Macromolecules **2007,** *40,* 4854−4858

Synthesis of Poly(vinylene−phosphine)s: Ring-Collapsed Radical Alternating Copolymerization of Methyl-Substituted Cyclooligophosphine with Acetylenic Compounds

Kensuke Naka,* Tomokazu Umeyama, Akiko Nakahashi, and Yoshiki Chujo

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

Received February 1, 2007; Revised Manuscript Received May 7, 2007

ABSTRACT: A conjugated polymer containing a phosphorus atom in the main chain, poly(vinylene−phosphine), was synthesized by ring-collapsed radical alternating copolymerization (RCRAC) of a cyclooligophosphine and phenylacetylene (**1a**). Under a nitrogen atmosphere, pentamethylcyclopentaphosphine (*cyclo*-$(MeP)_5$) and **1a** were reacted in the presence of a catalytic amount of 2,2′-azobis(isobutyronitrile) (AIBN) at 78 °C in deaerated benzene for 8 h. Poly(vinylene−phosphine) (**2**) was obtained as a yellow powder after purification by reprecipitation into *n*-hexane three times and freeze-dried for 10 h. The number-average molecular weight of polymer **2** was 2500, which is estimated by gel permeation chromatographic (GPC) analysis (chloroform, PSt standards). The structure of **2** was supported by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopies, suggesting that *trans* isomers of diphosphaalkene units were mainly formed in the main chain. The UV−vis absorption spectrum of polymer **2** in chloroform showed small absorption at a visible region derived from the n−π^* transition in the main chain as well as strong absorption at a UV region derived from aromatic groups. The fluorescence spectrum of a dilute chloroform solution of **2** showed an emission peak at 470 nm, which derived from the *n*−π^* transition along the polymer backbone.

Introduction

To date, a number of inorganic polymers have been provided and exhibited interesting and useful properties.[1] However, a variation of inorganic polymer is relatively limited although an enormous kind of inorganic atoms exist. Synthesis of new polymers having inorganic elements in the backbone is still a challenging topic. General synthetic protocols of organic polymers that involve a chain-growth mechanism such as addition polymerization cannot be applied to the synthesis of inorganic polymer since suitably reactive but stable element−element multiple bonds for inorganic elements are difficult to prepare.[2] To obtain stable compounds with multiple bonds between inorganic elements or between an element and a carbon, the presence of sterically hindered substituents on the elements is required, which prevents spontaneous oligomerization.[3] The common methodology to obtain inorganic polymers like polysiloxsanes,[4] polyphosphazenes,[5] and poly(carbosilane)s[6] is a ring-opening polymerization (ROP) reaction. ROP for inorganic polymerization by heat, anionic or cationic initiators, or metal catalysts is now well-established and widely used. More recently, synthesis of a poly(vinylene−phosphine) via anionic ROP was reported by designing the strained ring structure.[7] The use of the inorganic rings for ring-opening homopolymerization has been studied and utilized well, and a few examples of the copolymerization of inorganic homocycles with organic comonomers have been reported by now.[8]

Cyclooligophosphines are monocyclic compounds of which backbone is constructed with only phosphorus atoms. Although interesting behaviors owing to their ability to form complexes with metal carbonyls and transition metal salts have been shown,[9] there are few reports of cyclooligophosphines about reactions with organic compounds.[9a,10] Recently, poly(vinylene−arsine)s and poly(vinylene−stibine)s were successfully synthesized by ring-collapsed radical alternating copolymerization (RCRAC) of cyclooligopnictogens with acetylenic compounds in our laboratory (Schemes 1 and 2).[11] Moreover, it was reported that the triple bond of phenylacetylene (**1a**) reacts with a diphosphine compound (R_2P-PR_2, R = Me or Ph) in the presence of a catalytic amount of 2,2′-azobis(isobutyronitrile) (AIBN) to produce disubstituted vinylenes, $R_2P-CPh=CH-PR_2$.[12] Utilizing cyclic phosphorus compounds instead of diphosphines, it can be speculated that a polymer with phosphorus elements in the main chain would be provided by the addition of phosphine units toward the ethynyl group of **1a**.

