J|A|C|S
ARTICLES

Synthesis of Poly(vinylene-arsine)s: Alternating Radical Copolymerization of Arsenic Atomic Biradical Equivalent and Phenylacetylene

Kensuke Naka,* Tomokazu Umeyama, and Yoshiki Chujo*

Contribution from the Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan

Received April 17, 2002

Abstract: Novel organoarsenic polymers, poly(vinylene-arsine)s, were synthesized by a free-radical alternating copolymerization of phenylacetylene with cyclooligoarsines as an atomic biradical equivalent. The polymerization between pentamethylpentacycloarsine (**1a**) or hexaphenylhexacycloarsine (**1b**) with phenylacetylene (**2**) in the presence of a catalytic amount of AIBN (in benzene; refluxing; for 12 h) gave the corresponding poly(vinylene-arsine)s. The obtained polymers were soluble in common organic solvents such as THF, chloroform, and benzene. From gel permeation chromatographic analysis (chloroform, PSt standards), the number-average molecular weights of the polymers from **1a** and **1b** were found to be 11500 and 3900, respectively. The structures of the polymers were supported by ^{1}H and ^{13}C NMR spectroscopies. The corresponding polymer was also obtained by irradiation of a benzene solution of **1a** and **2** with xenon lamp at room temperature. After the polymer from **1a** was stirred vigorously with 30% H_2O_2, the ^{1}H NMR spectrum of the polymer showed the methyl proton that was assigned to As(III)-Me, suggesting the insensitivity of the trivalent state arsenic in the main chain to the oxidation. The structures and the molecular weights of the polymers were insensitive to the feed ratio of the monomers. This result indicates that the addition of the arsenic radical to phenylacetylene was a rate-determining step in the copolymerization.

Introduction

To develop new polymerization methods for heteroatom-containing unsaturated polymers is of considerable interest because such polymers show unusual properties. Among various types of such polymers, the simplest one is heteroatom-containing polyvinylenes, of which properties might be attractive. However, no example of these polymers has been reported except poly(vinylene-sulfide),[1] because of synthetic difficulties. In this report, we describe a synthesis of poly(vinylene-arsine)s by a radical alternating copolymerization of phenylacetylene and cyclooligoarsines.[2]

Inorganic polymers or oligomers are known whose chains or ring skeletons are made up of only one inorganic element[2] such as silicon, germanium, phosphorus, arsenic, sulfur, and selenium. These compounds often occur homolysis of element−element bonds by stimulation such as light and heat.[3] We speculated that heteroatom-including polyvinylenes would be obtained by a radical copolymerization if atomic biradicals of the inorganic element obtained by the homolytic cleavage add to acetylenic compounds, and obtained biradical adducts couple in a head-to-tail manner (Scheme 1). On the basis of this concept, we first chose organoarsenic ring compounds, cyclooligoarsines,[4] as inorganic oligomers. Cyclooligoarsines are prepared quite easily by reduction of the corresponding arsonic acids or their salts with hypophosphorus acid. It is known that a methyl-substituted cyclooligoarsine is a five-membered ring and a phenyl-substituted one is a six-membered ring, because these ring structures are quite stable compared to other ring structures. Although a large number of studies have been made on the structural chemistry of cyclooligoarsines and their transition-metal complexes,[5] no radical reactions of cyclooligoarsines have been reported.[6] Here, we regarded cyclooligoarsines as monomers to prepare poly(vinylene-arsine)s by radical copolymerization. It should be noted that this is the first soluble polymer containing arsenic atoms in the main chain.

Results and Discussion

A typical polymerization procedure was conducted as follows (Scheme 2). Under a nitrogen atmosphere, a benzene solution

---

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

(1) (a) Ikeda, Y.; Ozaki, M.; Arakawa, T. *J. Chem. Soc., Chem. Commun.* **1983**, *24*, 1518. (b) Ikeda, Y.; Ozaki, M.; Arakawa, T.; Takahashi, A.; Kambara, S. *Polym. Commun.* **1984**, *25*, 79. (c) Ikeda, Y.; Ozaki, M.; Arakawa, T. *Mol. Cryst. Liq. Cryst.* **1985**, *118*, 431.

(2) We already reported the preliminary results. See: Umeyama, T.; Naka, K.; Chujo, Y. *5th Pacific Polymer Conference, Oaxaca* ***2001***, 17.

(3) *The Chemistry of Inorganic Homo- and Heterocycles*; Sowerby, D. B., Haidu, I., Eds.; Academic Press: London, UK, 1987.

