# Spontaneous Ring-Collapsed Alternating Copolymerization of a Homocyclic Arsenic Compound and Phenylacetylene

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ABSTRACT: Without any added catalyst or radical initiator at 25 °C, *cyclo*-$(MeAs)_5$ caused cleavage of the arsenic−arsenic bond spontaneously and copolymerized with phenylacetylene (PA) in chloroform to give a novel organoarsenic polymer having a methylarsine (MeAs) unit and a vinylbenzene unit alternating in the main chain, $-[AsMe-CH{=}CPh]_n-$. The rate of monomer consumption during the copolymerization was followed by a gas chromatography (GC) analysis, and the increase of the molecular weight of the resulting copolymer was monitored by GPC measurement. These analyses revealed that this system was step-reaction polymerization. The consumption of PA during the copolymerization with *cyclo*-$(MeAs)_5$ using AIBN was much faster as compared to the case without AIBN.

## Introduction

Many monomers which are reluctant to homopolymerize are often found to be capable of undergoing rapid copolymerization reactions with one another.[1] If a strong electron-donating monomer and a strong electron acceptor, such as *p*-methoxystyrene and maleic anhydride, are mixed together, a regular alternating copolymer is formed either by spontaneous initiation or more commonly in the presence of radical initiator, UV, or $\gamma$ radiation. The mechanism to regulate the comonomer sequence alternatingly is roughly divided into two models: the terminal model and the complex mechanism. In the terminal model, the copolymerization is dominated by the cross reactions of free monomers caused by differences either in polarity or charge-transfer reactions between the growing radical and the incoming comonomer. No free monomers are required in the complex mechanism, and the chain is propagated by the “head-to-tail” homopolymerization of the charge-transfer complex (CTC) of the donor−acceptor monomer pair. In practice, however, as neither mechanism is completely satisfactory, alternative approaches, which consider the simultaneous propagation through free monomers and the CTC, have gained favor. As an exception to the two models, Kobayashi et al. reported the copolymerization which yielded the polymer having a tetravalent germanium unit and a *p*-hydroquinone unit alternatingly in the main chain by utilizing germylenes and *p*-benzoquinone derivatives.[2] By this copolymerization system, they introduced a new concept of “oxidation−reduction alternating copolymerization” where a germylene acts as a reductant monomer and a *p*-benzoquinone derivative behaves as an oxidant monomer.

Recently, in a series of our work to develop polymerization methods which produce novel polymers containing main-group elements in the backbone,[3] we reported the synthesis of poly(vinylene-arsine)s by a radical reaction between cyclic organoarsenic compound, such as pentamethylcyclopentaarsine (*cyclo*-$(MeAs)_5$) or hexaphenylcyclohexaarsine (*cyclo*-$(PhAs)_6$), and phenylacetylene (PA) using 2,2′-azobisisobutyronitrile (AIBN) as a radical initiator (Scheme 1).[4] This is a novel type of radical alternating copolymerization, in which the arsenic ring compound fell into pieces and the arsenic unit was incorporated into the polymer backbone with no arsenic−arsenic bonds. Therefore, we have named this copolymerization system “ring-collapsed radical alternating copolymerization (*RCRAC*)”. The obtained poly(vinylene-arsine) is the first example of the soluble polymer containing arsenic atoms in the main chain with well-defined structure. We proposed in the previous paper that this unique alternating copolymerization proceeded as follows (Scheme 2). First, the radical species from AIBN react with the cyclooligoarsine to collapse the ring structure and produce the arsenic radical. Because the arsenic−arsenic bonds in the open-chain oligomer are unstable as compared to those in the ring structure, the homolysis takes place spontaneously. Next, the arsenic radical adds to the ethynyl group of phenylacetylene and the resulting unstable vinyl radical reacts immediately with the arsenic−arsenic bond or arsenic radical to form the carbon−arsenic bond. In this manner, the cleavage of diarsenic linkage and the addition of arsenic radical to phenylacetylene are repeated a number of times consequently to result in the alternating copolymer, poly(vinylene-arsine).

Although the history of the organoarsenic homocycles[5] dates back at least to the synthesis of *cyclo*-$(PhAs)_6$ by Michaelis and Schulte in 1881[6] and the discovery and study of the chemotherapic effects of “Salvarsan” and their derivatives[7] in the early part of the 20th century, only a few reactions of the organoarsenic homocycles with organic compounds[8] have been developed as compared to the extensive studies on the coordination chemistry of them as ligands in transition metal complexes.[9] No radical reactions of the cyclooligoarsines had been reported before our previous study. Re-evaluation the organoarsenic homocycles would open a unique chemistry.

Herein, we report the detail studies of *RCRAC* of the cyclooligoarsines with phenylacetylene as well as the reactivity of the cyclooligoarsines. Although the phenyl-substituted arsenic ring compound showed no reaction with phenylacetylene without AIBN in refluxing benzene, the methyl-substituted arsenic ring is found to react with phenylacetylene in the absence of any radical initiators or catalysts to produce the corresponding poly-

