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Ring-Collapsed Radical Alternating Copolymerization of Phenyl-Substituted Cyclooligostibine and Acetylenic Compounds

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ABSTRACT: We studied ring-collapsed radical alternating copolymerization (RCRAC) of hexaphenylcyclohexastibine (*cyclo*-(PhSb)$_6$) and several acetylenic compounds in the presence of a catalytic amount of 2,2′-azobis(isobutyronitrile) (AIBN) in tetrahydrofuran at 70 °C. Although the monosubstituted acetylenic monomers, phenylacetylene (**1a**), 4-cyanophenylacetylene (**1b**), and 4-methoxyphenylacetylene (**1c**), gave low molecular weight poly(vinylene stibine)s, RCRAC of dimethyl acetylenedicarboxylate (**1d**) and *cyclo*-(PhSb)$_6$ provided a corresponding poly(vinylene stibine) (**2d**) of which the number-average molecular weight was 4300 by gel permeation chromatographic analysis. The structure of **2d** was supported by ^{1}H and ^{13}C NMR spectra and elemental analysis. The structure and the molecular weight of **2d** were insensitive to solvents and the feed ratio of the monomers. When hexaphenylcyclohexaarsine (*cyclo*-(PhAs)$_6$) was used in RCRAC with **1d**, no polymerization proceeded. These results were derived from different reactivity of pnictogen radicals. When the results of RCRAC of *cyclo*-(PhAs)$_6$ and that of **2** are compared, the arsenic radicals had more reactivity to the ethynyl groups and the antimony radicals had more reactivity toward the vinyl radicals.

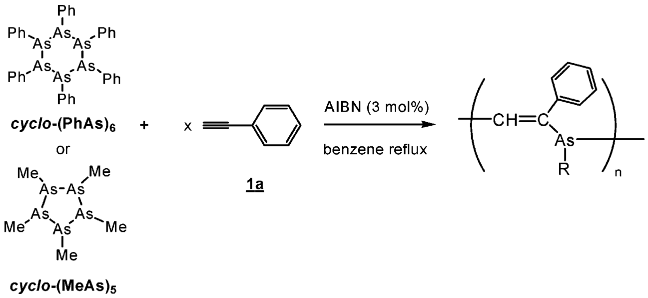
Introduction

Synthesis of polymers having inorganic elements in polymer backbones is of interest because they can offer interesting and useful properties such as electronic, photonic, biomedical, and flame-retardant properties.[1] Among them, the incorporation of inorganic elements into organic polymer main chains is currently of great interest and importance.[2] However synthetic methodology for incorporating a wide variety of inorganic elements in polymer main chain is limited. In particular, preparation of the polymers having metallic or metalloid elements in the backbone utilizes the classical methodologies[3−6] such as polyaddition using a metallic dihydride as a comonomer,[3] sodium coupling of a metallic dihalide,[4] or polycondensation of a dihydroxide and a dihalide.[5] The simplest type of the polymers featuring inorganic elements is heteroatom-including poly(vinylene)s. However, there was no report of the synthesis of such polymers except poly(vinylene sulfide)s.[7]

Recently, we have developed radical copolymerization of homocyclic arsenic compounds such as hexaphenylcyclohexaarsine (*cyclo*-(PhAs)$_6$) or pentamethylcyclopentaarsine (*cyclo*-(MeAs)$_5$) and phenylacetylene (**1a**)[8] (Scheme 1). This is a novel type of radical alternating copolymerization, in which the arsenic ring compounds fell into pieces and the arsenic unit was incorporated into the polymer backbone with no arsenic−arsenic bonds. Therefore, we have termed it as a ring-collapsed radical alternating copolymerization (RCRAC). The obtained polymers were first examples of well-defined organoarsenic polymers. The polymers showed fluorescent property attributable to n−π^* transition in the backbones.