Polymers containing phosphorus atoms showed a variety of important properties for flame retardants,[13] ionic conducting materials,[14] and easily separable supports for metal catalysts.[15] Moreover, the properties of the phosphorus-containing polymer can be tuned by changing the oxidation state or coordinating toward transition metals. Recently, several conjugated organophosphorus polymers have been reported and showed interesting features.[7,16−19] The phosphorus atoms participate in the conjugated system by virtue of their lone pairs. One of the most thoroughly investigated studies is phosphole-containing polymer due to their potential electronic application.[17] Poly(*p*-phenylene−phosphine)s[18] and polymers with P=C bonds in the polymer structure[19] were also reported with their interesting properties. This paper describes RCRAC of cyclooligophosphine with acetylenic compound which produced the simplest structure of the conjugated organophosphorus polymers, poly(vinylene−phosphine). Moreover, the results of the radical reactions would provide more information on compounds containing group 15 elements.

Results and Discussion

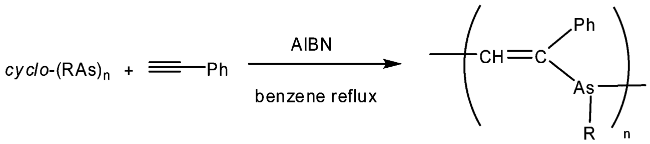
The methyl-substituted cyclooligophosphine was synthesized by the reduction of methyldichlorophosphine with lithium according to the literature procedure.[20] It is reported that the

---

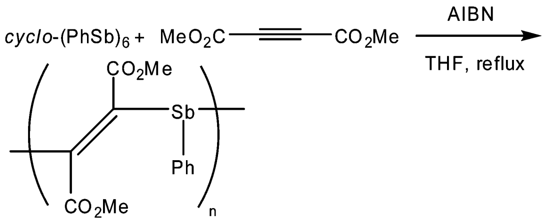
* Corresponding author. E-mail: ken@chujo.synchem.kyoto-u.ac.jp.

10.1021/ma0702795 CCC: $37.00

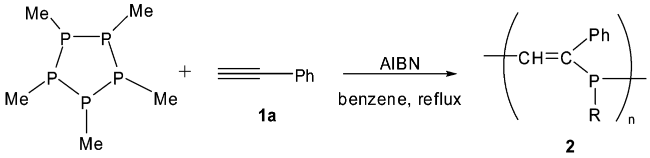
Scheme 1



Scheme 2



Scheme 3



five-membered ring structure, pentamethylcyclopentaphosphine, *cyclo*-(MeP)$_5$, is mainly formed by this method and exclusively obtained by distillation under reduced pressure. Under a nitrogen atmosphere, *cyclo*-(MeP)$_5$ and **1a** were reacted in the presence of 1.6 mol % of AIBN at 78 °C in deaerated benzene to provide a copolymer (**2**) (Scheme 3). The obtained polymer was purified by reprecipitation from benzene to *n*-hexane and then freeze-dried to give a light yellow powder in 46% yield. The relatively low yield was due to the removal of monomers and oligomers by the reprecipitation. The resulting polymer was soluble in common organic solvents such as chloroform, THF, benzene, and toluene. GPC analysis (chloroform) of **2** showed a single peak, and the number-average molecular weight (M_n) of **2** was estimated to be 2500 (vs polystyrene standards) with a polydispersity index (PDI; M_w/M_n) of 1.25. The degree of polymerization (DP) was 16.