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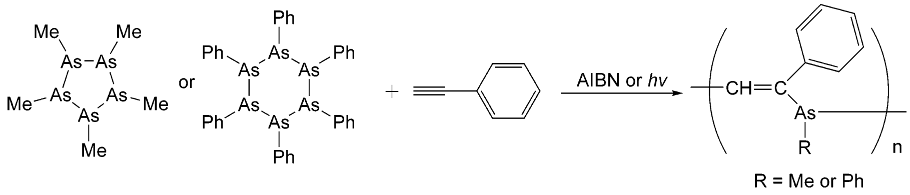
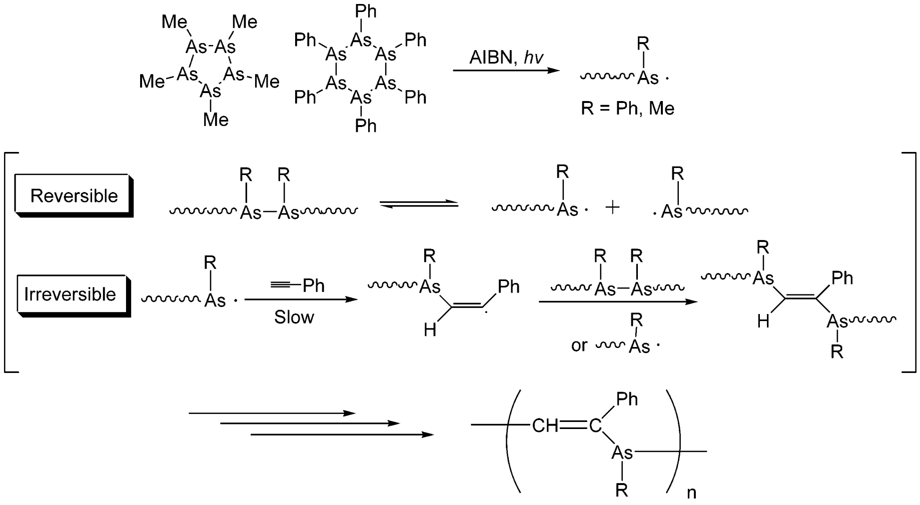
**Scheme 1**



**Scheme 2**



(vinylene-arsine) at 25 °C. The difference of the copolymerization behavior with and without AIBN is also a subject of this report.

## Experimental Section

**Materials.** Unless otherwise noted, all reagents and chemicals were purchased from Wako Pure Chemical Industries, Ltd. Toluene (water < 30 ppm) was bubbled with a stream of nitrogen before use. *n*-Hexane (water < 30 ppm), methanol (water < 50 ppm), and mesitylene were used without further purification. 2,2′-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Phenylacetylene (PA) was purchased from Aldrich and purified by distillation under reduced pressure. Pentamethylcyclopentaarsine (*cyclo*-(MeAs)$_5$)[10] and hexaphenylcyclohexaarsine (*cyclo*-(PhAs)$_6$)[11] were synthesized using literature procedures.

**Equipment.** All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using Schlenk techniques. $^1$H and $^{13}$C NMR spectra were obtained using a JEOL JNM-EX270 instrument (270 and 67.5 MHz, respectively) for solutions in CDCl$_3$ and were referenced to SiMe$_4$ (TMS). 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. Gas chromatography (GC) analyses were carried out on a SHIMADZU GC-17A using helium gas as a carrier gas. Thermogravimetric analysis (TGA) was performed on a TG/DTA6200, Seiko Instruments Inc. at the rate of 10 °C min$^{-1}$. Differential scanning calorimetry (DSC) thermograms were obtained with a DSC200, Seiko Instruments Inc., with a heating rate of 10 °C min$^{-1}$ under nitrogen atmosphere. The analysis of the low molecular weight compounds obtained was carried out on a recycling preparative high-pressure liquid chromatograph (HPLC) (Japan Analytical Industry Co. Ltd., model 918R) equipped with JAIGEL-1H and 2H columns (GPC) using chloroform as an eluent.

**Copolymerization in the Absence of AIBN.** A typical experimental procedure was conducted as follows. To a chloroform solution (3.0 mL) of *cyclo*-(MeAs)$_5$ (0.556 g, 1.24 mmol) was added PA (0.631 g, 6.18 mmol) all at once at room temperature. The reaction mixture was stirred for 12 h and then poured into *n*-hexane to precipitate a polymeric material. After reprecipitation from toluene into *n*-hexane twice, the resulting precipitate was freeze-dried for 10 h. A bright yellow powder was obtained (0.765 g) in 64% yield. $^1$H NMR ($\delta$, ppm): 0.80 (As−CH$_3$), 6.21 ((*E*)-C=CH), 6.43 ((*Z*)-C=CH), 6.81 (ArH$_o$), 7.24 (ArH$_m$, ArH$_p$). $^{13}$C NMR ($\delta$, ppm): 10.3 (As−CH$_3$), 126−129 ($C_{Ar}$H$_o$, $C_{Ar}$H$_m$, $C_{Ar}$H$_p$), 137−140 (C=*C*H), 140.1 ($C_{Ar}$−C), 155−159 (*C*=CH).

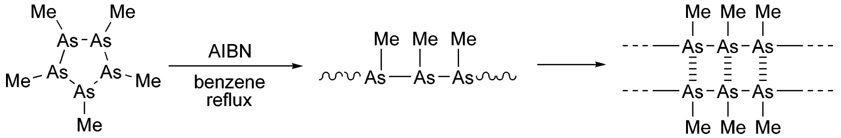
**Copolymerization in the Presence of AIBN.** A typical experimental procedure was conducted as follows. To a chloroform solution (3.0 mL) of *cyclo*-(MeAs)$_5$ (0.549 g, 1.22 mmol) were added AIBN (0.030 g, 0.018 mmol) and PA (0.623 g, 6.10 mmol) at room temperature. The mixture was stirred at 60 °C for 2 h and then poured into *n*-hexane to precipitate the polymeric material. After reprecipitation from toluene into *n*-hexane twice, the resulting precipitate was freeze-dried for 10 h. A bright yellow powder was obtained (0.588 g) in 50% yield. The $^1$H and $^{13}$C NMR spectra of the resulting polymer were identical to those of the copolymer obtained without AIBN.

