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Synthesis and Characterization of Esterified Poly[(aryloxy)phosphazene]s

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ABSTRACT: Four new phosphazene polymers were synthesized using an esterification methodology. It was found that poly[bis(4-carboxylatophenoxy)phosphazene] reacts with neat alcohols and catalytic acid at reflux to form polymers with varying chemical and physical properties. Esters were prepared from the following alcohols; 2-methoxyethanol, 2,2′-methoxyethoxyethanol, 2-ethoxyethanol, and 1-butanol. The resulting new polymers were characterized using nuclear magnetic resonance (NMR) spectroscopy and were found to have the expected ester pendant groups homogeneously substituted onto the phosphorus−nitrogen backbone. Laser light scattering (LLS) was used to determine that during the modification process molecular weight of the polymer is conserved, suggesting that under the conditions of the esterification process no chain scission occurs.

Introduction

The literature is replete with methods for the functionalization of linear poly[bis(chloro)phosphazene] with organic pendant groups. The predominant synthetic pathway involves nucleophilic attack of phosphorus with chloride acting as a leaving group.[1] The simplicity of this process endows polyphosphazenes with a wide variety of potential chemical functionalities, likewise providing a large array of physical and chemical characteristics. Modification of these polymers after attachment of organic side groups has been explored to a lesser degree.[2−4]

Numerous syntheses of polyorganophosphazenes have been reported.[5−7] These polymers can be made in a two-step process. First, linear dichlorophosphazene can be made using a ring-opening process[8] from the commercially available phosphonitrilic chloride trimer or a condensation process.[9] The second step is substitution of the backbone with the appropriate alkoxide or aryloxide.[7,8] In addition, various amines have been attached to the backbone[10] yielding polymers that are generally more glasslike and have characteristically higher glass transition (T_g) temperatures than corresponding alkoxides or aryloxides. Uses for (aryloxy)phosphazenes include membranes for the selective removal of organics from water[11] and organics from other organics,[12] and gas separations.[13] In addition, these materials have the potential to be used as flame retardants,[14] medical devices,[15] and ionic conductors.[16] The utility of these materials is dictated by the choice of pendant groups. Poly[bis((2,2′-methoxyethoxy)ethoxy)phosphazene] (MEEP)[16,17] is water soluble due to the polyether pendant groups, while poly[bis(2,2,2-trifluoroethoxy)phosphazene][8] is hydrophobic. Thus, the nature of the pendant group becomes the primary determining factor in creating a selected polymer morphology. For hydrophilic polymers, this becomes a greater concern since water swellable/soluble phosphazenes generally have very low glass transition temperatures that result in flowing or less than rigid physical attributes. In this paper, we report a novel method for the modification of poly[bis(4-carboxylatophenoxy)phosphazene] to give both hydrophobic and hydrophilic polymers that form thin films. This method entails the synthesis of a base polymer followed by pendant group modification. The advantage of this method is that it may be performed on a fully characterized polymer in order to yield a product with controlled chemical functionality.

Experimental Section

General. All NMR spectra were acquired using a Bruker AC-300P spectrometer operating at 75.5 MHz (^{13}C) and 121.5 MHz (^{31}P). All ^{13}C spectra were referenced to the center line of the $CDCl_3$ triplet at 77 ppm and taken at ambient temperature. All ^{31}P spectra were referenced to an external H_3PO_4. Glass transition temperatures were determined using a TA Instruments Model 2910 differential scanning calorimeter.

Dilute solution techniques were used to characterize the macromolecular structures of the esterified poly[(aryloxy)phosphazene]s. Tetrahydrofuran, filtered through a 0.02 μm filter was used as the solvent, and all experiments were performed at 22 °C. Solution refractive index increment, dn/dc, values were obtained using a Rainin Dynamax RI-1 differential refractive index detector. The instrument constant was determined via calibration using known concentrations of polystyrene standards whose dn/dc values are well-known. Laser light scattering (LLS) measurements were made using a Wyatt Technologies Dawn-DSP system, which uses polarized light having a wavelength of 633 nm and measures scattered light intensities at 18 angles ranging from 22.5° to 147°. The instrument was calibrated with toluene, which was filtered through a 0.02 μm filter. Dilute solutions in the 10^{-4} to 10^{-5} g/mL range were prepared in scintillation vials for scanning on the LLS instrument. Zimm and Debye plots were prepared to obtain weight-average molecular weights M_w, z-average square radii (mean square radii), and second-virial coefficients.