Cyclooligostibines are homocyclic compounds with rings built exclusively of antimony atoms, and have been well characterized.[9,10] However, the reactivity of cyclooligostibines was reported in few papers.[9] No reactions of cyclooligostibines with unsaturated compounds have been reported. Here, we report RCRAC of a cyclooligostibine and acetylenic compounds to organoantimony polymers, poly(vinylene stibine)s. Although several polymers containing antimony element in the main chain were reported,[11] most of the polymers were synthesized by polycondensation. Moreover, there was no organoantimony polymer except for poly(*p*-phenylene triphenylantimony)[12] whose degree of polymerization was 2. The antimony elements in those polymers were, however, all pentavalent because trialkyl-/triarylantimony dichloride/dinitrate were used as comonomers in the previous polymerization. The resulting polymers in this paper are first organic polymers which have trivalent antimony in the backbones. Because of a lone pair of trivalent antimony, the polymer should possess coordination ability[13] and potential for introduction of substitution via oxidative addition reaction.[14] Each trivalent antimony atom in the poly(vinylene stibine) is expected to have a less delocalized lone pair compared with an arsenic atom because of stronger s-character of the lone pair of the antimony atom. An array of radical cations with the simple rigid spacer would be generated by oxidation of the antimony atoms of the polymer.

Scheme 1



Results and Discussion

The phenyl-substituted cyclooligostibine, hexaphenylcyclohexastibine (*cyclo*-(PhSb)$_6$), was synthesized by reduction of phenylantimony dichloride using bis(cyclopentadienyl)cobalt(II) according to the literature procedure.[15] RCRAC of *cyclo*-(PhSb)$_6$ was studied with monosubstituted and disubstituted

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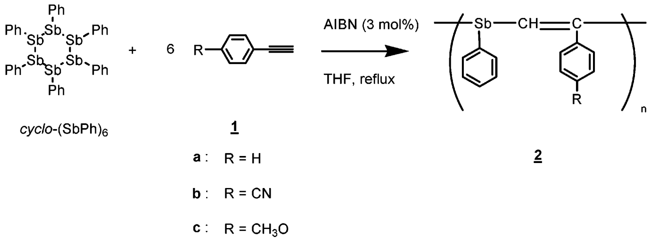
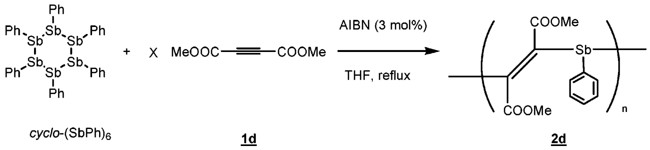
Scheme 2



Scheme 3



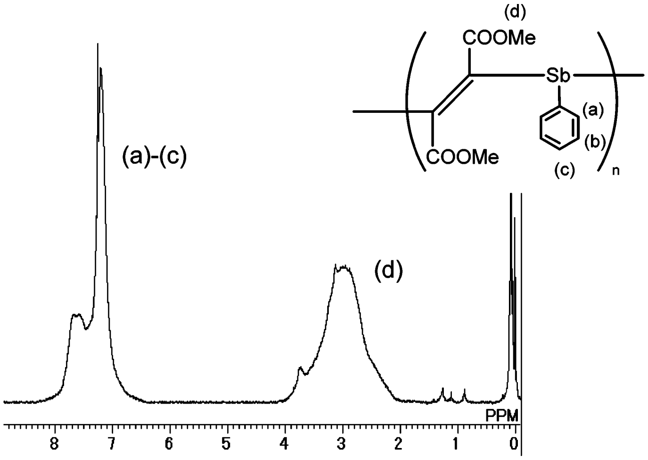


Figure 1. ^{1}H NMR spectrum of polymer **2d** (M_n = 4300, M_w = 6400) in $CDCl_3$ at room temperature.

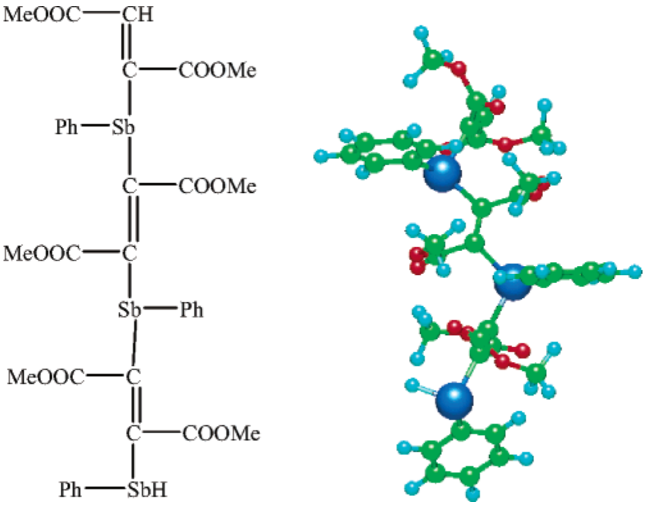


Figure 2. Trans isomer of a dimer model of **2d** (left) and its optimized geometry (right) calculated with the AM1 Hamiltonian.