**Emulsion Polymerization.** The reaction mixture of water (10.0 mL), *cyclo*-(MeAs)$_5$ (2.45 g, 5.44 mmol), PA (2.78 g, 27.2 mmol), sodium lauryl sulfate (0.5 g), and potassium peroxodisulfate (0.05 g) was stirred vigorously under a nitrogen atmosphere for 8 h at 80 °C. The mixture was then poured into methanol, and the precipitate was washed by methanol. The obtained polymer was purified by reprecipitation into *n*-hexane three times and freeze-dried for 10 h to yield the corresponding poly(vinylene-arsine) as a bright yellow powder (1.42 g, 27% yield). The $^1$H and $^{13}$C NMR spectra of the resulting polymer were identical to those of the copolymer obtained above.

**Stability of the Methyl-Substituted Poly(vinylene-arsine).** A chloroform solution (10 mL) of the methyl-substituted poly(vinylene-arsine) (0.54 g) was stirred for 24 h at 50 °C. During the stirring, a small amount of the solution was siphoned, diluted with chloroform, and analyzed by GPC, suggesting no decrease of the molecular weight. The $^1$H NMR spectrum of the polymer recovered after the stirring was identical to that of the starting polymer.

**GC Analysis of the Reaction Mixture during the Copolymerization without AIBN.** To a toluene solution (2.0 mL) of PA (0.623 g, 6.09 mmol) and mesitylene (0.50 mL) was

**Scheme 3**



added a toluene solution (0.50 mL) of *cyclo*-(MeAs)$_5$ (0.548 g, 1.22 mmol) all at once at 60 °C. The moment of the addition was defined as the start time of the copolymerization. During the copolymerization, a small amount of the reaction mixture was siphoned, diluted with chloroform, and analyzed by GC. The consumption rate of PA was calculated from the peak area ratio of PA and mesitylene.

**GC Analysis of the Reaction Mixture during the Copolymerization with AIBN.** To a toluene solution (1.0 mL) of *cyclo*-(MeAs)$_5$ (0.553 g, 1.23 mmol) and mesitylene (0.50 mL) was added a toluene solution (1.5 mL) of PA (0.628 g, 6.15 mmol) and AIBN (0.030 g, 0.018 mmol) all at once at 60 °C. The GC analysis was carried out as described above.

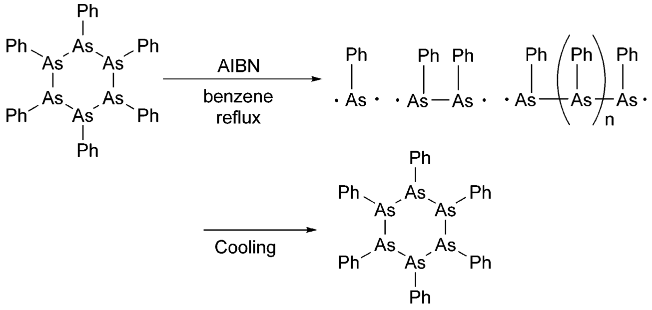
**GPC Analysis of the Reaction Mixture during the Copolymerization without AIBN.** To a chloroform solution (3.0 mL) of *cyclo*-(MeAs)$_5$ (0.563 g, 1.25 mmol) was added PA (0.639 g, 6.26 mmol) all at once, and then it was stirred at room temperature. The moment of the addition was defined as the start time of the copolymerization. During the copolymerization, a small amount of the reaction mixture was siphoned, diluted with chloroform, and analyzed by GPC.

**GPC Analysis of the Reaction Mixture during the Copolymerization with AIBN.** To a chloroform solution (1.0 mL) of *cyclo*-(MeAs)$_5$ (0.566 g, 1.26 mmol) was added a chloroform solution (2.0 mL) of PA (0.643 g, 6.29 mmol) and AIBN (0.030 g, 0.018 mmol) at 50 °C. The GPC analysis was carried out as described above.

## Results and Discussion

**Synthesis and Reactions of Cyclooligoarsines.** To examine the copolymerization mechanism, especially the spontaneous cleavage of the arsenic−arsenic bonds of the cyclooligoarsines, we discuss here the formation and reactions of the cyclooligoarsines. The methyl-substituted cyclooligoarsine, *cyclo*-(MeAs)$_5$, was synthesized by the reduction of sodium methylarsonate with hypophosphorus acid.[10] The five-membered arsenic ring was obtained exclusively, suggesting that this ring structure is stable as compared to other forms containing arsenic−arsenic bonds. The obtained *cyclo*-(MeAs)$_5$ is a yellow liquid with high viscosity. After *cyclo*-(MeAs)$_5$ was left under a nitrogen atmosphere at 25 °C for several days, a purple black precipitate appeared, which could be easily removed by filtration under a nitrogen atmosphere. The resulting precipitate was insoluble in any solvent and fuming in the air and, according to the literature,[12] should be a linear poly(methylarsine) with a ladder structure. The arsenic−arsenic bond of the ring compound was cleaved spontaneously, and then the open-chain oligoarsines stacked with each other to form the ladder structure (Scheme 3). Solutions of *cyclo*-(MeAs)$_5$ in organic solvents such as benzene, toluene, and chloroform also produced the purple-black precipitates after standing at 25 °C for several days. The formation of the precipitate was accelerated by heating in the presence of AIBN or by the irradiation with an incandescent lamp. In these conditions, a large quantity of the precipitate was obtained within a few hours, suggesting that the cleavage of the arsenic−arsenic bonds of *cyclo*-(MeAs)$_5$ was promoted by AIBN or *hν*. The precipitate showed no reaction due to the low solubility when a benzene solution of PA and a catalytic amount of AIBN was added to the precipitate and the mixture was stirred at 78 °C for several hours.