Materials. Hexachlorocyclotriphosphazene (Strem Chemical), **1**, was sublimed prior to use. Poly[bis(chloro)phosphazene], **2**, was prepared by the ring-opening polymerization of **1** at 250 °C for 56 h, Scheme 1, and isolated in 28% yield according to procedures previously described.[18] ^{31}P NMR gave a chemical shift for **1** of −18.0 ppm with respect to H_3PO_4. Anhydrous reagent grade solvents (toluene, hexane, tetrahydrofuran, 1,4-dioxane, diglyme) were stored under nitrogen. Sodium hydride (60% dispersion in mineral oil) and ethyl-4-hydroxybenzoate were obtained from Aldrich Chemical Co. and used as received.

Preparation of Poly[bis(4-(ethylcarboxylato)phenoxy)phosphazene] (3). Polymer **3** was prepared with modifica-

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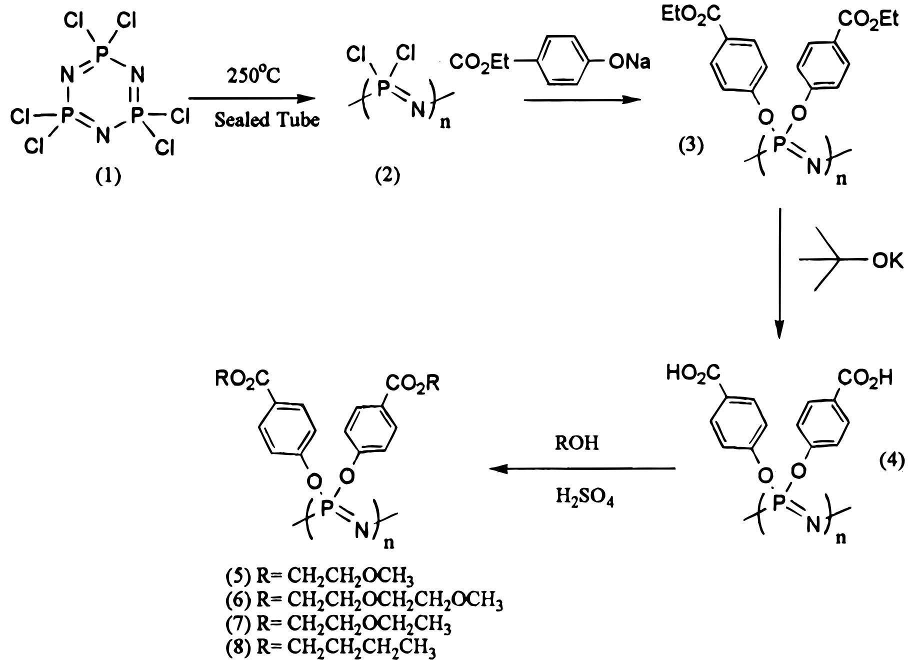
Scheme 1. Synthetic Pathway for the Esterification of *para*-Substituted (Aryloxy)phosphazenes



tions to the procedure originally described by Allcock.[19] A solution containing the sodium salt of ethyl-4-hydroxybenzoate was prepared from 24.04 g (0.144 mol) of the phenol and 5.31 g (0.132 mol) of NaH in 200 mL of 1,4-dioxane. This sodium salt solution was then slowly added to 7.0 g (0.060 mol) of polymer **2** dissolved in 70 mL of toluene and 100 mL of 1,4-dioxane. The reaction became increasingly viscous during the addition and resulted in a thick suspension. The reaction temperature was raised to 115 °C by adding 170 mL of diglyme and removing 1,4-dioxane−toluene azeotrope with a Dean-Stark trap. After heating the reaction at 115 °C for 18 h, ^{31}P NMR spectroscopy showed a single peak at −20.0 ppm for the bis(aryloxy)-substituted phosphorus, which indicated that the reaction was complete. The resulting product solution was cooled and added to several liters of methanol to precipitate polymer **3**. The product was washed several times with water and methanol to remove sodium chloride and excess ethyl-4-hydroxybenzoate. After a final wash with methanol, the white fibrous polymer was dried to a constant mass: 16.75 g, 74% yield based on polymer **2**; ^{31}P NMR ($CDCl_3$) −20.0 ppm (singlet); ^{13}C NMR 165.0, 153.9, 130.7, 126.8, 119.0, 60.8, 14.2 ppm; DSC T_g = 14 °C, T_1 = 141 °C. Anal. Calcd for $C_{18}H_{18}O_6PN$: C = 57.60, H = 4.83, N = 3.73. Found: C = 57.02, H = 4.76, N = 3.65. Molecular weight (weight average) = $(2.1 \pm 0.2) \times 10^6$, d*n*/d*c* = 0.124, rms radius = 105 ± 11 nm, second-virial coefficient = $(1.4 \pm 0.6) \times 10^{-4}$ mL mol/g^2.

