Synthesis of Polyphosphazene Block Copolymers Bearing Alkoxyethoxy and Trifluoroethoxy Groups

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ABSTRACT: Block copolymers were formed by the anionically initiated copolymerization of $(CH_3OCH_2CH_2O)(CF_3CH_2O)_2P{=}NSi(CH_3)_3$ or $(CH_3OCH_2CH_2OCH_2CH_2O)(CF_3CH_2O)_2P{=}NSi(CH_3)_3$, followed by the subsequent addition of $(CF_3CH_2O)_3P{=}NSi(CH_3)_3$. These materials were characterized by ^{31}P and ^1H NMR, SEC, and DSC. SEC traces show that these block copolymers exhibit monomodal molecular weight distributions. In addition, there is a gradient in thermal and mechanical properties which is dependent upon the repeating unit ratios. The properties are also different from those of the analogous random copolymers.

Introduction

Polyphosphazenes are a potentially enticing class of polymers which have thus far proven to be of limited commercial utility due to high production costs associated with limited yields, long polymerization times, and high reaction temperatures. These materials are interesting because of their unique combination of low-temperature flexibility and high-temperature stability which imparts serviceability over a wide range of temperatures. With the appropriate choice of functional groups, polyphosphazenes have excellent solvent resistance, inherent flame retardance, and good toughness and vibration-dampening properties.[1] The glass transition temperatures of polyphosphazenes are typically quite low. For example, poly(diisopropoxyphosphazene) possesses a T_g of −105 °C.[2] In general, polyphosphazenes have properties which are equaled only by those of polysiloxanes. Applications include high-performance seals, O-rings, gaskets, fuel hoses, and vibration shock mounts. Additionally, these polymers can be rendered biocompatible or biodegradable with the proper function groups.[3] Doped poly(bis(2-(2-methoxyethoxy))ethoxy)phosphazene (MEEP) has been used as a solid-phase electrolyte due to the cation solvating ability of the side groups.[4] MEEP has been considered for this application because of the higher ambient temperature conductivities obtained in comparison to poly(ethylene oxide), the classical solid-phase electrolyte. This has been attributed to greater backbone flexibility.

Polyphosphazenes are produced commercially by the ring-opening polymerization of hexachlorocyclotriphosphazene and the subsequent nucleophilic displacement of the resulting poly(dichlorophosphazene) by alkoxides, aryloxides, or amines. This method was first optimized in the mide-1960s by Allcock[5] and has been used to produce a tremendous variety of polymers. The primary drawbacks to this method include the aforementioned time and temperature constraints as well as high polydispersities and the inability to produce fully alkylated or arylated polymers. Additionally, conversion is limited to ca. 70% to suppress cross-linking. Similarly, the polycondensation of $Cl_3P{=}NP(O)Cl_2$ can be used to produce the dichloropolymer.[6]

A second route to polyphosphazenes involves the polymerization of phosphoranimines. Tris(2,2,2-trifluoroethoxy)-*N*-(trimethylsilyl)phosphoranimine was synthesized by Flindt and Rose using the Staudinger reaction[7] in 1977 and thermally polymerized at 200 °C for 1–2 days to produce polymers with moderate molecular weights ($M_n \approx 10000$).[8] Dimethyl(2,2,2-trifluoroethoxy)-*N*-(trimethylsilyl)phosphoranimine was used by Neilson in 1980 to produce poly(dimethylphosphazene).[9] This method has since been used to produce a number of other polymers.[10] The primary problem with the thermal polymerization of phosphoranimines is that 2 or more days at temperatures above 200 °C is required to produce high polymer.

Efforts in our group have concentrated on the anionically initiated or nucleophilically catalyzed polymerization of *N*-silylphosphoranimines.[11–19] Using this method, it is possible to completely convert phosphoranimines in as little as 3–5 h at 100 °C. Other advantages to this technique are that it is possible to control the molecular weights of these polymers, low polydispersities are obtained, and it is possible to produce telechelic polymers.

Although it has been possible to produce a number of polyphosphazene random copolymers from the anionically initiated polymerization of phosphoranimines[18] and random and graft copolymers using other methods,[10,20–23] the formation of block copolymers between two polyphosphazenes has not been previously reported. If the blocks were sufficiently incompatible and of the appropriate length, then it is conceivable that they might microphase-separate to provide tougher materials. For example, block copolymers formed with MEEP and bis(2,2,2-trifluoroethoxy)phosphazene segments might microphase-separate to form polymers in which the highly crystalline fluoroalkoxy segments may act as virtual cross-link points. Since commercial MEEP is a gooey, taffy-like material and the use of zirconates and titanates to toughen MEEP via dative cross-links to improve the mechanical strength of that polymer has been studied,[24] such materials could prove to be interesting.

The existence of a slow macrocondensation process in the anionically initiated polymerization of *N*-silylphosphoranimines suggested the existence of reactive end groups and gave rise to the possibility of making a subsequent addition of a second monomer after conversion of the first to produce A–B polyphosphazene block copolymers. In this study, the nature of the end group on the growing polyphosphazene chain and the preparation of polyphosphazene block copolymers by the addition of $(CF_3CH_2O)_3P{=}NSi(CH_3)_3$ (**1d**) to the products of the polymerization of $(CH_3OCH_2CH_2O)(CF_3CF_2O)_2P{=}NSi(CH_3)_3$ (**1a**) and $(CH_3OCH_2CH_2OCH_2CH_2O)(CF_3CH_2O)_2P{=}NSi(CH_3)_3$ (**1b**) will be discussed.

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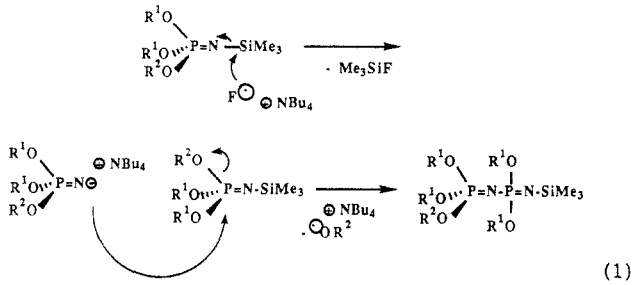
These phosphoranimines were chosen for this study because they behave similarly to each other during the polymerization process.