**Scheme 4**



The reduction of phenylarsonic acid with hypophosphorus acid yielded the six-membered arsenic ring compound,[11] but no other rings or chains of arsenic were formed by this reduction. The phenyl-substituted cyclooligoarsine, *cyclo*-(PhAs)$_6$, was obtained as a pale yellow crystal after recrystallization from chlorobenzene. The crystal showed poor solubility in benzene. When *cyclo*-(PhAs)$_6$ was treated with 3 mol % of AIBN in refluxing benzene, the heterogeneous reaction mixture became clear within 30 min. The stable ring structure was collapsed, and open-chain arsenic oligomers or arsenic atomic biradicals might be formed in the solution (Scheme 4). By cooling the clear solution to room temperature, *cyclo*-(PhAs)$_6$ was regenerated as a light yellow powder. The catalytic amount of AIBN was enough to homogenize the mixture, in other words, to collapse all of the stable six-membered ring structure, suggesting that the produced arsenic radial also contributed to the destruction of *cyclo*-(PhAs)$_6$. In contrast to *cyclo*-(MeAs)$_5$, *cyclo*-(PhAs)$_6$ was stable at room temperature in the air atmosphere in the solid state and showed no reaction even in refluxing benzene for several hours.

**Spontaneous Alternating Copolymerization of *cyclo*-(MeAs)$_5$ with PA.** The arsenic ring compound with methyl-substitution, *cyclo*-(MeAs)$_5$, reacted with PA in chloroform at 25 °C in the absence of any radical initiators or catalysts to produce the corresponding poly(vinylene-arsine) in moderate yield (Table 1, run 1). The copolymerization was initiated simply by mixing a chloroform solution of *cyclo*-(MeAs)$_5$ and PA. The resulting copolymer was purified by reprecipitation from toluene to *n*-hexane. The copolymer showed a single peak on the GPC trace. The number-average molecular weight of the copolymer was estimated to be 11 100 by GPC analysis (vs polystyrene standards). The structure of the resulting copolymer was determined by $^1$H NMR and $^{13}$C NMR spectra (see the Supporting Information). Both spectra were identical to those of the poly(vinylene-arsine) previously prepared using a catalytic amount of AIBN as a radical initiator.[4a] The ratio of the peak areas of the vinyl proton and the methyl proton in the $^1$H NMR spectrum showed that the copolymer consisted of a 1:1 unit of methylarsine (MeAs) and PA. The $^{13}$C NMR spectrum exhibited a single peak attributable to the methyl carbon at 10.3 ppm, suggesting that the

**Table 1. Copolymerization of *cyclo*-$(MeAs)_5$ with PA: Effect of Solvent and Reaction Temperature**[a]

| | | | resulting polymer | | |
|---|---|---|---|---|---|
| run | solvent | temp (°C) | yield (%)[b] | $M_n$[c] | $M_w/M_n$[c] |
| 1 | chloroform | 25 | 64 | 11 100 | 2.1 |
| 2 | chloroform | 0 | 56 | 9900 | 2.1 |
| 3 | chloroform | 50 | 52 | 8800 | 1.9 |
| 4 | toluene | 25 | 60 | 13 000 | 2.4 |
| 5 | toluene | 100 | 38 | 4000 | 1.6 |
| 6[d] | toluene | 25 | 63 | 11 500 | 2.1 |
| 7 | benzene | 25 | 59 | 11 300 | 2.2 |
| 8 | diethyl ether | 25 | 45 | 7400 | 2.1 |
| 9 | THF | 25 | 58 | 15 000 | 2.8 |
| 10[d] | none | 25 | 41 | 600 | 3.4 |

[a] Copolymerization was carried out with a 1:5 feed molar ratio of *cyclo*-$(MeAs)_5$ and PA for 12 h under nitrogen. [b] Isolated yield after reprecipitation from toluene into *n*-hexane. [c] Determined by GPC (chloroform, polystyrene standards). [d] Copolymerization was carried out in a light-resistant container. The reaction mixture was solidified within 15 min, and the reaction was ceased.

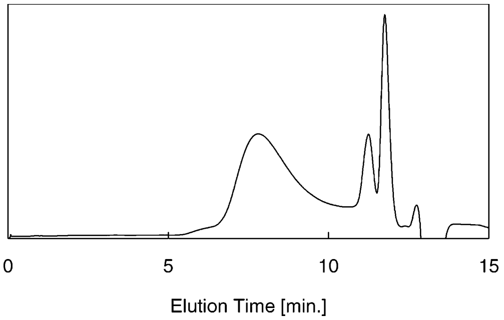


**Figure 1.** GPC trace (chloroform) of the reaction mixture after the copolymerization of *cyclo*-$(MeAs)_5$ with PA in chloroform at 25 °C in the absence of AIBN before the reprecipitation.

obtained copolymer possessed no arsenic−arsenic bonds or oxidized arsenic in the main chain.