Preparation of Poly[bis(4-carboxylatophenoxy)phosphazene] (4). Polymer **4** was synthesized[19] by hydrolysis using potassium *tert*-butoxide (Aldrich). The resulting solid was only soluble in basic water. The material was isolated by acidification followed by suction filtration and water washing (3×) of the white solid. The polymer was then dried under vacuum to give **4** in 94% yield.

Preparation of Poly[bis(4-(2-methoxy)ethylcarboxylatophenoxy)phosphazene] (5). A 4.1 g sample of **4** was placed in a 50 mL round bottom flask and treated with 50 mL of 2-methoxyethanol (Aldrich) and 2 mL of concentrated H_2SO_4. The resulting solution was heated to reflux for 45 min, where a clear solution was observed, indicating reaction completion. The solution was allowed to cool to room temperature, where it was precipitated into water to yield a tan-colored polymer. This was collected and dried under vacuum: Yield = 76%; ^{31}P NMR ($CDCl_3$) −19.7 ppm (singlet); ^{13}C NMR ($CDCl_3$) 165.0, 154.0, 131.0, 126.3, 119.7, 70.3, 63.7, 58.6 ppm; DSC T_g = 6 °C. Anal. Calcd for $C_{20}H_{22}O_8PN$: C = 55.18, H = 5.09, N = 3.22. Found: C = 54.11, H = 4.75, N = 3.45. Molecular weight (weight average) = $(7.2 \pm 0.5) \times 10^6$, d*n*/d*c* = 0.118, rms radius = 142.6 ± 8.4 nm, second-virial coefficient = $(2.8 \pm 3.0) \times 10^{-5}$ mL mol/g^2.

Preparation of Poly[bis(4-(2,2′-methoxyethoxyethyl)-carboxylatophenoxy)phosphazene] (6) and Poly[bis(4-(2-ethoxy)ethylcarboxylatophenoxy)phosphazene] (7). Polymers **6** and **7** were prepared in a similar manner; the preparation of **6** is shown here. A 1.2 g sample of **4** was placed in a 50 mL round bottom flask fitted with a condenser. To this was added 20 mL of 2-(2-methoxyethoxy)ethanol (Alfa) and 2 mL of concentrated H_2SO_4. The reaction was heated to reflux for 10 min. The resulting clear solution was cooled to room temperature, followed by addition of 30 mL of deionized water. Polymer **6** appeared as a tan sticky solid that was dissolved in THF and precipitated into water. The solid was dried under vacuum to give polymer **6** in 60% yield. Polymer **6**: ^{31}P NMR ($CDCl_3$) −20.0 ppm (singlet); ^{13}C NMR ($CDCl_3$) 165.0, 154.0, 130.9, 126.2, 119.8, 71.7, 70.3, 68.9, 63.8, 58.7; DSC T_g = −15 °C. Anal. Calcd for $C_{24}H_{30}O_{10}PN$: C = 55.07, H = 5.78, N = 2.68. Found: C = 53.98, H = 5.32, N = 3.00. Molecular weight (weight average) = $(1.51 \pm 0.06) \times 10^6$, d*n*/d*c* = 0.115, rms radius = 63.8 ± 3.3, second-virial coefficient = $(1.6 \pm 1.0) \times 10^{-4}$ mL mol/g^2. Polymer **7**: ^{31}P NMR ($CDCl_3$) −19.8 ppm (singlet); ^{13}C NMR ($CDCl_3$) 165.0, 154.0, 131.0, 126.4, 119.8, 68.2, 66.5, 64.0, 15.1; DSC T_g = −15 °C. Anal. Calcd for $C_{22}H_{26}O_8PN$: C = 57.02, H = 5.65, N = 3.02. Found: C = 56.52, H = 5.50, N = 3.09. Molecular weight (weight average) = $(1.4 \pm 0.2) \times 10^6$, d*n*/d*c* = 0.115, rms radius = 98.5 ± 7.1, second-virial coefficient = $(4.0 \pm 30.0) \times 10^{-5}$ mL mol/g^2.

