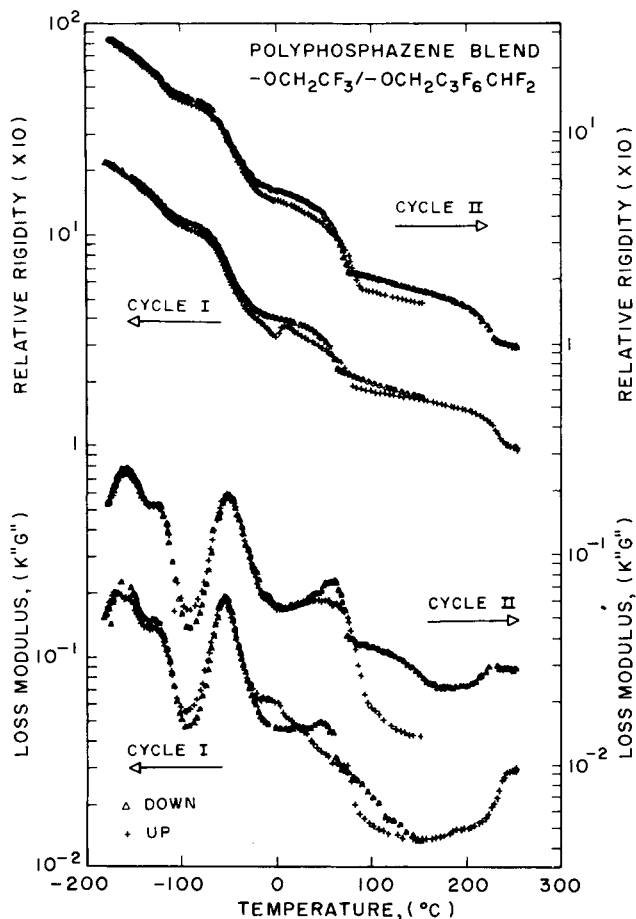
Fig. 10. Thermomechanical spectra: $[NP(OCH_2CF_3)_2]_n/[NP(OCH_2C_3F_6CHF_2)_2]_n$ blend, He atmosphere. Prehistory: dry, $25° \rightarrow 150°C$. Experiment: $150° \rightarrow -180° \rightarrow 250° \rightarrow -180° \rightarrow 150°C$. $\Delta T/\Delta t = 2.0°C/min$, $T > 0°C$; $\Delta T/\Delta t = 1.5°C/min$, $T < 0°C$.

higher-temperature loss peak, and an intense glassy-state doublet are also evident in the loss spectra. A decrease in rigidity which occurs with increasing temperature at about 200°C (cycle I) is presumably due to flow.

Both copolymeric materials appear to be completely amorphous, as indicated by the loss modulus and relative rigidity curves in the region above the glass transition.

Double glassy-state relaxations are observed for each copolymer. The T_{sec}/T_g (°K/°K) ratio for each copolymer is about 0.53, which is somewhat lower than the ratios for the heptafluorobutoxy and octafluoropentoxy homopolymers. The added free volume introduced by the presence of the fluoroethoxy groups in the copolymer structure may be responsible for reducing the temperature of the T_{sec} process.

Anomalies in the behavior in the glass transition region are to be noted. For each copolymer, the glass transition temperature lies close to that of the longer-substituent homopolymer, and a high-temperature peak or shoulder is present immediately above the T_g loss peak. Thermomechanical spectra of
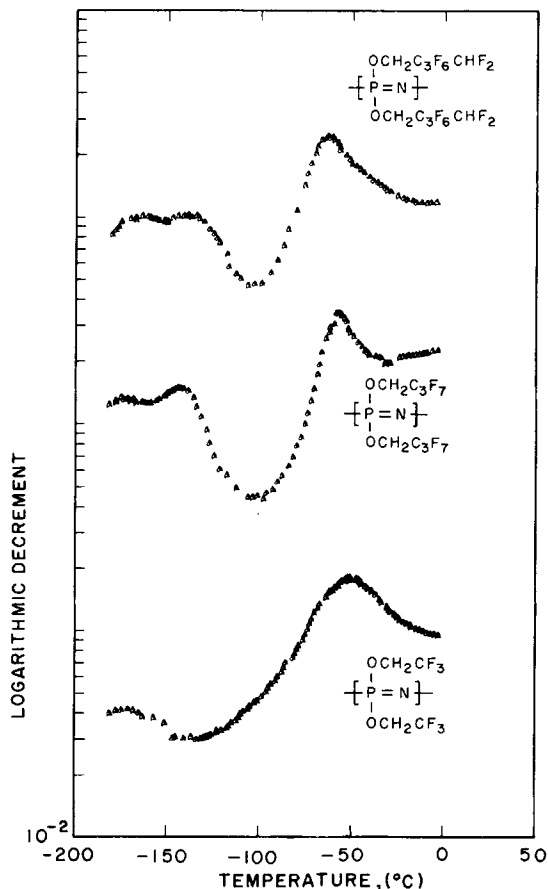
Fig. 11. Logarithmic decrement vs. temperature: $[NP(OCH_2CF_3)_2]_n$, $[NP(OCH_2C_3F_7)_2]_n$, $[NP(OCH_2C_3F_6CHF_2)_2]_n$. Experiment: $0° \rightarrow -180°C$. For purposes of clarity, data for $[NP(OCH_2C_3F_7)_2]_n$ are displaced by a factor of $\log_{10} 9.0$, and data for $[NP(OCH_2C_3F_6CHF_2)_2]_n$ are displaced by a factor of $\log_{10} 81.0$. Compare Fig. 11 with Figs. 4, 5, and 6, which include the same data plotted as $K''G''$ vs. temperature.