After the copolymerization of *cyclo*-$(MeAs)_5$ with PA in chloroform was carried out for 12 h, the reaction mixture was analyzed by GPC before the reprecipitation (Figure 1). Besides a peak assigned to the poly(vinylene-arsine) with high molecular weight, the GPC chart shows two peaks in the region of the molecular weight of several hundreds. By the recycling HPLC analysis using chloroform as an eluent, it was revealed that both of the two peaks in the lower molecular weight region consisted of several peaks.[13] Because the compounds accounting for the two peaks were soluble in *n*-hexane and polymeric material was not, they were separated from each other by pouring the reaction mixture after the copolymerization into *n*-hexane. The low molecular weight compounds were stirred in toluene at 25 °C for 12 h, and then no polymer was obtained. This result suggests that the polymer with high molecular weight was not formed via the compounds responsible for these peaks. Similar peaks were also observed in the GPC trace when we employed AIBN as a radical initiator of the copolymerization. The formation of these compounds decreases the isolated yield of the polymer with high molecular weight.

Table 1 summarizes the effect of solvents and temperature on the copolymerization of *cyclo*-$(MeAs)_5$ with PA. Various solvents were found usable for affording copolymers with number-average molecular weights of more than 10 000 in moderate yields at 25 °C (Table 1, runs 1, 4, 7, 9). The molecular weight and yield of the poly(vinylene-arsine) decreased when the copolymerization was carried out at 100 °C in toluene (Table 1, run 5), probably because chain-transfer reactions took place more often at higher reaction temperature. The use of diethyl ether also gave the copolymer with the same structure and slightly decreased molecular weight, although the reaction system was heterogeneous during the copolymerization because of the poor solubility of the poly(vinylene-arsine). The reaction of *cyclo*-$(MeAs)_5$ with PA in toluene at room temperature was carried out in a light-resistant container (Table 1, run 6) and produced the polymer with almost the same molecular weight and same structure as those in run 4. The possibility of light energy initiating the copolymerization is excluded by this result. The reaction between *cyclo*-$(MeAs)_5$ and PA without any solvent afforded a transparent yellow solid in 15 min (Table 1, run 10). The obtained solid contained the monomers and oligomer with low molecular weight, which was characterized by $^1$H NMR spectroscopy and GPC analysis.

**Table 2. Copolymerization of *cyclo*-$(MeAs)_5$ with PA in the Absence of AIBN: Effect of the Feed Ratios of Monomers**

| | feed ratio | resulting polymer | | |
|---|---|---|---|---|
| run[a] | MeAs[b]:PA | $M_n$[c] | $M_w/M_n$[c] | yield (%)[d] |
| 1 | 1:0.33 | 5200 | 2.6 | 17[e] (32)[f] |
| 2 | 1:0.67 | 5200 | 2.7 | 42[e] (52)[f] |
| 3 | 1:1 | 11 100 | 2.1 | 64[e] |
| 4 | 1:1.5 | 13 100 | 2.3 | 52[e] (65)[g] |
| 5 | 1:1.5 | 11 200 | 2.1 | 30[e] (61)[g] |

[a] Copolymerizations were carried out in chloroform at 25 °C for 12 h. [b] MeAs represents methylarsine ($CH_3As$). [c] Estimated by GPC analysis in chloroform on the basis of polystyrene standards. [d] Isolated yield after reprecipitation from toluene to methanol. [e] (Weight of polymer)/(total weight of monomers). [f] Based on the molar amount of PA. [g] Based on the molar amount of *cyclo*-$(MeAs)_5$.

The treatment of *cyclo*-$(PhAs)_6$ with PA in toluene without AIBN at 25 or 60 °C for several hours resulted in no polymer and the recovery of the monomers. The poor solubility of *cyclo*-$(PhAs)_6$ in toluene is attributable as described above.

**Spontaneous Copolymerization in Various Monomer Feed Ratios.** The copolymerization of *cyclo*-$(MeAs)_5$ with PA was conducted in chloroform at 25 °C in various monomer feed ratios (Table 2). In all cases, the copolymerization resulted in the corresponding alternating copolymer, poly(vinylene-arsine). Thus, the 1:1 alternating structure of MeAs and PA is controlled very strictly under a wide variety of copolymerization conditions. These results can be explained by the mechanism we proposed.[4] Because the vinyl radical reacts with the arsenic−arsenic bond or arsenic radical immediately after production due to the instability, almost all of the propagating radical in the copolymerization system is arsenic radical and the concentration of the vinyl radical is extremely low. Thus, the vinyl radical never reacts with another vinyl radical. It rarely attacks PA either because of the low homopolymerizability of PA. This is also the case for runs 4 and 5 in which the excess amount of PA was employed. Therefore, the resulting copolymers have no consecutive PA units in the main chain in all of the cases. The other propagating radical, the arsenic radical, can cause the recombination reaction as a termination. The resulting diarsenic linkage, however, is unstable and can bring about its homolytic cleavage to reproduce the arsenic radical as a propagating end-group. Consequently, even when the excess amount of *cyclo*-$(MeAs)_5$ was employed,