Preparation of Poly[bis(4-butylcarboxylatophenoxy)-phosphazene] (8). A 1.1075 g sample of **4** was placed in a 50 mL round bottom flask and to this was added 10 mL of 1-butanol (Fisher) and 2 mL of concentrated H_2SO_4. Heating to reflux was applied for 20 h. The resulting solution was cooled to room temperature. This solution was then transferred to a separatory flask containing 30 mL of toluene (Fisher). The solution was washed with three 50 mL portions of water. The organic phase was taken to dryness with a rotary evaporator. The residue was redissolved in 20 mL of THF and precipitated into a 200 mL volume of water. The solution was removed and polymer **8** was collected and dried under vacuum in 67% yield: ^{31}P NMR ($CDCl_3$) −20.3 ppm (singlet); ^{13}C NMR ($CDCl_3$) 165.0, 153.9, 130.7, 126.8, 119.9, 64.7, 30.6, 19.1, 13.7; DSC T_g = −36 °C, T_1 = 31 °C, decomposition exotherm observed at 170 °C. Anal. Calcd for $C_{22}H_{26}O_6PN$: C = 61.25, H = 6.07, N = 3.25. Found: C = 60.71, H = 6.22, N = 3.11. Molecular weight (weight average)

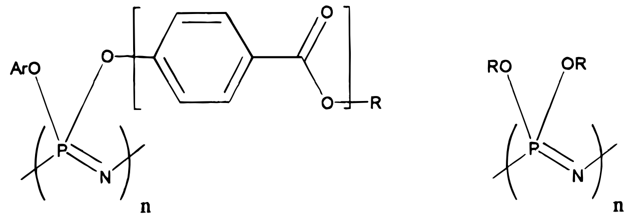


Figure 1. Comparison of esterified (left) and nonesterified polymers. Inserted "benzoate molecular fragment" is shown in brackets.

= $(1.9 \pm 0.3) \times 10^7$, d$n$/d$c$= 0.116, rms radius = 241.6 ± 22.5, second-virial coefficient = $(3.5 \pm 2.0) \times 10^{-5}$ mL mol/g^2.

Results and Discussion

The general synthetic approach (see Scheme 1) utilized in this work entails modification of aryloxy pendant groups on a phosphazene high polymer to make new materials with differing properties. Poly[bis-(4-ethylcarboxylatophenoxy)phosphazene] was synthesized by the method of Allcock[19] from linear poly[bis(chloro)-phosphazene] and the sodium salt of ethyl 4-hydroxybenzoate. This polymer is a white fibrous solid that was found to be fully soluble in tetrahydrofuran (THF) and 1,4-dioxane. The corresponding carboxylic acid derivative was made by de-esterification[19] with potassium *tert*-butoxide and THF in 94% isolated yield. As previously reported, this material is a white glassy polymer that is soluble in basic water. Esterification of this material to four new phosphazenes was achieved by exposure of the acidic polymer to four different alcohols with concentrated sulfuric acid as a catalyst, Scheme 1. Heating was generally required to achieve the reaction, with no esterified products observed in ambient-temperature experiments.

The reaction of **4** with neat 2-methoxyethanol proceeded within 45 min at a temperature of 119 °C to give a polymer solid, **5**. Initially, the acid polymer **3** was not soluble in the alcohol; the reaction was considered to be complete when insoluble material disappeared. ^{31}P NMR of the resulting polymeric solid revealed a singlet at −20.0 ppm that suggested that the phosphorus was homogeneously substituted along the backbone. The nature of the pendant group was confirmed by ^{13}C NMR spectroscopy. Eight carbon signals were observed that correlate to the expected ester. The most significant signal was the carbonyl resonance observed at 165.0 ppm, verifying the presence of the ester carbonyl carbon. Additional characterization using DSC revealed that the glass transition temperature of this new polymer was 6 °C and that there were no other thermal features observed, suggesting that the polymer is amorphous. A slight exotherm is noted at approximately 200 °C, indicating thermal decomposition. It should be noted that the decomposition is substantially lower than what is observed for poly[bis(phenoxy)phosphazene], approxi-