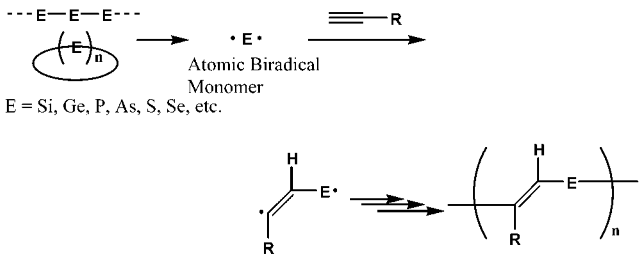
(4) For example: (a) Breunig, H. J. In *The Chemistry of Organic arsenic, Antimony and Bismuth Compounds*; Patai, S., Ed.; John Wiley & Sons: Chichester, UK, 1994; p 563. (b) Haiduc, I.; Sowerby, D. B. *The Chemistry of Inorganic Homo- and Heterocycles*; Sowerby, D. B., Haidu, I., Eds.; Academic Press: London, UK, 1987; Vol. 2, p 701. (c) Smith, L. R.; Mills, J. L. *J. Organomet. Chem.* **1975**, *84*, 1.

(5) DiMaio, A.-J.; Rheingold, A. L. *Chem. Rev.* **1990**, *90*, 169.

(6) There are a few reports on radical reactions of diarsenic compounds (R_2-As-AsR_2), see: (a) Tzschach, A.; Baensch, S. *J. Prakt. Chem.* **1971**, *313*, 254. (b) Gynane, M. J. S.; Hudson, A.; Lappert, M. F.; Power, P. P.; Goldwhite, H. *J. Chem. Soc., Dalton Trans.* **1980**, 2428. (c) Hitchcock, P. B.; Lappert, M. F.; Smith, S. J. *J. Organomet. Chem.* **1987**, *320*, C27.

10.1021/ja026578l CCC: $22.00 © 2002 American Chemical Society

Scheme 1



Scheme 2

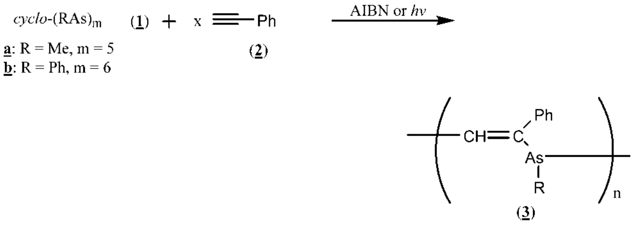


Table 1. Results of Polymerization

run	1	x^b	initiator	M_w^c	M_n^c	M_w/M_n^c	yield (%)[d]
1	*cyclo*-(AsMe)$_5$ (**1a**)	5.0	AIBN[e]	48700	11500	4.3	46
2	*cyclo*-(AsMe)$_5$ (**1a**)	5.0	*hν*[f]	11100	3400	3.3	48
3	*cyclo*-(AsPh)$_6$ (**1b**)	6.0	AIBN[e]	5600	3900	1.4	35
4	*cyclo*-(AsPh)$_6$ (**1b**)	6.0	*hν*[f]		no polymer		
5	*cyclo*-(AsPh)$_6$ (**1b**)	3.0	AIBN[e]	5000	3500	1.4	34[g]
6	*cyclo*-(AsPh)$_6$ (**1b**)	1.0	AIBN[e]	5600	3800	1.5	trace
7	*cyclo*-(AsPh)$_6$ (**1b**)	12.0	AIBN[e]	7300	4100	1.8	17[g]

[a] Runs 1 and 3: in benzene at 350 K. Runs 2 and 4: in benzene at room temperature. [b] Molar ratio of **2** to **1**. [c] GPC (CHCl$_3$). Polystyrene standards. [d] Isolated yields after reprecipitation into *n*-hexane. [e] 3 mol % of AIBN was employed. [f] Xenon lamp. [g] Based on the molar amount of ***2***.

of a catalytic amount of 2,2′-azobisisobutyronitrile (AIBN) was added to a refluxing solution of pentamethylpentacycloarsine (**1a**) and phenylacetylene (**2**) in benzene. After being stirred for 12 h, the reaction mixture was poured into *n*-hexane to precipitate the product, which was purified three times by reprecipitation from benzene to *n*-hexane. After freeze-drying for 10 h, polymer **3a** was obtained as a bright-yellow powder. From gel permeation chromatographic analysis (CHCl$_3$, PSt standards), the number-average molecular weight of **3a** was estimated to be 11 500 (Table 1). In the case of using hexaphenylhexacycloarsine (**1b**) instead of **1a**, corresponding poly(vinylene-arsine) (**3b**) was obtained as a white powder. The relatively low yields are due to removal of low molecular weight products by reprecipitation. Both polymers were readily soluble in common organic solvents such as THF, chloroform, and benzene.