Results and Discussion

Mechanism of the Anionically Initiated Polymerization of Phosphoranimines. Phosphoranimine monomers were synthesized by the Staudinger coupling[7] of the suitably substituted phosphite with azidotrimethylsilane. The preparation of these phosphoranimines and their precursors as well as the homopolymerization and random copolymerization has been previously reported.[13,14,16,19] The proposed polymerization mechanism involves the abstraction of the silyl group from the monomer by a "silylphilic initiator" (tetra-*N*-butylammonium fluoride (TBAF) has proven to be particularly effective) followed by the attack of the resultant "phosphazene anion" on another monomer.



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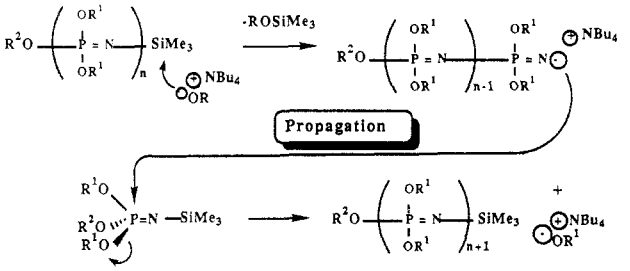
Propagation may proceed through the attack of the resultant trifluoroethoxide on the silyl group of the growing polymer chain, producing an anion which can then attack another monomer molecule.



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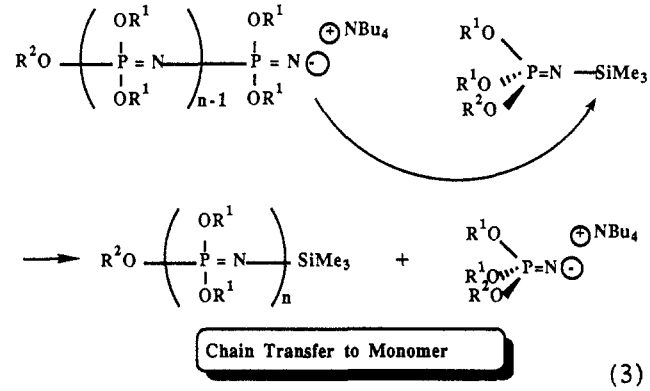
Another possibility is that some type of multicentered silicon intermediate may be involved in this process. These polymerizations obey first-order kinetics in monomer. The kinetic order in initiator/catalyst is dependent upon the solvent and the nature of the substituents on phosphorus. The polymerization of $(CH_3OCH_2CH_2O)(CH_3CH_2O)_2P{=}NSi(CH_3)_3$ (**1a**) is first order in TBAF in bulk. However, the polymerization of both $(CH_3OCH_2CH_2O)(CF_3CH_2O)_2P{=}NSi(CH_3)_3$ (**1a**) and $(CF_3CH_2O)_3P{=}NSi(CH_3)_3$ (**1d**) in diglyme is half-order in TBAF, and low orders (<0.2) are obtained when *N*-methylimidazole is used as a catalyst.

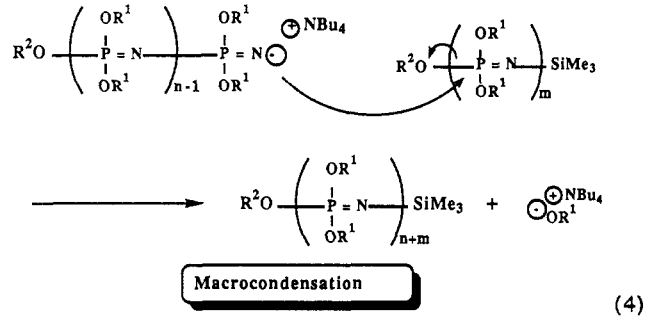
Molecular weight vs time studies have shown that high polymer is formed at low conversions. This indicates that the polymerization occurs via a chain growth process with slow initiation and fast propagation. One possible explanation for this phenomenon is that the N–Si bond on the monomer is stronger than the analogous bond on the growing chain. Molecular weights seem to be limited by chain transfer to monomer which may involve the attack of the active species on the monomer silyl group, resulting in the temporary and reversible termination of that chain and the initiation of a new chain.



(3)

This would lead to lower molecular weights during the chain growth phase which vary between $M_n \approx 20000$ for $(CF_3CH_2O)_3P{=}NSi(CH_3)_3$ and ≈ 2000 for $(CH_3OCH_2CH_2OCH_2CH_2O)_2(CF_3CH_2O)P{=}NSi(CH_3)_3$. This can be attributed to inductive effects in the phosphoranimine monomers.

A slow increase in molecular weight vs time is also observed even after complete conversion of monomer. This has been attributed to a much slower macrocondensation process resulting from the attack of the active site on the P-terminal end of an existing chain. The M_n of these materials can increase to as high as 200 000 by this process.



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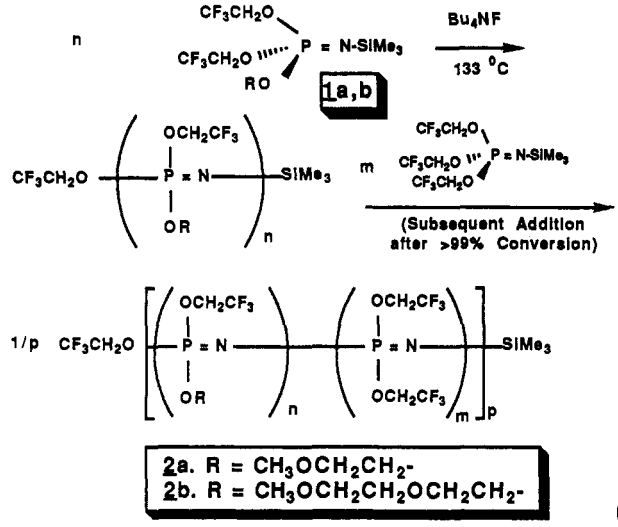
Nature of the End Group. $(CH_3OCH_2CH_2OCH_2CH_2O)_2(CF_3CH_2O)P{=}NSi(CH_3)_3$ (**1c**) was chosen for end group studies as the molecular weight obtained from the bulk polymerization of this compound after 100% conversion is only 1800 by SEC ($X_n \approx 7$) and thus the end groups should be readily identifiable by NMR. This phenomenon is attributed to the high rates of transfer to monomer **1c** by the attack of the active site on the silyl group of a monomer molecule. Solution polymerization ^1H NMR studies of **1c** in 4:1 diglyme:$CD_3S(O)CD_3$ with 1% TBAF after 112 min at 133 °C show the presence of monomer (δ = 0.25; 46% conversion), the $ROSi(CH_3)_3$ condensate (δ = 0.36), and peaks at δ = 0.27 and δ = 0.285 (see Figure 1). The first is probably $(CH_3)_3SiOSi(CH_3)_3$ formed by the hydrolysis of the phosphoranimine, and the latter may be attributed to a trimethylsilyl peak on the end of a polymer chain. The small amount of hydrolysis products present results from the presence of water in the TBAF initiator. Water acts a transfer agent in the anionically initiated polymerization of phosphoranimines. This phenomenon has been previously discussed.[26]