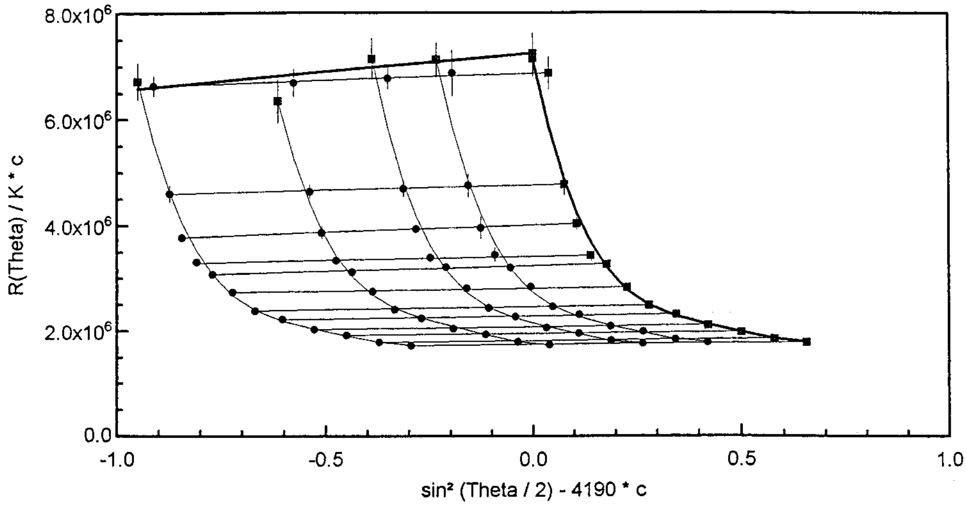


Figure 2. Debye plot (lower 12 angles) for polymer **5**.

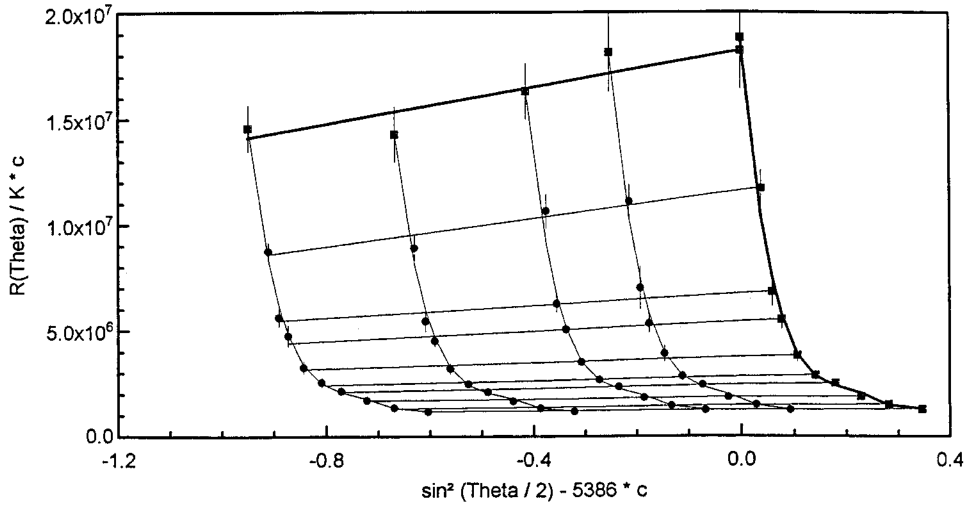


Figure 3. Debye plot (lowest nine angles) for polymer **8**.

mately 390 °C,[20] suggesting that the decomposition observed occurs at the ester linkage.