Structural characterization of the polymers was provided by ^{1}H and ^{13}C NMR spectroscopies.[7] In the ^{1}H NMR spectrum of **3a** (Figure 1), the integral ratio of two peaks in a vinyl region (6.1 to 6.4 ppm) confirmed that the trans isomer was predominantly obtained.[5a] From the peak area ratio of an aromatic (6.6 to 7.5 ppm) and a methyl region in the ^{1}H NMR and the elemental analysis, a copolymer composition of **3a** was nearly 1:1 (phenylacetylene:methylarsine). Analysis of **3a** by ^{13}C NMR spectroscopy (Figure 2) showed only one sharp resonance for the methyl carbon at 11.6 ppm, suggesting that the arsenic in **3a** existed in a trivalent state and no arsenic−arsenic bond or no oxidized arsenic was present.[8,9] These results revealed that the copolymerization proceeded alternatingly. After **3a** was stirred vigorously with 30% H$_2$O$_2$ at 60 °C for 3 h, the ^{1}H NMR spectrum and the GPC curve of **3a** were the same as those for the starting polymer. These results suggest that the trivalent state of arsenic in the main chain was insensitive to the oxidation.

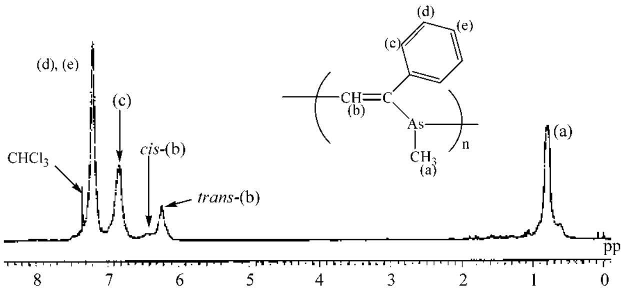


Figure 1. ^{1}H NMR spectrum of **3a** in CDCl$_3$.

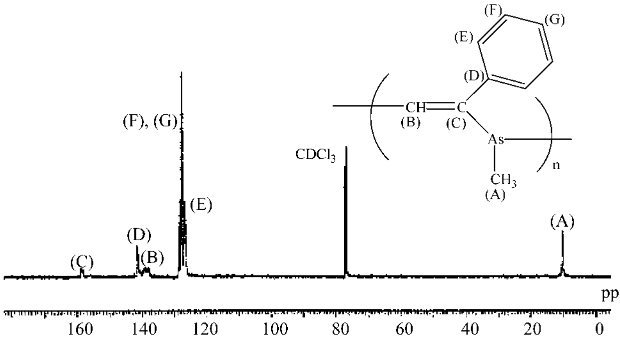


Figure 2. ^{13}C NMR spectrum of **3a** in CDCl$_3$.

After purification of polymer **3b** by reprecipitation into *n*-hexane, the soluble part in *n*-hexane was investigated by GPC and ^{1}H NMR. It contained only low molecular weight materials by GPC. The ^{1}H NMR spectrum showed many peaks assigned to aromatic protons and a small broaden peak of the vinyl proton. These results suggested that the *n*-hexane soluble part was mainly residual cyclooligoarsines and a small amount of low molecular weight oligomers. The consumption of **2** under the copolymerization conditions with **1b** was monitored by gas chromatography. The limit of the consumption of **2** was about 80%.

Polymer **3a** was also obtained by irradiation of a benzene solution of **1a** and **2** with a xenon lamp at room temperature (Table 1, Run 2). In Run 4 where we employed **3b** and a xenon lamp, however, no polymer was obtained. In contrast to the case with **1a**, the reaction mixture of Run 4 was heterogeneous because of the poor solubility of **1b** at room temperature. Effective reaction did not proceed under heterogeneous conditions.