**Table 3. Copolymerization of *cyclo*-(MeAs)$_5$ with PA in the Presence of AIBN: Effect of the Feed Ratios of Monomers**

| | feed ratio | resulting polymer | | |
|---|---|---|---|---|
| run[a] | MeAs:PA | $M_n$[b] | $M_w/M_n$[b] | yield (%)[c] |
| 1 | 1:0.33 | | | 0[d] |
| 2 | 1:0.67 | 3900 | 1.7 | 21[d] (26)[e] |
| 3 | 1:1 | 11 300 | 1.8 | 50[d] |
| 4 | 1:1.5 | 12 200 | 1.4 | 42[d] (53)[f] |
| 5 | 1:3 | 11 000 | 2.4 | 26[d] (54)[f] |

[a] Copolymerizations were carried out in toluene at 60 °C for 2 h. [b] Estimated by GPC analysis in chloroform on the basis of polystyrene standards. [c] Isolated yield after reprecipitation from toluene to methanol. [d] (Weight of polymer)/(total weight of monomers). [e] Based on the molar amount of PA. [f] Based on the molar amount of *cyclo*-(MeAs)$_5$.

the copolymerization yielded the copolymer with no consecutive MeAs units in the backbone.

While the excess amount of PA (Table 2, runs 4 and 5) was found to remain unchanged after the completion of the reaction, the excess amount of MeAs (Table 2, runs 1 and 2) decreased the molecular weights and yields of the obtained polymers in comparison to those in the equivalent case (Table 2, run 3). Because almost all of the propagating radical is the arsenic radical even in the case that the excess PA was employed, the copolymerization in runs 4 and 5 proceeded comparably to the equivalent case. When an amount of PA that is less than that of MeAs was employed, all PA was consumed before the sufficient growth of the copolymer chain. Thus, the copolymerization in runs 1 and 2 yielded the alternating copolymer with low molecular weight, and hence in low yield, after the removal of the oligomer by reprecipitation.

**Alternating Copolymerization of *cyclo*-(MeAs)$_5$ or *cyclo*-(PhAs)$_6$ with PA in the Presence of a Radical Initiator.** The copolymerization of *cyclo*-(MeAs)$_5$ with PA using a catalytic amount of AIBN produced the corresponding poly(vinylene-arsine) as reported in the previous paper.[4a] This time, we conducted the copolymerizations of *cyclo*-(MeAs)$_5$ and PA in various monomer feed ratios with 1.5 mol % of AIBN in toluene at 60 °C for 2 h. Table 3 summarizes the results of the copolymerizations. The molecular weights and yields were measured after the purification of the resulting polymers by reprecipitation into *n*-hexane. Similar to the copolymerization without AIBN, the excess amount of PA had no influence on the obtained polymer (Table 3, runs 4 and 5), while the excess amount of MeAs yielded the copolymer with low molecular weight and in low yield (Table 3, run 2) or no polymeric material (Table 3, run 1). As determined by the characterization with $^1$H and $^{13}$C NMR spectra, the obtained copolymers were the poly(vinylene-arsine) in all of the cases.

The difference in the production rate of the arsenic radicals with and without AIBN affected the results of the copolymerization of *cyclo*-(MeAs)$_5$ with PA fed in an excess amount of MeAs. In the feed ratio of MeAs:PA = 1:0.67, the copolymerization without AIBN (Table 2, run 2) yielded the alternating copolymer with higher molecular weight in higher yield than those of the copolymer produced with AIBN (Table 3, run 2). While the reaction without AIBN in the feed ratio of MeAs:PA = 1:0.33 (Table 2, run 1) produced the copolymer, the treatment of them in the same feed ratio with AIBN yielded no precipitation when the reaction mixture was poured into *n*-hexane (Table 3, run 1). In the presence of AIBN, the concentration of the arsenic radical became high in a few minutes, and hence all PA was consumed at the early stage of the copolymerization, yielding the low molecular-weight oligomer of the vinylene-arsine structure. In the absence of AIBN, on the other hand, the concentration of the arsenic radical was low at the initial stage, and hence during that period the growth of the polymer chain was accomplished although it was insufficient as compared to the equivalent case.

The copolymerization of *cyclo*-(PhAs)$_6$ with PA in various monomer feed ratios using AIBN was described in the previous report[4] and resulted in the copolymers having a 1:1 alternating structure with almost the same molecular weights in similar yields. The excess amount of the phenylarsine unit (PhAs) had no effect on the obtained copolymer in contrast to the case of MeAs. In the case of *cyclo*-(PhAs)$_6$, the concentration of the propagating arsenic radical was kept low as compared to the case of *cyclo*-(MeAs)$_5$ due to the poor solubility of *cyclo*-(PhAs)$_6$. It took about 30 min after the copolymerization was initiated by adding AIBN to make the reaction mixture homogeneous, in other words, to collapse all of the insoluble ring structure producing the arsenic radical. Therefore, the same copolymer as in the equivalent case was obtained even when an excess amount of PhAs was employed.

**Emulsion Polymerization.** The methyl-substituted cyclooligoarsine, *cyclo*-(MeAs)$_5$, afforded the corresponding poly(vinylene-arsine) by the copolymerization with PA using water as the reaction media. The copolymerization was carried out under a nitrogen atmosphere using water, *cyclo*-(MeAs)$_5$, PA, sodium lauryl sulfate as an emulsifier, and potassium peroxodisulfate as a water-soluble radical initiator in the weight ratio of 2:1:0.1:0.01. After vigorous stirring for 8 h at 80 °C, the obtained polymer latex was poured into methanol, and the precipitate was washed by methanol. The obtained polymer was purified by reprecipitation into *n*-hexane to yield the corresponding poly(vinylene-arsine) as a yellow-white powder (yield 27%). The number-average molecular weight ($M_n$) of the copolymer was 4700 with the polydispersity index ($M_w/M_n$) of 4.1. $^1$H NMR and $^{13}$C NMR spectra were employed to support the structure of the polymer. The fact that the copolymerization proceeded in the presence of water excludes the possibility that ionic species contribute to the propagation of the copolymerization.