The integration of the low-field peak indicates that X_n = 2.5 after 112 min. Even though GPC can only be used to get rough correlations in this molecular weight range, the ^1H NMR data are in good agreement with the SEC

data which show M_n = 600 (X_n = 2) at this stage of the reaction. After 13 h, X_n = 4.5 by ^{1}H NMR and 4 by SEC.

The M_n values of the polymers synthesized from monomer **1c** are considerably lower than those obtained for the bulk polymerization of $(CH_3OCH_2CH_2OCH_2CH_2O)(CF_3CH_2O)_2P{=}NSi(CH_3)_3$ (**1b**), which were M_n = 3600 after 2 h and 4300 (X_n = 18.5) after 8 h by SEC. The X_n by ^{1}H NMR was 16 for the bulk sample after 8 h at 133 °C. In this sample, the peak at δ = 0.285 is the only one which remains when the volatiles are removed by distillation at 0.5 mmHg and 150 °C for 4 h. The integration ratios did not change for this peak. These molecular weight differences are consistent with past comparisons between bulk and solution polymerization data and may be due to slower rates of polymerization in addition to enhanced rates of transfer to monomer in solution.[14,16] The results of this study indicate that there are indeed TMS end groups present on the polymer since good agreement is obtained between the SEC and ^{1}H NMR data. The TMS group has also been observed as an end group on polymer **2a**.

Copolymerization Reactions. Copolymerization reactions were carried out by polymerizing **1a** or **1b** at 133 °C using 1% TBAF and then, after complete conversion of the first monomer (determined by ^{31}P NMR), various amounts of $(CF_3CH_2O)_3P{=}NSi(CH_3)_3$ (**1d**) were added to make a series of block copolymers. Tetra(*n*-butyl)ammonium fluoride (TBAF) was used as an initiator in these studies because of the high propagation rates obtained with this initiator and the extensive kinetic data available for all of the phosphoranimines utilized.



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This scheme has been simplified by showing only $-[(CF_3CH_2O)_2P{=}N]-$ repeating units after the initial polymerization. As previously reported,[12,15,16,19] both $CF_3CH_2O^-$ and $CH_3OCH_2CH_2O^-$ are leaving groups, and 84% of the repeating units are $-[(CH_3OCH_2CH_2O)(CF_3CH_2O)P{=}N]-$ after this initial polymerization step. As in the case of the random copolymers,[18] the percentage of each repeating unit in the precipitated polymers (*n* is the fraction of repeat units bearing an alkoxy ether unit—see Table I for data) reflects the fact that some of the alkoxy ether groups are lost as leaving groups.

Copolymerization Kinetics. In situ ^{31}P NMR studies were utilized to investigate the polymerization of **1d** from converted **1b**. Since the following relationship holds, the polymerization is first order in monomer **1d** and initiator (in this case the "initiator" is the active site (end group)

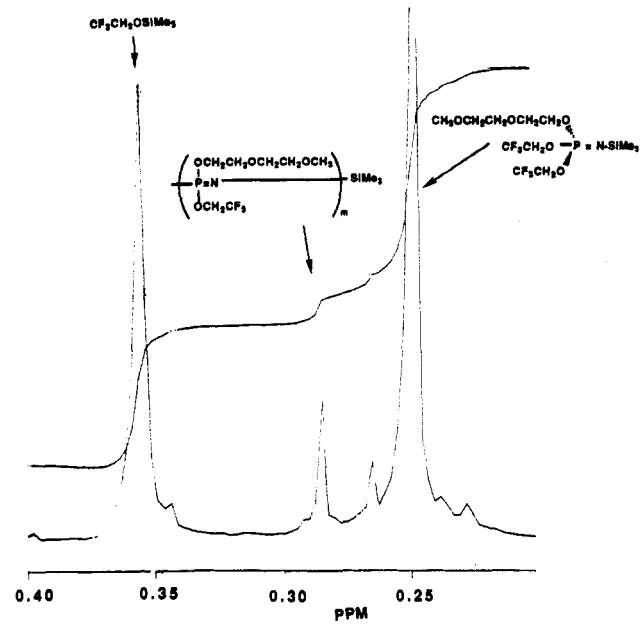


Figure 1. ^{1}H NMR spectrum of the polymerization of **1c** in 4:1 diglyme/DMSO-d_6 after 112 min at 133 °C.

on the polymer formed from **1b**):

$$R_p = -\frac{d[M]}{dt} = k_p^{app}[M][I]_0^n \qquad (6)$$

where k_p^{app} is the apparent rate constant calculated by the assumption that the "initiator" quantitatively produces active sites, [M] is the monomer concentration at a given time, *n* is the order in initiator, which varies between 0.5 and 1.0 for TBAF as previously discussed, and $[I]_0$ is the alkoxide concentration assuming quantitative formation from fluoride. Plots of $\ln([M]_0/[M])$ vs time (Figure 2) show that first-order kinetics are not followed for this system.

The homopolymerization of **1a–d** and the random copolymerizations are first order in [M]. Deviations from first-order kinetics in [M] using the "macromonomeric initiator" are due to precipitation of polymer after ca. 30% conversion. However, if one looks at the slopes of the initial $\ln([M]_0/[M])$ vs time curves to obtain an estimate of $d(\ln([M]_0/[M])/dt$, then the plot of $\ln(d(\ln([M]_0/[M])/dt)$ vs ln[I] (see Figure 3) gives a slope of 0.92, where [I] is the alkoxide concentration. This indicates that at early stages the polymerization is first order in alkoxide.