We propose here that the radical alternating copolymerization proceeds via the following pathways (Scheme 3). First, AIBN or light cleaved the arsenic−arsenic bond of the cyclooligoarsines to produce arsenic radicals. Second, the homolysis of the

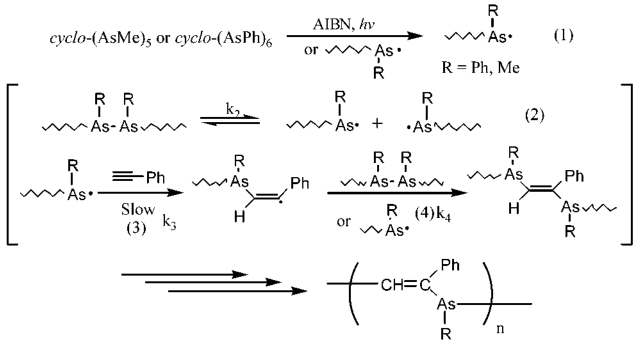
---

(7) The assignments of the peaks in the ^{1}H and ^{13}C NMR spectra for **3a** and **3b** were supported by the DEPT spectrum and ^{1}H−^{13}C COSY. See the Supporting Information.

(8) Elmes, P. S.; Middleton, S.; West, B. O. *Aust. J. Chem.* **1970**, *23*, 1559.

(9) (a) Borner, G. M.; Gagnon, C.; Whittern, D. N. *J. Organomet. Chem.* **1983**, *243*, 305. (b) Armstrong, R. S.; Aroney, M. J.; Le Fèvre, R. J. W.; Pierens, R. K.; Saxby, J. D.; Wilkins, C. J. *J. Chem. Soc. (A)* **1969**, 2735.

Scheme 3



other arsenic−arsenic bonds proceeded spontaneously due to their instability by the destruction of the quite stable five- or six-membered-ring structure. In competition with this reaction, the arsenic radical added to phenylacetylene to give a vinyl radical. Next, the vinyl radical reacted immediately with the arsenic−arsenic bond or with the arsenic radical to form a new carbon−arsenic bond.

To support the proposed mechanism for the polymerization, we carried out several experiments. When a benzene solution of cyclooligoarsine (**1a** or **1b**) and **2** was refluxed in the absence of AIBN or *hν*, the corresponding poly(vinylene-arsine) was not produced. Because of the poor solubility of **1b** in benzene, the mixture of **1b** and benzene was heterogeneous at 78 °C. After 3 mol % of AIBN was added, the mixture became homogeneous in a few tens of minutes. The stable six-membered-ring structure should collapse to form open chain oligoarsines (and atomic biradical arsenic) under reflux conditions with AIBN. When the homogeneous reaction mixture was cooled to room temperature, a large amount of the cyclooligoarsine was reproduced as white precipitates. These results indicate that the structure of **1b** undergoes homolytic cleavage by AIBN to produce arsenic radicals and the resulting arsenic radicals attacked the remaining ring structure. The catalytic amount of AIBN was enough to cleave the arsenic−arsenic bonds. The consumption of **2** monitored by gas chromatography under the copolymerization conditions with **1b** started after the reaction mixture was stirred for several minutes. These results suggest that the tertiary radicals derived from AIBN first reacted with the cyclooligoarsines followed by the reaction of the resulting arsenic radicals to phenylacetylene as shown in Scheme 3.

We carried out the copolymerization in different feed ratios ($x = {}^1/_6$ to12) of the two monomers, **1b** and **2** (Table 1, Runs 5−7). In Run 5, the polymerization with 3 equiv of **2** to **1b** gave a polymer that had almost the same molecular weight and the same structure. The polymerization with an equivalent of **2** to **1b** also gave a polymer with almost the same molecular weight and the same structure. If the rate of the arsenic−arsenic bond cleavage is comparable to the rate of eq 3, some arsenic−arsenic bonds should be included in the polymer structure under the conditions of Run 5 or 6, and the molecular weight of the polymer should be reduced due to labile As−As bonds in the structure during isolation. Thus, the addition rate (k_3) of the arsenic radical to phenylacetylene is much lower than the homolysis rate (k_2) of the arsenic−arsenic bond. When we employed an excess amount of **2**, the copolymer composition and the molecular weight of the polymer obtained were almost the same as those of the polymer obtained in Run 3. If the reaction rate of the vinyl radical to the arsenic is comparable to the rate of formation of the vinyl radical, the resulting copolymer should have more vinylene units than arsenic units in the main chain. Therefore, the addition rate of the vinyl radical toward the arsenic−arsenic bonds or the arsine radicals should be much higher than the rate of eq 3. Thus, the addition reaction (eq 3) should be a rate-determining step in the copolymerization. Due to the fast cleavage of the arsenic−arsenic bonds, the cyclooligoarsines are regarded as atomic biradical equivalents.

