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A New Polymeric Intermediate for the Synthesis of Hybrid Inorganic−Organic Polymers

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The search for synthetic methods that yield new hybrid polymers is an area of growing interest in response to the need for novel materials in advanced technology. We report here a new approach to the synthesis of inorganic−organic macromolecules that provides access to a broad range of new polymers with unique and potentially useful properties. A hybrid polymer architecture with considerable promise consists of organic macromolecules that bear inorganic units as side structures. Organic polymers with pendent cyclophosphazene units are especially interesting because not only can the properties be controlled through the organic main chain structure but, more significantly, they can be tailored via the substituents on the cyclophosphazene rings (Figure 1). The cyclotriphosphazene pendent unit is known to react through nucleophilic substitution with a wide variety of reagents.[1]

Several examples exist where polymers have been functionalizated after polymerization. Previous work has focused on poly(dicarboximide) functionlized either with alkyl groups[2] or through "click" chemistry.[3] Weck and co-workers[4] have developed several architectures capable of functionalization through noncovalent interactions. Although these methods are successful functionalization strategies, they do not offer the versatility of an inorganic−organic hybrid system.

Two methods have been developed to access such structures. The first, pioneered by Allen,[5] involves the free radical polymerization of cyclophosphazenes with one vinyl or allyl substituent per ring. The second requires the ring-opening metathesis polymerization (ROMP) of a norbornene-substituted organocyclotriphosphazene such as **2**.[6−9] The free radical processes do not allow precise control of the polymer molecular weight but do permit copolymerization reactions. The ROMP alternative is a "living" polymerization which permits molecular weight control and either random or block copolymerization.

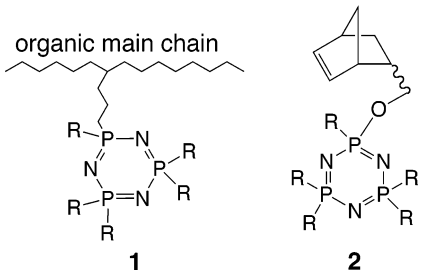

Figure 1. Final polymer structure **1** and ROMP monomer **2**.

Monomers of type **2** for the ROMP process are typically synthesized via nucleophilic replacement of one chlorine atom in hexachlorocyclotriphosphazene by potassium 5-norbornene-2-methoxide[1,3−5] followed by replacement of the remaining five chlorines with nonfunctional organic units, before polymerization through a typical ROMP procedure. Replacement of all the chlorine atoms in hexachlorocyclotriphosphazene by organic substituents is carried out to avoid potential interference to the ROMP process by the highly reactive P−Cl bonds. This constitutes a serious limitation because bulky or reactive organic cosubstituent groups on the phosphazene ring often inhibit polymerization during the ROMP reaction. For example, when monomer **2** (R = $-O(CH_2CH_2O)_2CH_3$) is polymerized, a high PDI (>5) polymer is obtained. This is thought to be a direct result of steric or chemical interactions between the oligoethylenoxy groups and the ROMP catalyst.

Contrary to mechanistic intuition, we have found that the ROMP process occurs without initiator deactivation even when each monomer molecule bears one norbornyl unit and five P−Cl bonds (monomer **3**).[10] After polymerization of this monomer,[11] the chlorine atoms can be replaced by a wide variety of organic groups to vary properties such as polymer solubility or glass

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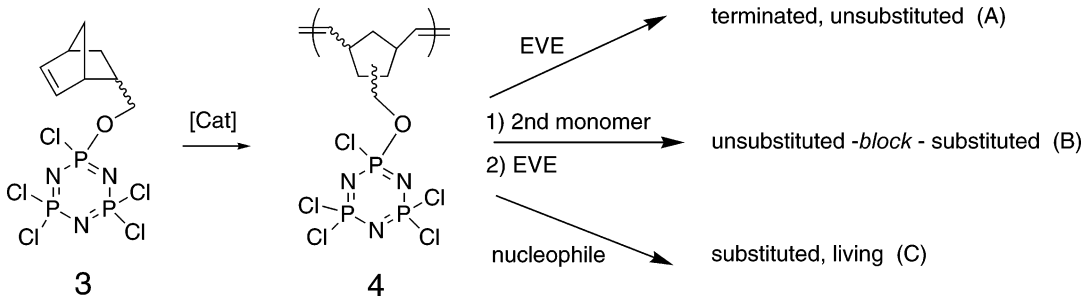
Scheme 1. Polymer Synthesis via Living Macromolecular Intermediate 4



transition temperature or to introduce functional groups. The significance of this is that more than 250 different reagents are known to react cleanly to replace chlorine atoms in phosphazene cyclic trimers.[8] This provides access to a large number of different polymers through reactions carried out on one easily accessible macromolecular intermediate. The following examples illustrate the scope of the process.