It is also possible to compare the apparent rate constant for the bulk polymerization of **1d** taken from the random copolymerization kinetic studies[19] (k_p^{app} = 1.8 × 10^{-2} s^{-1} M^{-1}) to that obtained from the most concentrated sample shown in Figure 3 (k_p^{app} = 0.11 s^{-1} M^{-1}) at 133 °C as calculated from eq 6. This indicates that the polymerization of **1d** is 6 times faster from the silyl group on the end of an existing chain when compared to the polymerization of monomer **1d** only. This is additional supporting evidence that the chain growth kinetics observed in the anionically initiated polymerization of phosphoranimines can be explained by the possibility that the strength of the N–Si bond on a growing chain is weaker than that on a monomer molecule.[18]

Solubilities. The homopolymers formed from **1a** and **1b** are soluble in $CHCl_3$, while poly(bis(2,2,2-trifluoroethoxy)phosphazene) formed from **1d** is not. All three are soluble in THF. Thus, if the subsequently added **1d** were simply homopolymerizing after addition, then there should not be an alkoxyalkoxy groups incorporated after

Table I. Properties for Various Polyphosphazene Random and Block Copolymers[a]

monomer feed ratio	type	n	yield (%)	M_n (×10⁻³)	M_w/M_n	$T(1)$ (°C)	ΔH (mJ/mg)
1a only	N/A	0.827		15.5	1.60	N/A	N/A
30 **1a**:70 **1d**	R, S	0.166	32.4	44.9	1.41	54	7
20 **1a**:80 **1d**	R, S	0.101	48.5	43.9	1.55	57	20
10 **1a**:90 **1d**	R, S	0.053	56.1	59.6	1.59	64	33
1 **1a**:19 **1d**	R, S	0.019	82.3	37.7	2.34	67	35
45 **1a**:55 **1d**	B, S	0.294	15.9	28.8	1.54	69	21
36 **1a**:64 **1d**	B, S	0.197	65.1	35.1	1.52	71	21
22 **1a**:78 **1d**	B, S	0.113	76.3	36.2	1.51	75	32
8 **1a**:92 **1d**	B, S	0.043	79.6	43.0	1.44	73	40
5 **1a**:95 **1d**	B, S	0.028	81.8	41.2	1.44	74	40
22 **1a**:78 **1d**	B, L	0.134	51.7	46.4	1.34	*	*
15 **1a**:85 **1d**	B, L	0.126	88.4	49.1	1.52	66	27
10 **1a**:90 **1d**	B, L	0.080	95.7	73.4	1.56	68	39
4 **1a**:96 **1d**	B, L	0.047	87.6	127.4	1.36	80	46
1d only	N/A	0	85.5	81.5	1.87	71	39
1b only	N/A	0.995		4.5	1.31	N/A	N/A
3 **1b**:7 **1d**	R, S	0.118	32.0	9.2	1.71	*	*
2 **1b**:8 **1d**	R, S	0.051	76.7	18.7	1.61	59	28
1 **1b**:9 **1d**	R, S	0.026	83.4	17.5	1.45	68	37
1 **1b**:19 **1d**	R, S	0.013	97.0	17.3	1.40	68	38
4 **1b**:6 **1d**	B, S	0.089	15.8	22.6	1.58	*	*
22 **1b**:78 **1d**	B, S	0.050	67.3	22.7	1.56	66	32
12 **1b**:88 **1d**	B, S	0.019	74.9	21.1	1.54	67	32
6 **1b**:94 **1d**	B, S	0.012	81.1	22.7	1.67	71	40

[a] R = random; B = block; S = 13 h of polymerization time; L = 44 h of polymerization time. Molecular weight data are determined by SEC vs polystyrene standards, and the thermal properties are quoted for the second heating cycle. Asterisks indicate multiple transitions near $T(1)$.

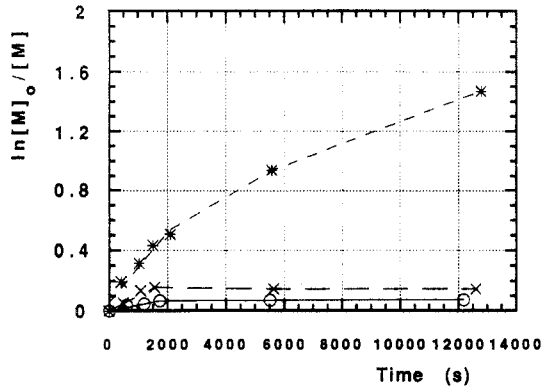


Figure 2. Kinetics of the bulk polymerization of **1d** from the products of the polymerization of **1b** at 133 °C: (*) $[RO^-] = 2.7 \times 10^{-3}$ M, **1b**:**1d** = 1.6:1; (x) $[RO^-] = 9.5 \times 10^{-4}$ M, **1b**:**1d** = 10:1; (O) $[RO^-] = 3.8 \times 10^{-4}$ M, **1b**:**1d** = 15:1.

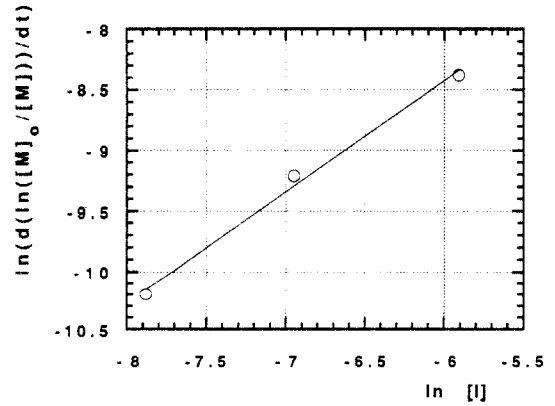
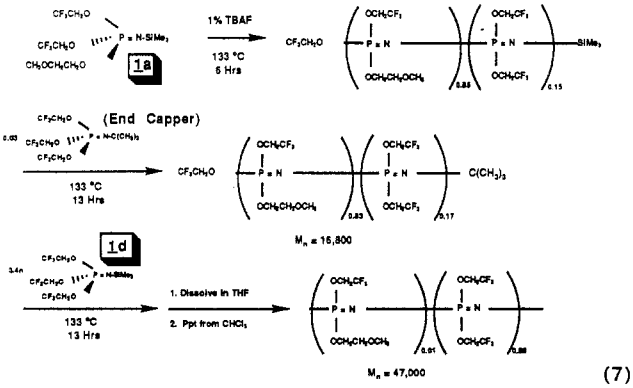


Figure 3. Effect of the active species concentration on the kinetics of polymerization of **1d** from the products of the polymerization of **1b** at 133 °C.

dissolving the samples in THF and precipitating from $CHCl_3$. To gain evidence for this, equal masses of the polymers formed from **1a** and poly(bis(2,2,2-trifluoroethoxy)phosphazene) from **1d** were dissolved in THF and precipitated from chloroform. There were no detectable 2-methoxyethoxy groups by ^1H NMR in the precipitated polymer. This is evidence that the block with alkoxyalkoxy repeating units is covalently bound to the block with bis(trifluoroethoxy) units.