The 1:1 alternating structure of methylphosphine (MeP) and vinylbenzene units was supported by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopies of **2**. The ^{1}H NMR spectrum (Figure 1 (I)) showed peaks in aromatic (δ 6.6−7.6 ppm) and vinyl regions (δ 5.89 ppm) and a peak assignable to the methyl proton at δ 0.80 ppm. The chemical shift of the vinyl proton suggested that a *trans* isomer was predominantly obtained.[12] Small peaks at δ 1.2−1.6 ppm can be attributed to the terminal methyl proton derived from the AIBN fragment. The integral ratio of the peaks of the methyl protons attributed to the phosphine unit and the peaks attributed to the AIBN fragment and the vinyl protons was 3.0_0:0.6_6:1, indicating the polymer main chain structure with the AIBN fragment as an end group. The integral ratio suggests that the polymer structure is the 1:1 alternating methylphosphine unit and the vinylene unit with a DP of 17 (calculated on the assumption that both the end groups are isobutyronitrile groups). The result of the end-group analysis in NMR spectrum is in agreement with the GPC analysis. In the case of poly(vinylene−arsine)s, however, no obvious peaks attributable to end groups were observed in the methyl region in ^{1}H and ^{13}C NMR spectra.[11a,b] The results show that the phosphine−carbon (sp^3) bond is strong enough to be intact during the reaction. The phosphorus radical with the isobutyronitrile group acted as an end-capping agent during the copolymerization; in contrast, few terminating groups were observed in the copolymerization of *cyclo*-(MeAs)$_5$ with **1a**. This fact is one reason for the lower molecular weight of **2** than that of a methyl-substituted poly(vinylene−arsine) synthesized by the same methodology (M_n = 11 500, yield 46%). The ^{13}C NMR spectrum (Figure 1 (II)) showed only one sharp resonance for the methyl carbon at δ 11.9 ppm. The peak of vinyl carbon (C) was observed around δ 160 ppm. The ^{31}P NMR (Figure 1 (III)) spectrum exhibited one peak at δ 28.4 ppm. The ^{31}P NMR spectrum of *cyclo*-(MeP)$_5$ showed a peak at 20 ppm. These results were compatible with the fact that the polymer backbone possessed no oxidized phosphorus atom and no phosphorus−phosphorus bond.

Poly(vinylene−phosphine) **2** is reasonably air- and moisture-stable in the solid state; no change was observed in the GPC trace, and the ^{31}P NMR spectrum after **2** in the solid state was exposed to air for several days. On the other hand, when polymer **2** was left in $CHCl_3$ for 12 h, a new peak appeared around δ 25 ppm in the ^{31}P NMR spectrum, which suggests the oxidation of the phosphine unit. The peak of the vinyl proton became smaller in the ^{1}H NMR spectrum, suggesting decomposition of the vinylene−phosphine structure. After being exposed to air in the solution state for several days, the polymer decomposed to show no polymeric peaks in a GPC trace. Polymer **2** was reacted with elemental sulfur in dichloromethane to yield phosphine sulfide, of which the ^{31}P NMR spectrum showed a peak at δ 39.8 ppm and no peak around δ −28 ppm. In this case, the GPC trace exhibited no significant change compared to that before the sulfuration.

No RCRAC of *cyclo*-(MeP)$_5$ with **1a** without AIBN proceeded even when heating up at 80 °C or under the bulk condition. This result suggests that AIBN would be required for RCRAC of *cyclo*-(MeP)$_5$, in contrast with RCRAC of *cyclo*-(MeAs)$_5$.[21] A phosphorus−phosphorus bond is stronger than an arsenic−arsenic bond, and the phosphorus−phosphorus bond in *cyclo*-(MeP)$_5$ cannot cleave spontaneously. The radical reaction of *cyclo*-(MeP)$_5$ with 4-cyanophenylacetylene (**1b**) and dimethyl acetylenedicarboxylate (**1c**) gave only oligomeric products. In the case of **1b**, a broad peak assignable to vinyl protons was observed at δ 6.5−5.5 ppm. The addition of **1c** toward *cyclo*-(MeP)$_5$ caused violent exothermic reaction to provide a black solid. As described in the previous work,[11c] radicals of lighter elements are expected to have less capture ability of vinyl radicals. The capture of the vinyl radicals is hardly achieved in RCRAC of *cyclo*-(MeP)$_5$ with electron-deficient acetylenes which provide less reactive vinyl radicals. Comparing the results in this paper with those of *cyclo*-(MeAs)$_5$[11a] and *cyclo*-(PhSb)$_6$,[11c] the capture ability of the vinyl radical is approved to be lower in the case of *cyclo*-(MeP)$_5$ than that in the case of *cyclo*-(MeAs)$_5$, and that in the case of *cyclo*-(PhSb)$_6$ to provide the corresponding poly(vinylene−phosphine) despite the reaction of *cyclo*-(MeP)$_5$ with **1b** or **1c** proceeds.