other phosphazene copolymers [e.g., $PN(OC_6H_5)_{0.5}(p\text{-}OC_6H_4C_2H_5)_{0.5}$] display a distinct loss peak above the main glass transition.[18] The unusual behavior may be the consequence of heterogeneities in the copolymer structure which arise through synthesis. Substitution of $[NPCl_2]_n$ using two alkoxides may have proceeded to give copolymers with some block character.

Blends

The unusual thermomechanical spectra in the glass transition region of the two phosphazene copolymers prompted an investigation of blends of the homopolymers. Equimolar (based on repeat units) physical blends of poly[bis-(trifluoroethoxy)phosphazene] with poly[bis(heptafluorobutoxy)phosphazene] and poly[bis(trifluoroethoxy)phosphazene] with poly[bis(octafluoropentoxy)phosphazene] were prepared, corresponding to the composition of the two phosphazene copolymers. The dispersion on the high-temperature
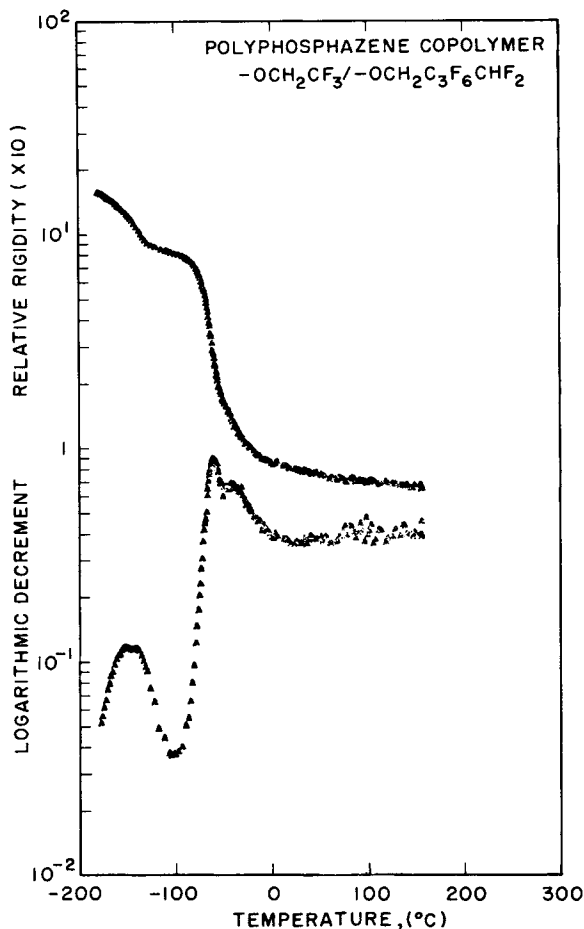
Fig. 12. Logarithmic decrement and relative rigidity vs. temperature: (OCH_2CF_3)/ $(OCH_2C_3F_6CHF_2)$ copolymer. Experiment: $150° \rightarrow -180°C$. Compare Fig. 12 with Fig. 8, which includes the same data plotted as $K''G''$ vs. temperature.

side of the glass transition loss peak of the copolymers is similar to the behavior which is to be expected from an incompatible mixture of two polymers with close glass transition temperatures. The study of polyphosphazene blends was undertaken in an effort to simulate possible irregularities in the copolymer structure.

$[NP(OCH_2CF_3)_2]_n/[NP(OCH_2C_3F_7)_2]_n$ (Fig. 9; Table II). Transitions are observed which correspond to the crystal/crystal and crystal/melt transitions of the ethoxy homopolymer and the crystal/melt transition of the butoxy homopolymer. A single glass transition, between the glass transition temperatures of the component homopolymers, and two glassy-state transitions are observed.

$[NP(OCH_2CF_3)_2]_n/[NP(OCH_2C_3F_6CHF_2)_2]_n$ (Fig. 10; Table II). Transitions are observed which correspond to the transitions of the crystalline regions of the ethoxy homopolymer. A single glass transition, between the glass transition temperatures of the component homopolymers, and two glassy-state transitions are evident.

Thermomechanical spectra for the polymer blends exhibit the transitions of the constituent homopolymers (except for the glass transitions which were presumably too close for resolution). Most significantly, the crystal/melt and crystal/crystal transitions of the trifluoroethoxy-substituted homopolymer are evident. The implication of their presence is that the blends exist as two-phase mixtures rather than as a single-phase polymer solution. As such, the results obtained for the polyphosphazene blends fail to explain the anomalous behavior of the copolymers.

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