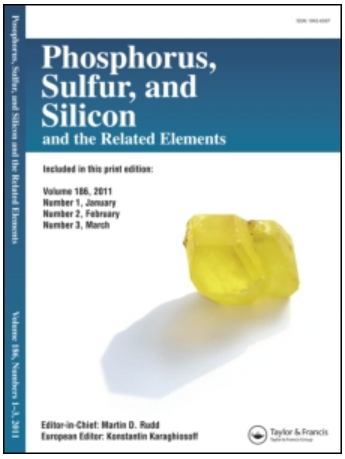

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New Ring-Opening Polymerization of Phosphorus-Containing Cyclic Monomers

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NEW RING-OPENING POLYMERIZATION OF PHOSPHORUS-CONTAINING CYCLIC MONOMERS

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A living cationic ring-opening polymerization of a six-membered cyclic phosphonite initiated with a new catalyst system of a halobenzene with $NiBr_2$ is disclosed. Furthermore, we report a cationic ring-opening polymerization of a three-membered cyclic phosphine, giving rise directly to the polyphosphine derivative.

Keywords: Living polymerization; phosphorus-containing cyclic monomer; polyphosphine; ring-opening polymerization

INTRODUCTION

Cyclic phosphorus compounds are good starting monomers for preparing functional polymers that have phosphorus moieties in the main chain. They are known to undergo ring-opening polymerization via cationic, anionic, or thermal processes. The polymerization of trivalent phosphorus-containing cyclic monomers by a cationic initiator generally proceed involving propagation via the Arbuzov-type reaction to produce polymers having pentavalent phosphorus in the main chain. Such cyclic monomers, however, have been difficult to polymerize in a living manner, and thus the molecular weights of the product polymers were not controlled. In contrast to the above polymers having pentavalent phosphorus, the preparation of polymers containing trivalent phosphorus in the main chain, such as polyphosphine, by ring-opening polymerization was not well established.

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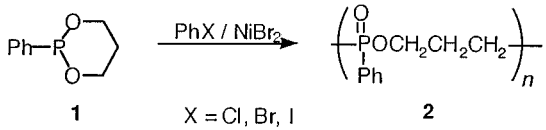
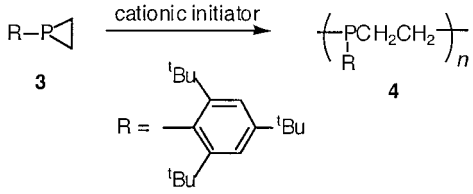
The first topic of this paper deals with the polymerization of a six-membered cyclic phosphonite **1** initiated with PhX/$NiBr_2$ system, which is a new polymerization catalyst (Scheme 1). The polymerization initiated with this catalyst proceeded in a living nature to give poly (phosphinate) **2** with a controlled molecular weight.[1,2] As a second topic, we describe the cationic ring-opening polymerization of a three-membered cyclic phosphine **3** to produce directly the polyphosphine derivative **4** (Scheme 2).[3]



1 **2**

SCHEME 1



3 **4**

SCHEME 2

RESULTS AND DISCUSSION

Polymerization of Six-Membered Cyclic Phosphonite 1

Polymerization of **1** initiated with $NiBr_2$/iodo-, bromo-, or chlorobenzene proceeded in a living nature, in which the degree of polymerization (DP) was close to the monomer/halobenzene feed ratio and the M_w/M_n values were relatively small. The polymerization did not proceed with only PhX or $NiBr_2$. The feed ratio of $NiBr_2$ and the monomer did not affect the DP. The living nature of the present polymerization was also confirmed by the relationships of DP and M_w/M_n values in terms of the monomer conversion. The DP is proportional to the monomer conversion, and the M_w/M_n values stayed less than 1.3. An additional evidence of the living nature is given by a monomer-addition experiment. When the same amount of monomer was added after the complete consumption of the first monomer at the final stage, the propagation still continued to give **2**, having the double DP value at the second final stage. The structure of the product polymer was determined to be a

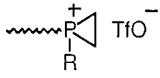
poly(phosphinate) **2** having the end groups of diphenyl phosphinate and a halomethylene on the basis of the ^{1}H NMR, ^{13}C NMR, IR spectroscopy, and elemental analysis, as well as the alkaline hydrolysis experiment.

In contrast to the above polymerization, the polymerization of seven- and five-membered cyclic phosphonites were also examined by using the PhI/$NiBr_2$ system. The polymerization of the seven-membered monomer proceeded at 100°C for 72 h to give the corresponding polymer in 100% conversion. However, the DP values were not close to the feed ratio of PhI and the monomer, indicating that the polymerization is not a living nature. On the other hand, the polymerization of five-membered cyclic phosphonite did not proceed at all under similar reaction conditions.

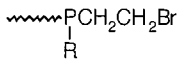
The polymerization of **1** initiated with polyhalobenzene/$NiBr_2$ system was carried out. Polyhalobenzenes employed as multifunctional initiators were 1,4-dihalobenzene, 1,3,5-trihalobenzene, 1,2,4,5-tetrahalobenzene, and hexahalobenzene. The reaction proceeded smoothly to produce linear and star-shaped poly(phosphinate)s.[4]

Polymerization of Three-Membered Cyclic Phosphine 3

Polymerization of **3** was examined with cationic, anionic, and radical initiators. Cationic initiators such as MeI, $PhCH_2Br$, and MeOTf are effective for the polymerization of **3** (Table I). An anionic initiator (MeMgBr) and a radical initiator (AIBN) did not induce the polymerization of **3**. The structure of polymer **4** was established on the basis of NMR and IR analysis. In the IR spectrum of the polymer, a strong absorption at around 1200 cm^{-1} due to P=O was not observed. These data indicate that the oxidation of the phosphorus atom in the polymer did not take place during the polymerization and the work-up procedure. To shed light on the polymerization mechanism, the equimolar model reaction of the monomer with an initiator was carried out. The structure of the propagation species depends upon the nucleophilicity of the counter anion from the initiator. The propagating ends are phosphonium ions **5** in the polymerization with MeOTf, whereas the propagating ends are alkyl bromide species **6** when $PhCH_2Br$ was used as the initiator. In the polymerization with MeI, there are two possibilities of phosphonium and covalent types for the propagating species.



5



6

TABLE I Cationic Ring-Opening Polymerization of **3**[a]

Entry	Initiator (mol% for **3**)	Temperature (°C)	Time (h)	Yield[b] (%)	M_n[c]
1	CH_3OTf (4.1)	50	739	31	7800
2	CH_3I (5.6)	35	230	27	7800
3	CH_3I (5.6)	50	118	45	6600
4	$PhCH_2Br$(9.7)	50	66	47	2500

[a]Dichloromethane as solvent.
[b]Residue after sublimation of the reaction mixture.
[c]Determined by VPO.

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