Scheme 1 illustrates three different routes that allow the conversion of polymeric intermediate **4** to derivative macromolecules. All polymerizations and subsequent substitutions for routes A−C were carried out in a single reaction vessel without purification of intermediates. First (route A), an unsubstituted living polymer was terminated by the addition of ethyl vinyl ether (EVE) to a solution of intermediate **4**. The ^{31}P NMR spectrum (Figure 2A) was identical to that of the unreacted monomer **3**.[12] This macromolecule served as a source of reactive polymer that can be used for linkage of one or more different side groups to the phosphazene rings by nucleophilic replacement of the chlorine atoms. Thus, macromolecules can be prepared with a wide range of different properties depending on the substituents introduced at this postpolymerization stage. This allows access to polymers with side groups that would interfere with the ROMP process through steric or other constraints. As an example, polymer **4** was substituted with 2,2,2-trifluoroethoxy groups to give a macromolecule with a ^{31}P NMR spectrum B (Figure 2).

Second (route B), the "living" polymeric intermediate **4** may be employed to produce a diblock structure utilizing any ROMP-compatible comonomer. For example, living polymer **4** was used to initiate a block copolymer by the addition of a monomer **2** where R was methoxyethoxyethoxy groups. ^{31}P NMR spectra provided evidence for a product polymer that contained a diblock structure with P−Cl and $POCH_2CH_2OCH_2CH_2OCH_3$ units in two separate blocks (Figure 2C). This reaction can be repeated to produce multiblock polymers. Thus, continued living polymerizations may be carried out without replacement of the P−Cl bonds on the initial phosphazene block since these have little or no effect on the catalyst activity. A delayed substitution of the initial phosphazene block is particularly beneficial when the final phosphazene pendent unit will bear highly polar or sterically bulky side groups that could affect the efficiency or rate of polymerization. Because nucleophilic halogen replacement is carried out after completion of the copolymerization, the number of repeating units in each block and the polymer architecture are unaffected.

A final synthetic option (route C) is substitution of the living macromolecule (**4**) *before* termination of the polymerization process to carry out block copolymerization at the terminus of a substituted polymer. This further diversifies the opportunities to control the polymer structure. Preliminary evidence has been obtained that strong nucleophiles such as sodium trifluoroethoxide react with polymer **4** without substantial deactivation of the living chain ends. A ^{31}P NMR spectrum of this product (Figure 2D) indicated that complete halogen replacement had occurred,[13] but this polymer was still capable of initiating the growth of a second block following the addition of monomer **2** where $R = OCH_2CH_2OCH_2CH_2OCH_3$. Some initiator deactivation was detected by the isolation of higher molecular weight polymers than expected and from the increased polydispersity, as compared to a control.[14] This survival of the living end groups following substitution is noteworthy and unexpected. The GPC trace for the diblock polymer synthesized through route C was monomodal and had a polydispersity (M_w/M_n) of <2.

To summarize, this new synthetic route via the polymerization of mono(5-norborene-2-methoxy)pentachloro cyclotriphosphazene (**3**) provides several advantages over existing pathways to inorganic−organic hybrid polymers. First, it creates an efficient means for producing organic backbone polymers with properties that are supplemented by those of the pendent inorganic ring systems. For example, one property of general interest is fire resistance. Second, the fact that compound **3** can be polymerized eliminates problems encountered in earlier work where the polarity and steric effects of some organic side groups