**Gas Chromatography (GC) and Gel Permeation Chromatography (GPC) Analysis.** We carried out a GC study of the copolymerization system to investigate the consumption rate of PA. The spontaneous alternating copolymerization of *cyclo*-(MeAs)$_5$ with PA in toluene at 60 °C was conducted in the presence of mesitylene as a standard material. During the copolymerization, a small amount of reaction mixture was siphoned, diluted with chloroform, and analyzed by the GC. The conversion of PA was calculated by the peak area ratio of PA and mesitylene. The conversion rate of PA during the copolymerization with *cyclo*-(MeAs)$_5$ in toluene at 60 °C in the presence of 3 mol % of AIBN was also analyzed by the GC. Both of the results are plotted in Figure 2. The spontaneous copolymerization took nearly 4 h to convert 90% of PA, while the conversion of PA reached 100% within 40 min by the reaction with *cyclo*-(MeAs)$_5$ in the presence of AIBN. The GC analysis during the copolymerization without AIBN at 25 °C in chloroform

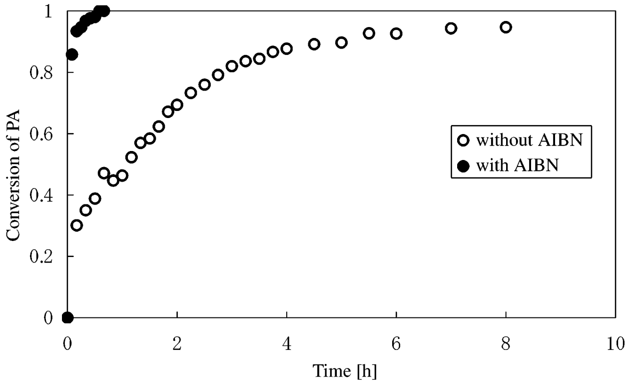


**Figure 2.** Conversion rate of PA during the copolymerization with *cyclo*-(MeAs)$_5$ in the absence (○) or presence (●) of AIBN in toluene at 60 °C. Mesitylene was employed as a standard material.

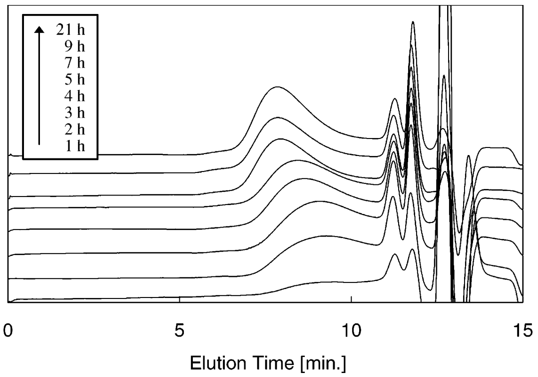


**Figure 3.** GPC traces of the reaction mixture during the copolymerization of *cyclo*-(MeAs)$_5$ with PA in the absence of AIBN in chloroform at 25 °C.

was also performed and exhibited no significant difference with the spontaneous copolymerization in toluene at 60 °C (see the Supporting Information). The effect of the reaction temperature and solvent on the rate of the copolymerization was small. The large difference in the conversion rate of PA between those with and without AIBN is explained by the difference in the rate of the collapse of the ring structure. The cleavage of the arsenic–arsenic bonds of the cyclooligoarsines was accelerated by a catalytic amount of AIBN, which was proved by the reaction of the cyclooligoarsines with AIBN in the absence of PA. The large contribution of a radical initiator suggests that the copolymer chain propagates via radical species.

To examine the growth process of the copolymer chain during the copolymerization in chloroform at room temperature, the molecular weight change was monitored by GPC analysis. Similar to the GC analysis, during the copolymerization in chloroform at 25 °C, a small amount of the reaction mixture was siphoned, diluted with chloroform, and analyzed by the GPC (Figure 3). As the reaction proceeded, the peak assigned to the poly(vinylene-arsine) gradually shifted to left, suggesting the progressive growth of the polymer chain. The two peaks that appeared in the region of the molecular weight of several hundreds (elution time; 11–12 min) showed no change in the molecular weight during the copolymerization. The GPC analysis of the spontaneous copolymerization in chloroform at 50 °C was also carried out and exhibited no significant difference of the rate of the chain growth as compared to the copolymerization in chloroform at 25 °C (see the Supporting Information). The molecular weight of the copolymer at the peak top ($M_p$) in the GPC trace (vs polystyrene standards) is plotted as a function of the conversion rate of PA in Figure 4. The steep increase of the molecular weight of the polymer with the increase of the conversion rate of PA was observed in the range of high conversion. This is a typical feature of step-reaction polymerizations such as polycondensation and polyaddition.