End-Capping Experiments. A series of reactions were done to show that block copolymerization occurs from the silyl end group located on the original polymer and not to any significant extent by the attack of the active site on a growing bis(trifluoroethoxy)phosphazene chain (which could be formed from the subsequently added monomer (**1d**) initiated by alkoxide leaving group residues) on the P-terminal end of the first homopolymer or by some sort of branching mechanism. Since it has been previously shown that the use of phosphoranimines with non-leaving groups on the nitrogen (such as *tert*-butyl) can be used to end-cap polyphosphazenes,[29] tris(2,2,2-trifluoroethoxy)-*N*-*tert*-butylphosphoranimine was utilized to block the N-terminal end of the first polymer before the addition of the second monomer.



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^{31}P NMR was used to confirm that the first monomer was consumed and to verify that the *tert*-butylphosphoranimine was incorporated. Residual *tert*-butylphosphoranimine was removed by vaccum distillation at 0.5 mmHg and 150 °C prior to the addition of **1d**. The ^1H NMR spectrum at this stage showed a peak at δ = 1.23 corresponding to the butyl group. The integration of this peak leads to a calculated X_n = 79 in comparison to X_n

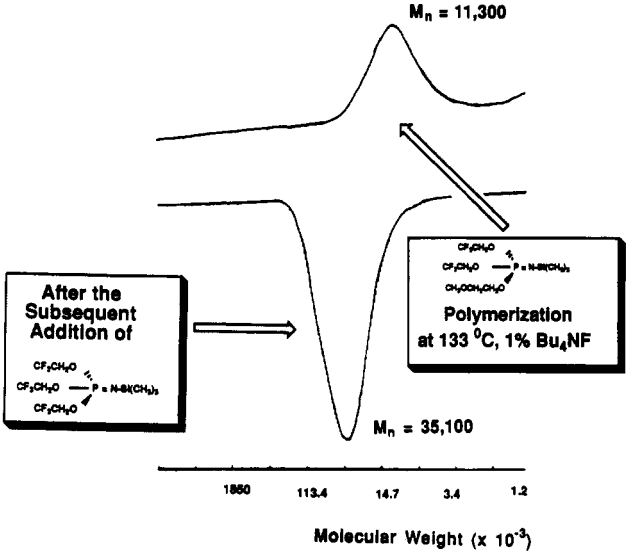

Figure 4. SEC traces of the polymerization of **1b** before and after the block copolymerization with **1d**.

= 73 (M_n = 16800) obtained from GPC and indicates that the polymer was quantitatively end-capped. The polymer synthesized from the subsequent addition of **1d** to end-capped **1a**, followed by precipitation with $CHCl_3$, shows that the precipitated polymer is largely poly(bis(2,2,2-trifluoroethoxy)phosphazene) formed by the initiation of **1d** with the alkoxide formed as leaving group from the homopolymerization of **1a**. A total of 1.1% of the repeating units in the precipitated polymer bear a 2-methoxyethoxy group. This is presumably due to a small amount of macrocondensation by the attack of a growing bis-(trifluoroethoxy)phosphazene chain on the P-terminal end of the end-capped polymer. The remainder of the latter polymer stays dissolved in the chloroform. If the reaction is done in an identical fashion without end-capping the first polymer, then 11% of the repeating units bear 2-methoxyethoxy groups.

Molecular Weights. Since chain growth kinetics for the anionically initiated polymerization of *N*-silylphosphoranimines have been observed, long runs of $-[(CF_3CH_2O)_2P{=}N]_n-$ can be expected after the addition of **1d**. This chain growth behavior has been explained by the N–Si bond on the monomer being stronger than the corresponding bond on the growing chain. In 13 h at 133 °C, little macrocondensation of polymer chains was noted. For instance, the polymerization of 1.27×10^{-4} mol of **1a** gives a polymer with M_n = 11300 by SEC vs polystyrene standards (M_w/M_n = 1.29) after 5 h (100% conversion) at 133 °C using 1% TBAF. After the subsequent addition of 1.38×10^{-3} mol of **1d** (10.9 **1d**:1 **1a**), the M_n had increased to 41 200 (M_w/M_n = 1.53) after 13 h. The SEC traces before and after the addition of **1d** are shown in Figure 4.

It is of importance to note that the refractive index of the homopolymer resulting from **1a** is positive and the refractive index of the homopolymer from **1d** is negative vs THF. All of the block copolymers formed from **1a** or **1b** with **1d** are monomodal and the molecular weights significantly increase after the second monomer addition, indicating that block copolymers are being formed. The refractive index of the copolymers is negative after conversion of the second monomer due to the incorporation of additional trifluoroethoxy groups. Samples from the polymerization of **1a** which were accidentally exposed to atmospheric moisture at 133 °C immediately after the addition of **1d** showed a bimodal molecular weight distribution with a low molecular weight peak which was

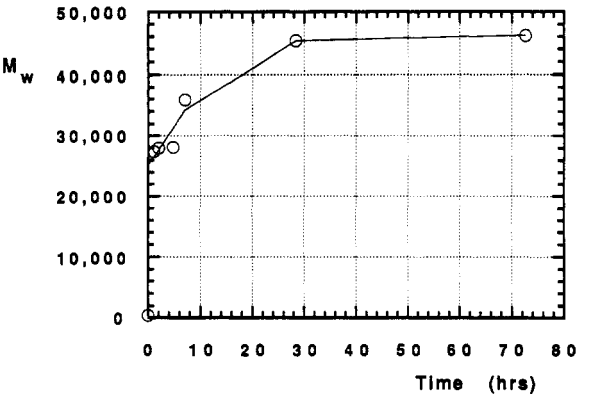

Figure 5. M_w vs time curves for a 3.86× molar excess of **1d** from the products of the bulk polymerization of **1a** at 133 °C.