acetylenic compounds. At first, the radical reactions of *cyclo*-$(PhSb)_6$ and various kinds of monosubstituted acetylenic compounds (**1a**−**1c**), which provided corresponding poly(vinylene arsine)s by RCRAC of the cyclooligoarsines,[16] were carried out (Scheme 2). A tetrahydrofuran (THF) solution of a catalytic amount (3 mol %) of 2,2′-azobis(isobutyronitrile) (AIBN), *cyclo*-$(PhSb)_6$, and the monosubstituted acetylenic compound was heated after deaeration in a sealed tube. After stirring the reaction mixture for 15 h at 70 °C, the reaction mixture was filtered to remove a white precipitate.[17] The filtrate was poured into *n*-hexane to precipitate a product, which was purified three times by reprecipitation. Although **1a**−**1c** were all copolymerized with *cyclo*-$(PhSb)_6$ estimated by ^{1}H NMR (as described later), yields of the corresponding products were all less than 10%, and the number-average molecular weights of the products determined by GPC analysis were around 1500. On the other hand, dimethyl acetylenedicarboxylate (**1d**) as a disubstituted electron-deficient acetylene gave polymer **2d** with a moderate yield and higher molecular weight by RCRAC with *cyclo*-$(PhSb)_6$ (Scheme 3). The polymer was purified by reprecipitation into diethyl ether. After freeze-drying, the polymer **2d** was obtained as a bright-yellow powder. From GPC analysis (DMF with 0.1 M LiBr, polystyrene standards), the number-average and weight-average molecular weights of **2d** were 4300 and 6300, respectively. The yield of **2d** (26%) was relatively low due to removal of low molecular weight products by reprecipitation and lower reactivity of stibine radical than an arsenic radical. The polymer **2d** was readily soluble in common organic solvents such as $CHCl_3$, THF, DMF, and toluene.

Structural characterization of **2d** was provided by ^{1}H and ^{13}C NMR spectroscopies. The ^{1}H NMR spectrum of **2d** showed broadening peaks at δ 8.0−6.7 ppm and δ 4.0−2.0 ppm attributed to the aromatic protons and the methyl protons, respectively (Figure 1). Considering the integral ratio of the methyl protons and the phenyl protons, the copolymer was found to have 1:1 of the stibine and the vinylene unit. The peak of the methyl protons was located in upper field than that of **1d** due to a ring current effect of the phenyl group on the antimony element. Molecular orbital calculations for optimized geometries of a cis and a trans isomers of a dimer model of **2d** were carried out (Figure 2). In the case of the cis isomer, calculation was not succeeded due to a steric hindrance of the two adjacent Sb atoms. The result of calculations of the optimized geometry of the trans isomer showed that the methyl protons can be located over the benzene ring. In the case of poly(vinylene arsine), the trans isomer was predominantly formed.[8] These results indicate that the trans configuration was the predominate structure of **2d**. A small peak appeared at around 3.8 ppm might be assignable to the methyl protons of the cis configuration. The ^{13}C NMR spectrum of the polymer showed a peak around 51 ppm attributed to the methyl group (Figure 3). A broad peak of the vinyl carbon appeared at around 143 ppm in the spectrum, which suggests the formation of the vinylene stibine units. The elemental analysis of **2d** confirmed 1:1 structure of the antimony element and the vinylene unit (see Experimental Section). This also suggests that the antimony element in **2d** existed in a trivalent state and no oxidated antimony was present.

The polymer **2d** was characterized by matrix-assisted laser desorption/ionization time-of-flight mass (MALDI−TOF−MS) measurement. Figure 4 shows the spectrum of **2d**. Although detected peaks attributed to the polymer with several repeating units, intervals between these peaks at high molecular weights are all 341, which is consistent with the value of the vinylene stibine unit. Moreover, the mass of the peaks corresponds to the weight of $[(C_6H_6O_4)_m(C_6H_5Sb)_{m+1}] + Na^+$ including isotope pattern for antimony. This result supports the premise that the polymer was terminated with the antimony units and not with the vinyl unit as well as the group from AIBN.

The polymer **2d** was air-stable in the solid state at room temperature. No changes in the molecular weight and the structure were observed in the GPC trace and ^{1}H NMR spectrum after exposing **2d** to air for several days. The GPC analysis and the ^{1}H NMR spectrum showed no change after leaving **2d** under inert atmosphere for several months.