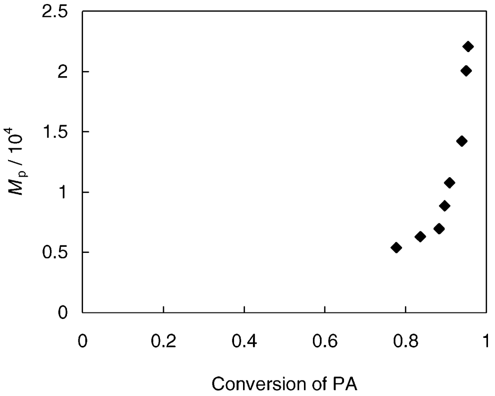


**Figure 4.** Plot of $M_p$ of poly(vinylene-arsine) in the GPC versus conversion rate of PA during the copolymerization of *cyclo*-(MeAs)$_5$ with PA without AIBN in chloroform at 25 °C.

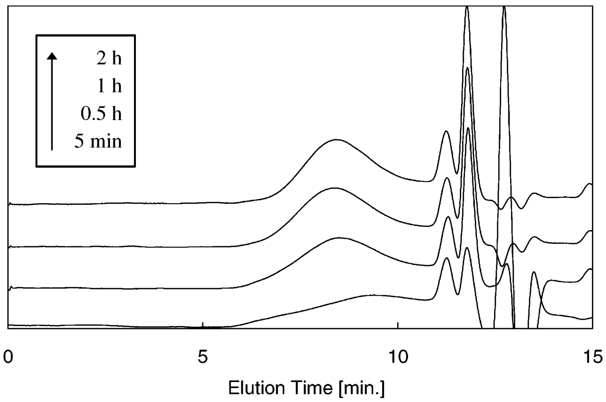


**Figure 5.** GPC traces of the reaction mixture during the copolymerization of *cyclo*-(MeAs)$_5$ with PA in the presence of AIBN in chloroform at 50 °C.

The copolymerization of *cyclo*-(MeAs)$_5$ with PA using AIBN in chloroform at 50 °C for 2 h also yielded the poly(vinylene-arsine) ($M_n = 6200$, $M_w/M_n = 1.8$), which was also analyzed by GPC (Figure 5). The growth of the polymer chain was completed within 30 min, which is consistent with the data of GC analysis (Figure 2).

**Stability of the Copolymers.** To investigate the thermal stability of the obtained polymers, a TGA analysis was carried out under nitrogen and air. The methyl-substituted poly(vinylene-arsine) showed a 10% weight loss at 265 °C (under $N_2$) and 205 °C (under air), and the phenyl-substituted one showed them at 284 °C (under $N_2$) and 250 °C (under air). The poly(vinylene-arsine) with phenyl-substitution was thermally more stable than that with methyl-substitution. The glass transition temperatures ($T_g$) of the methyl- and phenyl-substituted polymers were 58.2 and 92.9 °C, respectively, determined by DSC analysis. Both of the resulting copolymers are stable in the solid state at room temperature. No decrease of the molecular weight or no change of the structure was observed even after exposing them to air for several months. To examine the stability toward air moisture and oxidation more precisely, the chloroform solution of methyl-substituted poly(vinylene-arsine) was stirred in air atmosphere at 50 °C, and the molecular weight change was monitored by GPC (see the Supporting Information). The GPC analysis showed no decrease of the molecular weight after stirring for 24 h. The $^1$H NMR spectrum of the recovered copolymer indicated no change of the polymer structure.

## Conclusion

The synthesis of novel arsenic-containing polymers, poly(vinylene-arsine)s, has been achieved by ring-collapsed radical alternating copolymerization (*RCRAC*) of arsenic homocycles with PA. In the case of pentamethylcyclopentaarsine, *cyclo*-$(MeAs)_5$, the copolymerization took place without radical initiators or catalysts at room temperature to give 1:1 alternating copolymers with a number-average molecular weight of more than 10 000 in moderate yields. In the presence of a radical initiator, the copolymerization was accelerated and completed within 40 min. Although further investigations on the mechanism are needed such as ESR analysis, the results of the studies here strongly suggest that the copolymerization proceeds via radical propagating species. In addition, this copolymerization system showed a behavior of stepwise reaction polymerization in the conversion−molecular weight plot and a unique dependency on the monomer feed ratio; the excess MeAs decreases the molecular weight of the copolymer, while the excess PA has no effect on the obtained polymer. The present copolymerization can be regarded as a polyaddition of MeAs having biradical structure with phenylacetylene.

Besides the cyclooligoarsines, a number of cyclic compounds or polymers are known of which ring or chain skeletons are made up of only one inorganic element such as silicon, germanium, phosphorus, antimony, sulfur, and so on.[14] These compounds often cause homolytic cleavage by stimulation such as light or heat. The present methodology, which involves the homolytic cleavage of the element−element bond of inorganic homocycles or homochains and the addition of the produced inorganic radicals to the organic monomers, would be applicable to the preparation of various inorganic polymers containing inorganic elements in the main chain. Studies on the expansion of the scope of this methodology are now in progress.

**Supporting Information Available:** $^1$H NMR and $^{13}$C NMR spectra of the methyl-substituted poly(vinylene-arsine) obtained by the spontaneous copolymerization in chloroform at 25 °C, conversion rate of PA during the spontaneous copolymerization in toluene at 60 °C, and GPC traces of the reaction mixture during the spontaneous copolymerization in chloroform at 50 °C. This material is free of charge via the Internet at http://pubs.acs.org.

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(13) We assume from the $^1$H NMR analysis that these peaks are attributable to the cyclic compounds with the ring structure of vinylene-arsine. Now the precise isolation and the characterization of each peak are in progress.

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