The phenyl-substituted cyclooligophosphine, *cyclo*-(PhP)$_5$, was also treated with **1a** in the presence of AIBN in a refluxing benzene. The reaction suspension (due to poor solubility of *cyclo*-(PhP)$_5$ toward benzene) became homogeneous within about 30 min, suggesting the collapse of the ring structure of *cyclo*-(PhP)$_5$. However, no polymer was obtained after stirring the mixture for 8 h. Phenyl-substituted phosphorus radicals had too low reactivity toward the ethynyl group of **1a** to yield a poly(vinylene−phosphine).

The RCRAC of *cyclo*-(MeP)$_5$ with the acetylenic compounds should have proceeded in a similar way to that of *cyclo*-(MeAs)$_5$[11a] (Scheme 4). The difference with the case of RCRAC of *cyclo*-(MeAs)$_5$ is that AIBN is necessary to initiate RCRAC of *cyclo*-(MeP)$_5$. First, AIBN cleaved the phosphorus−

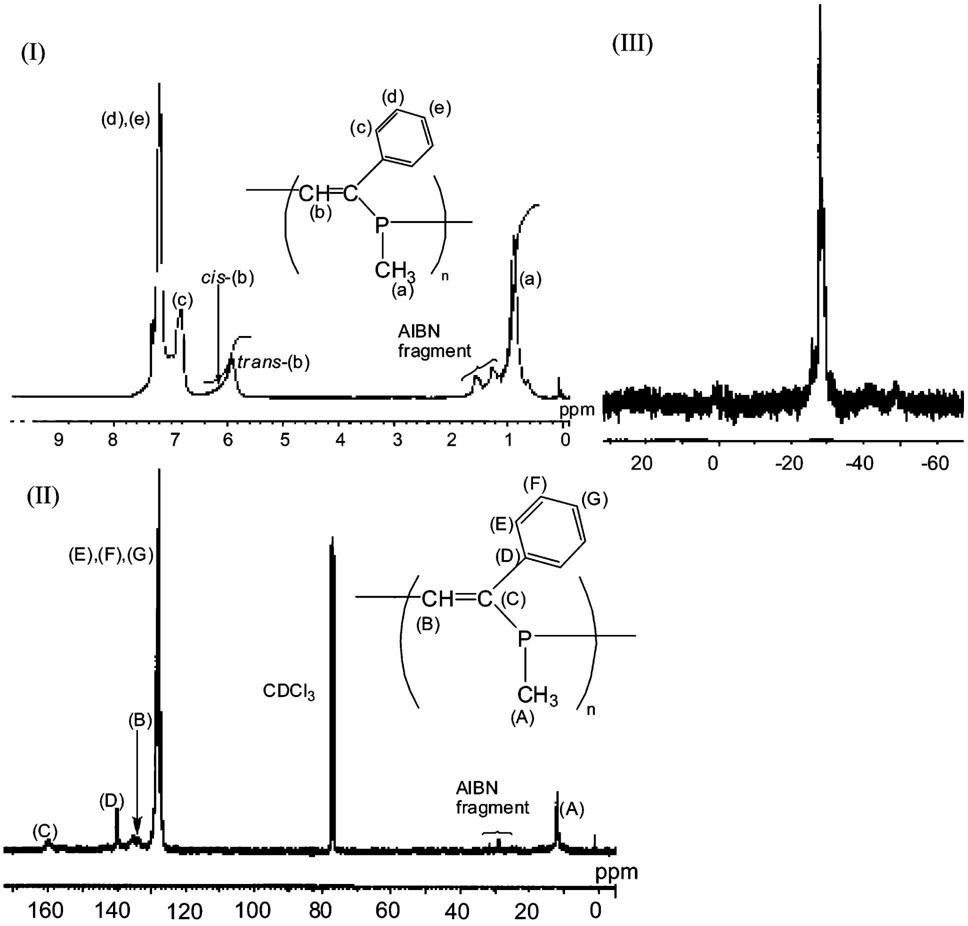
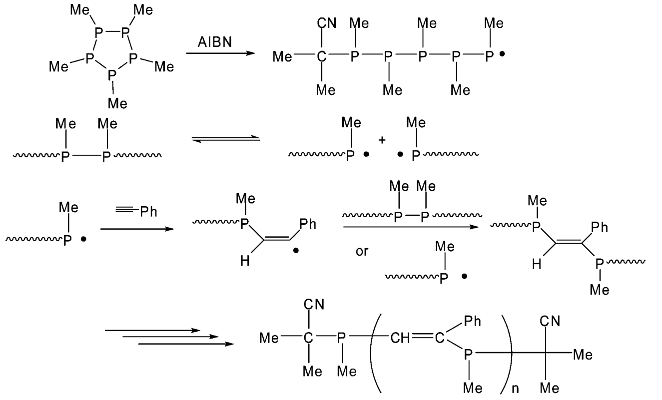


Figure 1. (I) ^{1}H, (II) ^{13}C, and (III) ^{31}P NMR spectra of polymer **2** in CDCl$_3$.