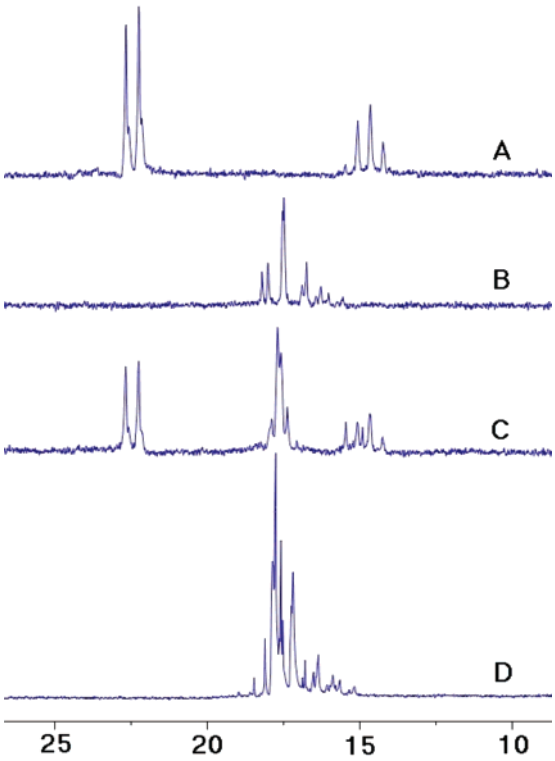


Figure 2. ^{31}P NMR spectra of reaction mixtures derived from **4**: (A) unsubstituted polymer **4**; (B) terminated polymer **4** fully substituted with trifluoroethoxy groups; (C) unsubstituted first *block*-methoxyethoxyethoxy-substituted second block polymer; (D) trifluoroethoxy-substituted-*block*-methoxyethoxyethoxy-substituted polymer.

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on the phosphazene rings in **2** interfered with the polymerization process. Third, the polymerization of **3** is reproducible from experiment to experiment and allows predictable chain lengths to be obtained. Compound **3** can be polymerized in a variety of common solvents such as tetrahydrofuran, dichloromethane, acetone, benzene, or chloroform. Fourth, intermediate **3** is quite stable in solution. After 1 month storage in dichloromethane under an atmosphere of nitrogen, the polymer characteristics were identical to those of a freshly prepared sample. This would facilitate scale-up of the process. Fifth, the intermediate can be utilized via one-pot syntheses to produce a variety of polymer architectures such as diblock, multiblock, star, comb, and linear polymers.

We anticipate that a broad development of this synthesis route will provide access to improved lithium ion and proton conductors, new separation membranes, and novel photonic materials.

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Supporting Information Available: Experimental procedure and characterization data for compounds **3** and **4** and routes A, B, and C. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Synthesis of monomer **3**: An excess of hexachlorocyclotriphosphazene was used to ensure monosubstitution. This is important toprevent subsequent cross-linking. Disubstitution was also avoided by carrying out the addition of the nucleophile to the phosphazene cyclic trimer at −78 °C. The reaction was monitored by ^{31}P NMR spectroscopy, which indicated the presence of mono(5-norbornene-2-methoxypentachlorocyclotriphosphazene (**3**) and unreacted hexachlorocyclotriphosphazene. Potassium chloride was removed through standard extraction workup, and the excess hexachlorocyclotriphosphazene was removed by sublimation. ^{31}P NMR spectra confirmed the absence of hexachlorocyclotriphosphazene to less than 0.1%. However, a small amount of hexachlorocyclotriphosphazene can be tolerated because it can be removed at later stages after full substitution by either precipitation or dialysis.
(11) A typical polymerization was carried out using dichloromethane as a solvent at a concentration between 0.2 and 0.02 g of monomer /mL of solvent. The monomer, mono(5-norbornene-2-methoxy)-pentachlorocyclotriphosphazene **3**, was degassed before polymerization. It was then diluted with dichloromethane, and the catalyst (bis(tricyclohexylphosphine)ruthenium benzylidene dichloroide), dissolved in dichloromethane, was added to the monomer solution. Reactions were typically complete within several hours at 25 °C, although most reactions were allowed to proceed for up to 72 h to ensure completion of the polymerization.
(12) Living polymer **4** cannot be evaluated by GPC without replacement of chlorine groups on the phosphazene rings. It has been found that P−Cl bonds interact with GPC columns and must be replaced prior to molecular weight characterization. Thus, the living monomer may be terminated with ethyl vinyl ether, substituted by nucleophilic replacement of the chlorine atoms, and *then* the molecular weight is estimated by gel permeation chromatography.
(13) Polymer intermediate **4** was first treated with sodium 2,2,2-trifluoroethoxide before a second monomer (**2**, where R = 2-(2-methoxyethoxy)ethoxy) was allowed to react with the living polymer. Gel permeation chromatography showed a single peak. Dialysis over several days failed to remove either block. Thus, ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy indicated the presence of a diblock copolymer. A separate experiment showed a similar spectrum when sodium 2,2,2-trifluoroethoxide and monomer **2** (R = 2-(2-methoxyethoxy)-ethanoxide) were added at the same time.
(14) A control polymer was synthesized to evaluate the effects of a nucleophile on the living chain end. The control targeted the same block length but proceeded through route B; i.e., nucleophilic substitution occurred *after* termination of the polymer.

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