positive vs THF ($M_n \approx 11000$) and a high molecular weight peak ($M_n \approx 30000$) which had a negative refractive index vs THF before precipitation. The copolymers which were not exposed to air were monomodal before precipitation. This can be explained by the hydrolysis of the more labile silyl group on the chain end of the polymer and the initiation of **1d** by the alkoxide leaving group which lead to the formation of a significant amount of poly(bis(2,2,2-trifluoroethoxy)phosphazene) homopolymer. The lower molecular weight material was soluble in $CHCl_3$ and remained in the filtrate during the precipitation process. ^1H NMR showed that the filtrate contained polymer **2a**. This can be seen as further evidence that block copolymers are being formed instead of two homopolymers.

There is also evidence that these materials essentially have an $[(CF_3CH_2O)_2P{=}N)]_m[((CH_3OCH_2CH_2O)(CF_3CH_2O)P{=}N)_{0.84}((CF_3CH_2O)_2P{=}N)_{0.16}]_n$ structure, where n is the number of repeating units obtained from the homopolymerization of **1a** (bearing in mind that this segment will have two different repeating units due to the presence of two leaving groups) and m is the number of repeating units which result from the subsequently added **1d**. For the sample in which 78% **1d** was block copolymerized from 22% **1a** (M_n = 11300; X_n = 49), the M_n was 36 200 (X_m = (36200 − 11300)/243 = 102 additional repeating units vs (78/22) × 49 = 174 expected) after 13 h. This molecular weight difference can be explained by the fact that all of the monomer had not been consumed at that time. After 33 h the monomer was completely consumed (M_n = 46400; X_n = 193). Since the molecular weight was still slightly lower than expected, this indicates that little macrocondensation has taken place and that there may be some poly(bis(2,2,2-trifluoroethoxy)phosphazene) present due to the initiation of **1d** by alkoxide or from chain transfer to monomer by the attack of the active site on the silyl group on a monomer molecule. The M_w vs time curve for the block copolymerization of 78% **1d** from 22% **1a** at 133 °C is shown in Figure 5.

The rate of polymerization ($d(\ln([M_0]/[M]))/dt$) of **1d** from **1a** or **1b** is low due to the low active site concentration for the ratios used. Even at 44 h, monomer conversion was incomplete for the polymerization of 96% **1b** polymerized from 4% **1a**. There is a significant difference in the physical properties of the samples which were heated for 44 h at 133 °C. In addition to higher yields resulting from higher conversions and higher molecular weights (see Table I), the samples which were polymerized for longer times are considerably more crystalline than the analogous polymers which were isolated after shorter polymerization times. The lower molecular weight materials are qualitatively better film formers and the resulting films are tougher. Thus, some potential exists for controlling the

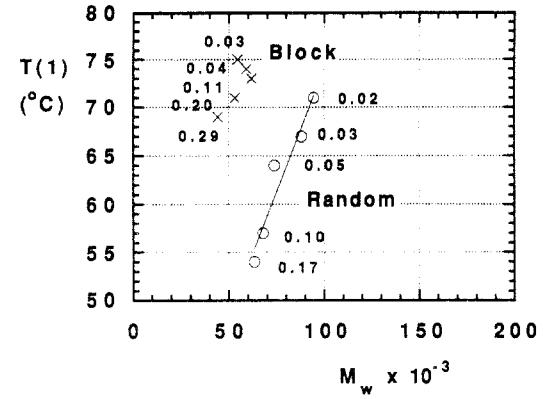

Figure 6. Effect of M_w on $T(1)$ for the copolymers made from **1a** and **1d**: (O) = random copolymers; (×) = block copolymers. The numbers next to the data points represent the molecular weight fraction of the repeating units bearing 2-methoxyethoxy moieties as calculated from ^{1}H NMR.

physical properties of the material by varying polymerization time as well as monomer feed ratios.

The polymerization of **1b** led to polymer with M_n = 8100 (M_w/M_n = 1.56) after 4 h (100% conversion), and the molecular weights for the copolymer with all feed ratios were M_n = 22000 (M_w/M_n = 1.56–1.67) 13 h after the addition of **1d**. Molecular weight vs time studies indicate that this molecular weight is reached within 2 h and does not increase even after 89 h. The reason for the difference in behavior between **1a** and **1b** is unclear, although it is probable that some type of unknown termination process is occurring. As discussed above, this termination reaction may also contribute to the deviation from first-order kinetics for the polymerization of **1d** from the products of the polymerization of **1b**.

Thermal Properties. It is well known that poly(bis(2,2,2-trifluoroethoxy)phosphazene) undergoes a thermal transition to a columnar mesophase at $T(1) \approx 80$ °C.[28] This polymer then becomes isotropic at $T_i \approx 240$ °C. All of the random and block copolymers formed from **1a** or **1b** with **1d** exhibit $T(1)$ and T_i in addition to T_g transitions. The existence of the $T(1)$ transition in the random copolymers has been confirmed by X-ray diffraction and optical microscopy.[18] As in the case of the random copolymers, the thermal properties are dependent upon the percentage of each repeating unit present and are affected by molecular weight and the nature of the substituents (see Figure 6 and Table I).

These materials may be low enough in molecular weight that the end group concentration influences $T(1)$. Copolymers bearing bulkier $CH_3OCH_2CH_2OCH_2CH_2O$ substituents have a higher $T(1)$ at a given M_w than those with $CH_3OCH_2CH_2O$ groups, which are in turn higher than polyphosphazenes bearing solely CF_3CH_2O groups. This is in agreement with results reported for poly[bis(halophenoxy)phosphazenes] where the size of the halogen influences $T(1)$.[27] The enthalpy of the mesophase transition decreases dramatically as the percentage of the alkoxyalkoxy groups increases. The fact that the polymers in the **2b** series have practically identical molecular weights and still have $T(1)$ values which are dependent upon the repeating unit ratios is indicative that, although molecular weight certainly plays a role, the repeating unit ratios also influence $T(1)$ to some extent.