Scheme 4



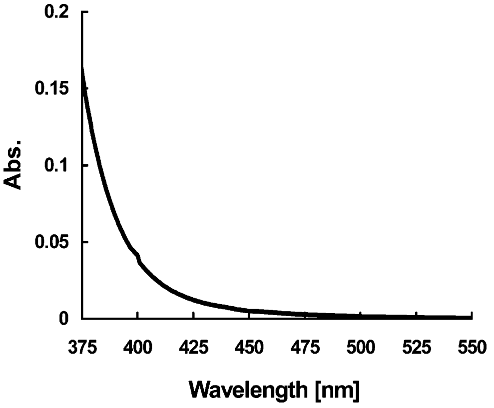


Figure 2. UV−vis absorption spectrum of **2** in CHCl$_3$ at room temperature.

phosphorus bond of *cyclo*-(MeP)$_5$ to produce an open-chain phosphorus oligomer with phosphorus radical. Once the ring structure of *cyclo*-(MeP)$_5$ was collapsed by isobutyronitrile radical or other phosphorus radical, the spontaneous cleavage of the phosphorus−phosphorus bond occurred to yield phosphorus radicals. The provided phosphorus radical attacked the ethynyl group to produce a vinyl radical, which reacted immediately with the phosphorus radical or the phosphorus−phosphorus bond to result in the formation of a new carbon−phosphorus bond. During the copolymerization, the phosphorus radical with the isobutyronitrile group acted as an end-capping agent. Since the vinyl radicals are less stable than the phosphorus radicals, they might immediately reacted with the phosphorus−phosphorus bond or the phosphorus radical to form the C=C−P unit. Thus, no C=C−C=C moieties in the backbone would be formed. The obtained copolymer **2** had no phosphorus−phosphorus bonds in the main chain since the cleavage of the phosphorus−phosphorus bonds occurs to generate the phosphorus radical because of the instability of the phosphorus−phosphorus bond in a linear chain.

The electronic structure of polymer **2** was investigated by using UV−vis spectroscopy (Figure 2). Figure 2 shows strong absorption in the UV region which comes from the $\pi-\pi^*$ transition of the benzene ring. Although no obvious peak is observed in the visible region, the lower energy absorption edge is located at around 480 nm. The absorption in the visible region is derived from n$-\pi^*$ transition in the main chain as seen in the case of poly(phenylene−phosphine)s.[16]

When a diluted chloroform solution of polymer **2** was excited at 430 nm, the emission was observed in the visible blue-green

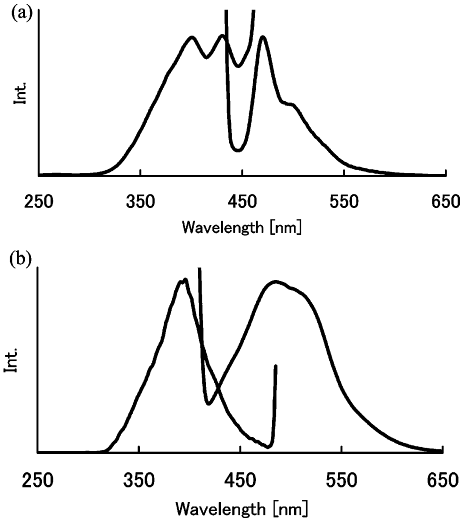
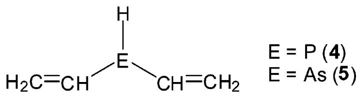


Figure 3. (a) Emission (right) (excited at 430 nm) and excitation (left line) (emitted at 470 nm) spectra of **2**. (b) Emission (right line) (excited at 400 nm) and excitation (left line) (emitted at 485 nm) spectra of **3**. All measurements were carried out in chloroform at room temperature.