The UV−vis absorption spectrum of polymer **3a** in chloroform showed small absorption in the visible region besides strong benzene-ring absorption in the UV region. The lower energy absorption edge was located at 550 nm. We assume that this lower energy absorption results from a delocalized n−π* transition in the main chain.[10] The fluorescence emission spectrum of a dilute chloroform solution of **3a** showed an emission peak at 485 nm. In the excitation spectrum of **3a**, monitored at 485 nm, the absorption peak was observed at 396 nm corresponding to the n−π* transition.

Summary

We have described here the synthesis of novel organoarsenic polymers, poly(vinylene-arsine)s, by the free-radical alternating copolymerization of phenylacetylene with the cyclooligoarsines. This polymerization system should be regarded as a new example of radical alternating copolymerizations. Although further detailed studies on the mechanism of the copolymerization are required, we believe that the present method provides a unique mechanism for designing new heteroatom-containing polymers, especially heteroatom-containing polyvinylenes. We are currently further evaluating physical and chemical properties of the poly(vinylene-arsine)s.

Experimental Section

Materials and Instruments. 2,2′-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Phenylacetylene (**2**) was distilled under reduced pressure. Benzene was dried over CaH_2, distilled, and bubbled with a stream of nitrogen before use. ^{1}H NMR spectra were recorded on a 270 MHz JEOL-JNM-GX270 NMR spectrometer. ^{13}C NMR spectra were recorded on a 67.5 MHz JEOL-JNM-GX270 NMR spectrometer. Gel permeation chromatographic analysis was carried out on a Shodex K-803 with $CHCl_3$ as an eluent after caribration with polystyrene standards.

Cyclooligoarsines. 1a and **1b** were prepared according to refs 8 and 11, respectively. **1a**: ^{1}H NMR (δ, ppm) 1.63, 1.64, 1.67 (lit.[4] 1.62, 1.63, 1.66). **1b**: mp 208−211 °C (lit.[5] mp 204−208 °C).

Polymerization. A typical experimental procedure is as follows. Under a nitrogen atmosphere, a benzene solution (1 mL) of AIBN (0.24 g, 1.5 mmol) was added to a refluxing solution of pentamethylcyclopentaarsine (**1a**) (4.38 g, 9.74 mmol) and phenylacetylene (**2**) (4.96 g, 48.6 mmol) in benzene (30 mL). After being stirred for 12 h, the reaction mixture was poured into *n*-hexane to precipitate the product, which was purified three times by reprecipitation from benzene to *n*-hexane. After freeze-drying for 10 h, the corresponding polymer **3a** was obtained as a bright-yellow powder (4.35 g, 22.6 mmol) in 46% yield.

3a: ^{1}H NMR (δ, ppm) 0.78 (As−CH_3), 6.21 ((*E*)-C═CH), 6.43 ((*Z*)-C═CH), 6.83 (ArH$_o$), 7.19 (ArH$_m$, ArH$_p$). ^{13}C NMR (δ, ppm) 10.7 (As−CH_3), 126.0−129.0 (C_{Ar}H$_o$, C_{Ar}H$_m$, C_{Ar}H$_p$), 137.9−139.7 (C═*C*H),

---

(10) Weiner, M. A.; Pasternack, G. *J. Org. Chem.* **1967**, *32*, 3707.
(11) Reesor, J. W. B.; Wright, G. F. *J. Org. Chem.* **1957**, *22*, 382.

141.4 (C_{Ar}−C), 158.9 (C=CH). Anal. Calcd for $[C_8H_6(CH_3As)_{1.07}]_n$: C, 54.9; H, 4.7. Found: C, 54.3; H, 4.8.

3b: ^{1}H NMR (δ, ppm) 6.24 (C=CH), 6.3−7.6 (ArH). ^{13}C NMR (δ, ppm) 127.7−130.1, 133.7−134.3 (C_{Ar}H), 138.0−139.8 (CH=C), 141.5−142.0 (C−C_{Ar}, As−C_{Ar}), 161.1 (CH=C). Anal. Calcd for $[C_8H_6(C_6H_5As)_{1.2}]_n$: C, 64.2; H, 4.3. Found: C, 63.3; H, 4.3.

Supporting Information Available: Characterization of **3a** and **3b** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA026578L