It may be noted that the block copolymers have a higher $T(1)$ at a given molecular weight and repeating unit ratio than their random analogs and that $T(1)$ is not greatly influenced by these factors in the blocky materials while it is significantly affected in the random copolymers (Figure 6). One possible explanation for this phenomenon is that only the bis(trifluoroethoxy) regions are undergoing a transition to a columnar mesophase (the homopolymers formed from **1a** and **1b** are completely amorphous and the only thermal transition exhibited by these materials is a T_g at ca −62 °C) and that while the random copolymers can tolerate a certain number of disrupting alkoxyalkoxy groups in the backbone, the $T(1)$ transition temperatures and the corresponding ΔH values of those transitions fall off rapidly as the number of disrupting groups increases. In the case of the block copolymers, there are long runs of bis(trifluoroethoxy) repeating units, and therefore the $T(1)$ is relatively unaffected when compared to the analogous random materials. This difference in behavior can be seen as evidence for the formation of block copolymers. It is not entirely clear why the **3a** block copolymers display higher $T(1)$ values for the $[(CF_3CH_2O)_2P{=}N]_m[((CH_3OCH_2CH_2CH_2O)(CF_3CH_2O)P{=}N)_{0.88}((CF_3CH_2O)_2P{=}N)_{0.12}]_n$ polymers formed after 13 h than for the 44-h samples where macrocondensation has produced materials with the formula $([(CF_3CH_2O)_2P{=}N]_m[((CH_3OCH_2CH_2O)(CF_3CH_2O)P{=}N)_{0.88}((CF_3CH_2O)_2P{=}N)_{0.12}]_n)_x$. It may be that since the trifluoroethoxy groups are localized on one end of the chain, they can associate and form a more ordered structure in the mesophase, whereas the presence of alkoxyethoxy groups in the middle of the chain decreases the order in the system. Another possibility is that some randomization of the block copolymers by the nucleophilic attack of the alkoxide residues is occurring over time.

A Comparison of Polyphosphazene Random and Block Copolymers. There are distinct differences in the thermal and physical properties of the block copolymers in comparison to the random copolymers. For example, the block copolymer sample **2a** which has M_n = 10400 has physical properties very different from those of the random copolymer with M_n = 9200. Both materials have the formula $[(CF_3CH_2O)_2P{=}N]_{0.89}[(CH_3OCH_2CH_2O)(CF_3CH_2O)P{=}N]_{0.11}$ as estimated by ^{1}H NMR. (A good correlation of the ^{1}H NMR data with elemental analysis has been obtained.) The blocky polymer is a tough, flexible material which forms good films when cast from THF solution. The random copolymer is a soft pliable material with a very low tensile strength. A comparison of the thermal properties for analogous materials can be made by viewing Table I and Figure 6.

Another phenomenon which warrants further study is that there are two distinct $T(1)$ peaks noted in the DSC for the block copolymers bearing high concentrations of 2-(2-methoxyethoxy)ethoxy side groups. Although one might expect that there would be two T_g transitions for the block copolymers, this is not observed because the T_g's for both of the homopolymers are in the range of −60 to −65 °C.[19] The block and random copolymers with higher percentages of bis(trifluoroethoxy) repeating units have only one $T(1)$ transition on the second DSC heating cycle after annealing above $T(1)$. Two transitions are present at 5–10 °C below ($T(1)$ before annealing above T_i in the random samples with larger amounts of (2-(2-methoxyethoxy)ethoxy groups and bis(alkoxyalkoxy) repeating units.[18] The reason for this behavior is unclear but may involve some type of transition between two different crystalline packing arrangements. Further studies are currently underway.

Conclusions. It has been demonstrated that it is possible to produce block A–B polyphosphazenes by the addition of a second monomer after consumption of the first by using the anionically initiated polymerization of

phosphoranimines. These block copolymers exhibit monomodal molecular weight distributions and have physical and thermal properties which are dependent upon the repeating unit ratios in addition to having properties distinctly different from those of the analogous random copolymers. It is also possible to control the properties of these materials by varying the monomer feed ratio and polymerization times. A comparison of the rates of polymerization from silyl groups on the ends of existing chains and from monomer molecules is cited as evidence that the difference in the N–Si bond strengths of these species is responsible for the observed chain growth kinetics in the anionically initiated polymerization of phosphoranimines. Further microscopy, X-ray diffraction, and conductivity studies are currently underway to better understand the microstructure and properties of these materials.

Experimental Section

Measurements. NMR spectra were recorded on an IBM NR-300 FTNMR 300-MHz instrument versus TMS and 85% H_3PO_4 standards for ^1H and ^{31}P, respectively. ^{31}P NMR spectra were generated by placing the sample in a 5-mm NMR tube which was then held in place inside a 10-mm tube containing $CDCl_3$ with a Teflon insert. GPC data were collected using a Waters 510 HPLC pump fitted with 100-Å, 1000-Å, and linear Ultrastyragel columns in series with a Waters Model 450 UV detector and a 410 refractive index detector and analyzed vs polystyrene standards. Polystyrene standards varying between M_n = 760 and M_n = 2300000 were purchased from Waters. Toluene was used as a low molecular weight standard. A 0.1% solution of $(n\text{-}C_4H_9)_4NBr$ in THF was used as a carrier solvent to prevent tailing of the chromatograms as described by Neilson.[6] A Seiko 5200 DSC and TGA/DTA 300 were used to gather thermal data. Two 10 °C/min heating and 20 °C/min cooling cycles were used for all DSC measurements. Elemental analysis was performed by M/M Laboratories in Indianapolis, IN, and IR spectra were generated on a Nicolet DX FTIR.

Materials. $(CF_3CH_2O)_3P{=}NSi(CH_3)_3$ (**1d**) was synthesized by the literature method.[8] The synthesis of $(CH_3OCH_2CH_2O)(CF_3CH_2O)_2P{=}NSi(CH_3)_3$ (**1a**), $(CH_3OCH_2CH_2OCH_2CH_2O)(CF_3CH_2O)_2P{=}NSi(CH_3)_3$ (**1b**), and $(CH_3OCH_2CH_2OCH_2CH_2O)_2(CF_3CH_2O)P{=}NSi(CH_3)_3$ (**1c**) by the Staudinger coupling of azidotrimethylsilane with the suitable phosphite was previously reported.[19] The synthesis of $(CF_3CH_2O)_3P{=}NC(CH_3)_3$ was also previously reported.[29] Tetra(*n*-butyl)ammonium fluoride (1.0 M in THF) was used as received. Diglyme was distilled from CaH_2 to CaH_2, and DMSO-d_6 was stirred over CaH_2 for 1.5 h before use.