Chart 1



region with a peak at 470 nm and a shoulder peak at 500 nm (Figure 3). In the excitation spectrum of **2** monitored at 470 nm, the absorption peak was not observed in the UV region but in the visible region with two peaks at 400 and 430 nm. The absorption of **2** in the UV region and the absorption in the visible region originate from the $\pi-\pi^*$ transition and the $n-\pi^*$ transition, respectively. When the dilute chloroform solution was irradiated at 400 nm, the same spectrum as in Figure 3a was observed. The emission of **2** results from only the absorption of the $n-\pi^*$ transition. The methyl-substituted poly(vinylene−arsine) (**3**), the arsenic analogue of **2**, also exhibited a blue-green emission by excitation at 400 nm (Figure 3b). The excitation spectrum of **3** showed a peak at 396 nm. It is assumed that the bathochromic shift observed in the excitation spectrum of **2** compared with that of **3** is attributed to the conformation of phosphorus or arsenic atom in the main chain. A calculation using the PM3 Hamiltonian suggested that the bond angle C−E−C in divinylphosphine **4** is larger than that in the arsenic analogue **5** (Chart 1).[22] This leads to the assumption that **2** should take a more linear conformation than **3**, inducing a more effective delocalization along the main chain. The s-character of the lone pair on a phosphorus atom is weaker than that of an arsenic atom. This might lead to increase delocalization between the lone pair electron and the π electon of the vinylene unit.

Summary

The poly(vinylene−phosphine) was synthesized by ring-collapsed radical alternating copolymerization (RCRAC) of *cyclo*-$(MeP)_5$ with phenylacetylene (**1a**). The experiments with other electron-withdrawing acetylenes showed that the phosphorus radical or the phosphorus−phosphorus bond has less capture ability of the carbon radical than the arsenic analogues. The obtained polymer **2** exhibited emission attributed to the $n-\pi^*$ transition in the main chain.

Experimental Section

Materials. Unless otherwise noted, all reagents and chemicals were purchased and used without further purification. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. Phenylacetylene (**1a**) and dimethyl acetylenedicarboxylate (**1c**) were distilled before use. 4-Cyanophenylacetylene (**1b**),[24,25] pentamethylcyclopentaphosphine (*cyclo*-$(MeP)_5$),[20] and pentaphenylcyclopentaphosphine (*cyclo*-$(PhP)_5$)[20] were synthesized using literature procedures.

Equipment. All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using Schlenk techniques. ^1H, ^{13}C, and ^{31}P NMR spectra were obtained using a JEOL JNM-EX270 instrument (270 and 67.5 MHz) for solutions in $CDCl_3$ and were referenced to $SiMe_4$ (TMS) or H_3PO_4. Gel permeation chromatography (GPC) was carried out on a TOSOH UV-8011 and RI-8000 (Shodex K-803L column) using $CHCl_3$ as an eluent after calibration with standard polystyrene. The UV−vis spectrum was obtained on a JASCO V-530 spectrometer. Photoluminescence spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer.

Polymerization. Under a nitrogen atmosphere, a benzene solution of 2,2′-azobis(isobutyronitrile) (AIBN) (30 mg, 0.18 mmol) was added to a refluxing solution of *cyclo*-$(MeP)_5$ (0.529 g, 2.29 mmol) and **1a** (1.17 g, 11.5 mmol) in benzene (4.0 mL). After stirring for 8 h, the reaction mixture was poured into *n*-hexane to precipitate a polymeric material. The resulting polymer was purified by reprecipitation into *n*-hexane three times and freeze-dried for 10 h to yield the corresponding poly(vinylene−phosphine) (**2**) as a bright yellow powder (0.78 g, 46% yield). ^1H NMR (δ in $CDCl_3$, ppm): 7.12 (m, p-H_{Ar}), 6.75 (o-H_{Ar}), 5.83 ($C{=}CH$), 0.80 ($P-CH_3$). ^{13}C NMR (δ in $CDCl_3$, ppm): 159.5 ($C{=}CH$), 139.8 ($C_{Ar}-C$), 136−133 ($C{=}CH$), 130−126 (C_{Ar}), 11.9 ($P-CH_3$). ^{31}P NMR (δ in $CDCl_3$, ppm): −28.5.