The ester formed from 2-(2-methoxyethoxy)ethanol (**6**) appeared more rubbery than the shorter chain polymer **5**, and the T_g was measured to be −15 °C, approximately 20 °C lower. There were no other thermal features, supporting the amorphous nature of this polymer. Polymer **7**, the ester formed from 2-ethoxyethanol, shared much with polymer **6** including a T_g measured at −15 °C. Comparison of these data to that for polymer **5** suggests that the longer side chains enjoy a higher degree of motional freedom, as expected. ^{31}P NMR spectra of polymers **5** and **6** gave singlets at −20.0 and −19.8 ppm, respectively. ^{13}C NMR also revealed the carbonyl functionality of both polymers at 165.0 ppm as well as spectra that correspond to the expected esters.

Polymers **5**, **6**, and **7** were found to be hydrophilic, as expected. It is interesting to note that polymer **6** is similar in structure to MEEP where a "benzoate molecular fragment" has been inserted between the polyether pendant group and the polymer backbone; see Figure 1. Thus, a comparison of the polymers is afforded where the influence of the inserted molecular fragment may be assessed. The influence is most significantly reflected in the T_g measurement. A glass transition for MEEP has been reported at −84 °C, approximately 70 °C lower than the measurement for **5**. In addition, the T_g for poly[bis(2-methoxyethoxy)phosphazene] (MEP) was reported[20] at −75 °C, approximately 80 °C lower than the measurement for polymer **5**. These increases in T_g are a result of the fundamental change in the polymer structure while retaining its hydrophilic character. In addition, it should be noted that while MEEP and MEP are soluble in water, **5** and **6** are not, and this lower solubility is a direct result of the inserted fragment. Another ramification is an increased level of structural integrity. MEEP flows readily, and methods to stabilize it such as radiation[21] and ultraviolet cross-linking[22] have been reported. A direct result of increased cross-linking is an elevated T_g when compared to the original polymer as motional freedom is limited. The net effect of the inserted molecular fragment is to raise the T_g by raising the activation energy required for backbone and pendant group motion.

A hydrophobic polymer, **8**, was synthesized using similar methodology. Polymer **4** was refluxed in 1-butanol for 20 h. This increased reaction time, as compared to the polyether esters, is attributed to the lower boiling point of 1-butanol. Isolated polymer **8** is a nonflowing solid rubber. The T_g was measured at −36 °C, approximately 80 °C higher than the corresponding poly[bis(butoxy)phosphazene] (−105 °C)[20]. As opposed to the polyether ester polymers, a thermal T_1 also was observed using DSC at 31.3 °C, suggesting some degree of crystallinity of the polymer. Additional characterization was provided using ^{13}C NMR, where nine carbons were assigned to the expected ester pendant group. As with the polyether esters, a peak at 165.0 ppm was indicative of the ester carbonyl carbon.

The LLS technique consistently yielded molecular weights in the 10^6 g/mol range and sizes (rms radii) in the 64−242 nm range, suggesting that there is no scission of the phosphorous−nitrogen polymer backbone due to either the deesterification or reesterification steps. Second-virial coefficients, indicators of the solute/solvent and solute/solute interactions, were all in the 10^{-4} to 10^{-6} mL mol/g^2 range, indicating near Θ solvent conditions. Both the Zimm and Debye formalisms were used to present the LLS data. However, most of the data were best fitted to second order to fourth order in $\sin^2(\Theta/2)$. As a result, the molecular weights, sizes, and second-virial coefficients reported here are all extracted from the Debye plots. Examples of Debye plots for polymers **5** and **8** are shown in Figures 2 and 3.

Conclusion

Outlined in this paper is a novel method for the synthesis of esterified poly[(aryloxy)phosphazene]s using a common stable polymer as the immediate precursor. It has been observed that both the physical and chemical properties of these polymers may be varied depending on the chosen ester. This technique proved to be inert to the polymer backbone, as witnessed by the conservation of polymer molecular weight and size. In the cases of polymers **5**, **6**, and **8**, comparison to nonesterified analogues gave a consistent 70−80 °C increase in T_g, suggesting that the insertion of the aromatic moiety serves to increase the temperature at which the backbone and pendant groups will undergo significant motion. It should be noted that this is consistent with data observed for other phenoxy-substituted phosphazenes, where the T_g's are observed from −10 °C to as high as 93 °C. The higher T_g for phenoxy polymers in general and for esterified phenoxy polymers in specific is proposed to be due to the increased steric bulk that limits molecular motion as compared to linear alkoxy and polyether alkoxy pendant groups. Thus, this methodology produces materials that are better film formers and have greater structural integrity than corresponding nonesters.

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