Copolymerization Reactions. A typical bulk copolymerization procedure utilized was to syringe 1.78 g (4.55×10^{-3} mol) of $(CH_3OCH_2CH_2O)(CF_3CH_2O)_2P{=}NSi(CH_3)_3$ (**1a**) and 45 μL (4.5×10^{-5} mol) of 1.0 M tetra(*n*-butyl)ammonium fluoride into a 25-mL round-bottom flask fitted with a septum which had been flame dried under Ar. The samples were heated at 133 °C for 5 h. Complete conversion of monomer was confirmed by ^{31}P NMR. Samples (0.0301, 0.0501, 0.1369, 0.2654, and 0.6450 g (7.7×10^{-5}, 1.28×10^{-4}, 3.50×10^{-4}, 6.79×10^{-4}, and 1.64×10^{-3} mol, respectively)) were then removed from the reaction flask with a syringe and placed in independent, preweighed, flame-dried, Ar-purged, 10-mL round-bottom flasks. $(CF_3CH_2O)_3P{=}NSi(CH_3)_3$ (**1d**) (0.5994, 0.5744, 0.5091, 0.5063, and 0.8273 g (1.44×10^{-3}, 1.38×10^{-3}, 1.23×10^{-3}, 1.22×10^{-3}, and 1.99×10^{-3} mol)) was then syringed into the respective flasks. The samples were then heated for an additional 13 h at 133 °C, dissolved in THF, and precipitated from $CHCl_3$ for purification. The samples were subsequently filtered on a frit and then dried in a vacuum oven overnight. DSC, SEC, gravimetric yield, and ^1H NMR integration data are summarized in Table I. Polymer **2a**: ^1H NMR ($CD_3C(O)CD_3$): 4.53 (m, broad), 4.19 (m, broad), 3.61 (m, broad), 3.34 ppm (s, broad). ^{31}P NMR ($CDCl_3$): −7.3 ppm (broad). IR (neat, precipitate from THF): 1291 (P=N, P–O–C), 1177, 1044 (C–O–C), 969, 1089 (P–O–C), 799, 838 cm^{-1} (P–N–P). For the 44-h sample in which the formula was estimated to be $-[(CF_3CH_2O)_2P{=}N)]_{0.864}/[(CH_3OCH_2CH_2O)(CF_3CH_2O)P{=}N]_{0.136}-$ by ^1H NMR: Calcd: F, 44.30; C, 20.72; H, 1.96; P, 12.92; N, 5.84. Anal. (found): F, 44.17; C, 21.06; H, 2.00; P, 13.13; N, 5.85. Polymer **2b**: ^1H NMR ($CD_3C(O)CD_3$): 4.50 (m, broad), 4.19 (m, broad), 3.70 (m, broad), 3.62 (m, broad), 3.51 (m, broad), 3.32 ppm (s, broad). ^{31}P NMR ($CDCl_3$): −7.1 ppm (broad).

Kinetic studies on the rates of polymerization were performed using similar techniques in NMR tubes which were dried in a 150 °C oven for a minimum of 16 h and then purged with Ar. Sample tubes were placed in an oil bath at the appropriate temperature controlled to ±1 °C and then removed at various times for analysis via ^{31}P NMR. ^{31}P NMR ($CDCl_3$): $-[(CF_3CH_2O)_2P{=}N]_n-$, −7.9; $-[(CF_3CH_2O)(CH_3OCH_2CH_2O)P{=}N]_n-$, −7.2; $-[(CF_3CH_2O)(CH_3OCH_2CH_2OCH_2CH_2O)P{=}N]_n-$, −6.9 ppm.

End-Capping Experiments. A typical procedure was to add 0.5 mL (1.5×10^{-3} mol) of $(CH_3OCH_2CH_2O)(CF_3CH_2O)_2P{=}NSi(CH_3)_3$ (**1a**) and 15.5 μL of TBAF to an Ar-purged 25-mL round-bottom flask which had been dried in a 150 °C oven overnight and then fitted with a septum. Similar samples were prepared in 5-mm NMR tubes for the ^{31}P NMR studies. The samples was heated for 6 h at 133 °C. Less than 1% residual monomer at $\delta(CDCl_3)$ = −9.8 was noted by ^{31}P NMR. $(CF_3CH_2O)_3P{=}NC(CH_3)_3$ (**1d** (0.014 mL (4.9×10^{-5} mol)) was added by microsyringe. The polymer ($\delta(CDCl_3)$ = −6.7 and −7.9; two different repeating units) to $(CF_3CH_2O)_3P{=}NC(CH_3)_3$ ($\delta(CDCl_3)$ = −29.1) integration ratio was 31:1. After 13 h at 133 °C, this ratio had increased to 77.8:1. After heating, the samples were subjected to a vacuum of 0.5 mmHg and a temperature of 150 °C for 4 h to remove the condensation byproducts of the polymerization and the residual $(CF_3CH_2O)_3P{=}NC(CH_3)_3$. The M_n was determined to be 16 800 (M_w/M_n = 2.23) by GPC vs polystyrene standards. ^1H NMR ($CD_3C(O)CD_3$): 4.53 (m, broad, 0.89 H), 4.19 (m, broad, 0.72 H), 3.61 (m, broad, 0.71 H), 3.34 (s, broad, 1.12 H), 1.23 ppm (s, broad, 0.05 H). $(CF_3CH_2O)_3P{=}NSi(CH_3)_3$ (2.0 mL (5.1×10^{-3} mol)) was then added, and the sample was heated for 13 h at 133 °C, then dissolved in THF, and precipitated from $CHCl_3$ at °C. GPC: M_n = 47000 (M_w/M_n = 1.49). ^1H NMR ($CD_3C(O)CD_3$): 4.53 (m, broad, 148.4 H), 4.19 (m, broad, 1 H), 3.61 (m, broad, 1 H), 3.34 ppm (s, broad, 1.5 H).

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