Sulfuration of 2. A solution of **2** (0.30 g, 2.0 mmol) in dichloromethane (20 mL) was added to a suspension of S_8 (0.15 g, 0.58 mmol) in dichloromethane (10 mL). The suspension was stirred for 48 h, and then the excess sulfur was removed by filtration. The solvent was distilled away, and the obtained polymer was analyzed by ^{31}P NMR spectroscopy. ^{31}P NMR (δ in $CDCl_3$, ppm): 39.8; $M_n = 2350$, $M_w = 3800$.

Acknowledgment. We thank the 21st century COE program, COE for a United Approach to New Material Science, for supporting this work.

References and Notes

(1) For example: (a) Mannars, I. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1603−1621. (b) Mannars, I. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 179−191. (c) Gates, D. P. *Annu. Rep. Prog. Chem., Sect. A* **2003**, *99*, 453−466. (d) Turner, M. L. *Annu. Rep. Prog. Chem., Sect. A* **2000**, *96*, 491−503. (e) *Inorganic Polymers*, 2nd ed.; Mark, J. K., Allcock, H. R., West, R., Eds.; Oxford University Press: New York, 2005.

(2) For example: (a) Sundararaman, A.; Victor, M.; Varughese, R.; Jäkle, F. *J. Am. Chem. Soc.* **2005**, *127*, 13748−13749. (b) Jin, Z.; Lucht, B. L. *J. Am. Chem. Soc.* **2005**, *127*, 5586−5595. (c) Smith, R. C.; Prorasiewicz, J. D. *J. Am. Chem. Soc.* **2004**, *126*, 2268−2269. (d) Tsang, C. W.; Yam, M.; Gates, D. P. *J. Am. Chem. Soc.* **2003**, *125*, 1480−1481. (e) Wright, V. A.; Gates, D. P. *Angew. Chem., Int. Ed.* **2002**, *41*, 2389−2392.

(3) For example: (a) Sasamori, T.; Takeda, N.; Tokitoh, N. *J. Phys. Org. Chem.* **2003**, *16*, 450−462. (b) Sasamori, T.; Arai, Y.; Takeda, N.; Okazaki, R.; Furukawa, Y.; Kimura, M.; Nagase, S.; Tokitoh, N. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 661−675. (c) Lee, V. Y.; Sekiguchi, A. *Organometallics* **2004**, *23*, 2822−2834. (d) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463−3504. (e) Weber, L. *Chem. Rev.* **1992**, *92*, 1839−1906. (f) West, R. *Angew. Chem.* **1987**, *99*, 1231−1241.

(4) For example: (a) *Siloxane Polymers*; Semlyen, J. A., Cjarson, S. J., Eds.; Prentice Hall: Englewood Cliffs, NJ, 1991. (b) *Silicon and Silicones*; Rochow, E. G., Ed.; Springer: Heidelberg, 1987.

(5) For example: (a) Allcock, H. R. *Chem. Eng. News* **1985**, *63*, 22−36. (b) Allcock, H. R. *J. Inorg. Organomet. Polym.* **1992**, *2*, 197−211. (c) *Chemistry and Applications of Polyphosphazenes*; Allcock, H. R., Eds.; John Wiley and Sons: New York, 2003.

(6) For example: (a) Weyenberg, D. R.; Nelson, L. E. *J. Org. Chem.* **1965**, *30*, 2618−2621. (b) Cundy, C. S.; Eaborn, C.; Lappert, M. F. *J. Organomet. Chem.* **1972**, *44*, 291−297.

(7) Vanderark, L. A.; Clark, T. J.; Rivard, E.; Manners, I.; Chris Slootweg, J.; Lammertsma, K. *Chem. Commun.* **2006**, 3332−3333.

(8) Reddy, N. P.; Yamashita, H.; Tanaka, M. *J. Am. Chem. Soc.* **1992**, *114*, 6596−6597.

(9) (a) Baudler, M.; Glinka, K. In *The Chemistry of Inorganic Homo- and Heterocycles*; Haiduc, I., Sowerby, D. B., Eds.; Academic Press: London, 1987; Vol. 2, p 423. (b) Baudler, M. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 492−512. (c) Maier, L. In *Organic Phosphorus Compounds*; Kosolapoff, G. M., Maier, L., Eds.; Wiley-Interscience: New York, 1972; Vol. 1, p 339.

(10) Schmidt, U.; Boie, I.; Osterroht, C.; Schoer, R.; Grutzmacher, H.-F. *Chem. Ber.* **1968**, *101*, 1381−1397.

(11) (a) Naka, K.; Umeyama, T.; Chujo, Y. *J. Am. Chem. Soc.* **2002**, *124*, 6600−6603. (b) Umeyama, T.; Naka, K.; Nakahashi, A.; Chujo, Y. *Macromolecules* **2004**, *37*, 1271−1275. (c) Naka, K.; Nakahashi, A.; Chujo, Y. *Macromolecules* **2006**, *39*, 8257−8262.

(12) Tzschach, A.; Baensch, S. *J. Prakt. Chem.* **1971**, *313*, 254−258.

(13) Henderson, W. A.; Epstein, J. M.; Seichter, F. S. *J. Am. Chem. Soc.* **1963**, *85*, 2462−2466.

(14) DuPont, T. J.; Mills, J. L. *Inorg. Chem.* **1973**, *12*, 2487−2489.

(15) Weiner, M. A.; Pasternack, G. *J. Org. Chem.* **1967**, *32*, 3707−3709.

(16) (a) Tsang, C.-W.; Yam, M.; Gates, D. P. *J. Am. Chem. Soc.* **2003**, *125*, 1480−1481. (b) Dorn, H.; Rodezno, J. M.; Brunnhöfer, B.; Rivard, E.; Massey, J. A.; Mannars, I. *Macromolecules* **2003**, *36*, 291−297. (c) Dorn, H.; Singh, R. A.; Massey, J. A.; Nelson, J. M.; Jaska, C. A.; Lough, A. J.; Mannars, I. *J. Am. Chem. Soc.* **2000**, *122*, 6669−6678.

(17) For example: (a) Morisaki, Y.; Aiki, Y.; Chujo, Y. *Macromolecules* **2003**, *36*, 2594−2597. (b) Mao, S. S. H.; Tilley, T. D. *Macromolecules* **1997**, *30*, 5566−5569. (c) Deschamps, E.; Ricard, F.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1158−1161.

(18) (a) Lucht, B. L.; St. Onge, N. O. *Chem. Commun.* **2000**, 2097−2098. (b) Lucht, B. L.; St. Onge, N. O. *J. Organomet. Chem.* **2002**, *653*, 167−176.

(19) (a) Weight, V. A.; Gates, D. P. *Angew. Chem., Int. Ed.* **2002**, *41*, 2389−2392. (b) Smith, R. C.; Chen, X.; Protasiewicz, J. D. *Inorg. Chem.* **2003**, *42*, 5468−5470. (c) Smith, R. C.; Protasiewicz, J. D. *Eur. J. Inorg. Chem.* **2004**, *126*, 998−1006. (d) Weight, V. A.; Patrick, B. O.; Schneider, C.; Gates, D. P. *J. Am. Chem. Soc.* **2006**, *128*, 8836−8844. (e) Smith, R. C.; Protasiewicz, J. D. *J. Am. Chem. Soc.* **2004**, *126*, 2268−2269.

(20) Baudler, M.; Hammerström, K. *Z. Naturforsch.* **1965**, *B20*, 810−811.

(21) Umeyama, T.; Naka, K.; Chujo, Y. *Macromolecules* **2004**, *37*, 5952−5958.

(22) The angle C−P−C (**3**) = 101.227°, and the angle C−As−C (**4**) = 99.671°. Calculated by use of the Spartan Package; Wavefunction, Inc., Irvin, CA. The molecular orbital surfaces were created after calculation of geometry optimization by the PM3 semiempirical molecular orbital method.

(23) Nagase, S. *The Chemistry of Organic Arsenic, Antimony and Bismuth Compounds*; Patai, S., Ed.; John Wiley & Sons: Chichester, UK, 1994; p 8. Inversion barriers calculated for MH_3 (M = P, As) at several levels of theory are listed here.

(24) Takahashi, S.; Sonogashira, K.; Higahara, N. *Synthesis* **1980**, 627−630.

(25) Moroni, M.; Lemoigne, J.; Luzzati, S. *Macromolecules* **1994**, *27*, 562−571.

MA0702795