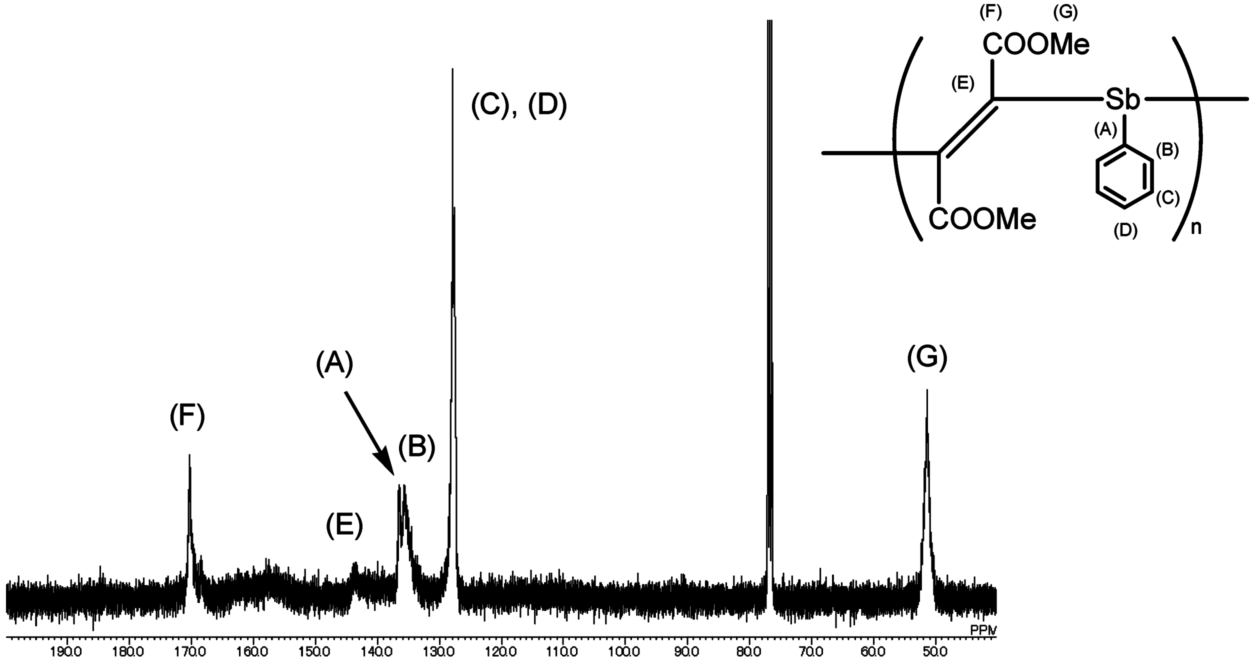


Figure 3. ^{13}C NMR spectrum of polymer **2d** ($M_n = 4300$, $M_w = 6400$)in $CDCl_3$ at room temperature.

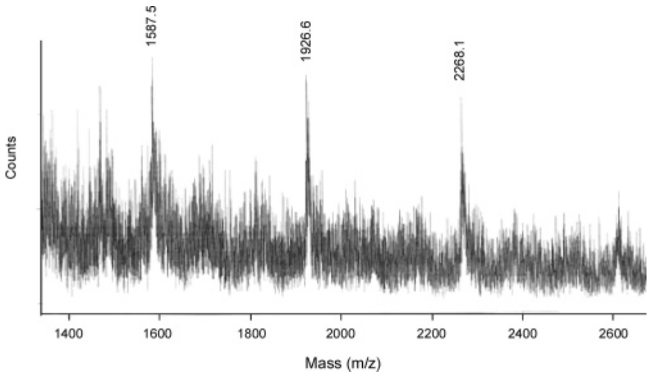


Figure 4. Matrix-assisted laser desorption/ionization time-of-flight mass spectrum of polymer **2d** ($M_n = 4300$, $M_w = 6400$). The measure peaks are labeled with their measured molecular weights.

Table 1. Solvent Effect of Copolymerization of 1d with *cyclo*-(PhSb)$_6$

run[a]	solvent	x[b]	M_w[c]	M_n[c]	M_w/M_n[c]	yield (%)[d]
1	THF	6	6400	4300	1.5	26
2	THF	60	5400[e]	3300[e]	1.6	N.A.[f]
3	toluene	6	7300	4600	1.6	18
4	toluene	10	8100[e]	4100[e]	2.0	N.A.[f]
5	DMF	6	4100	3000	1.4	20

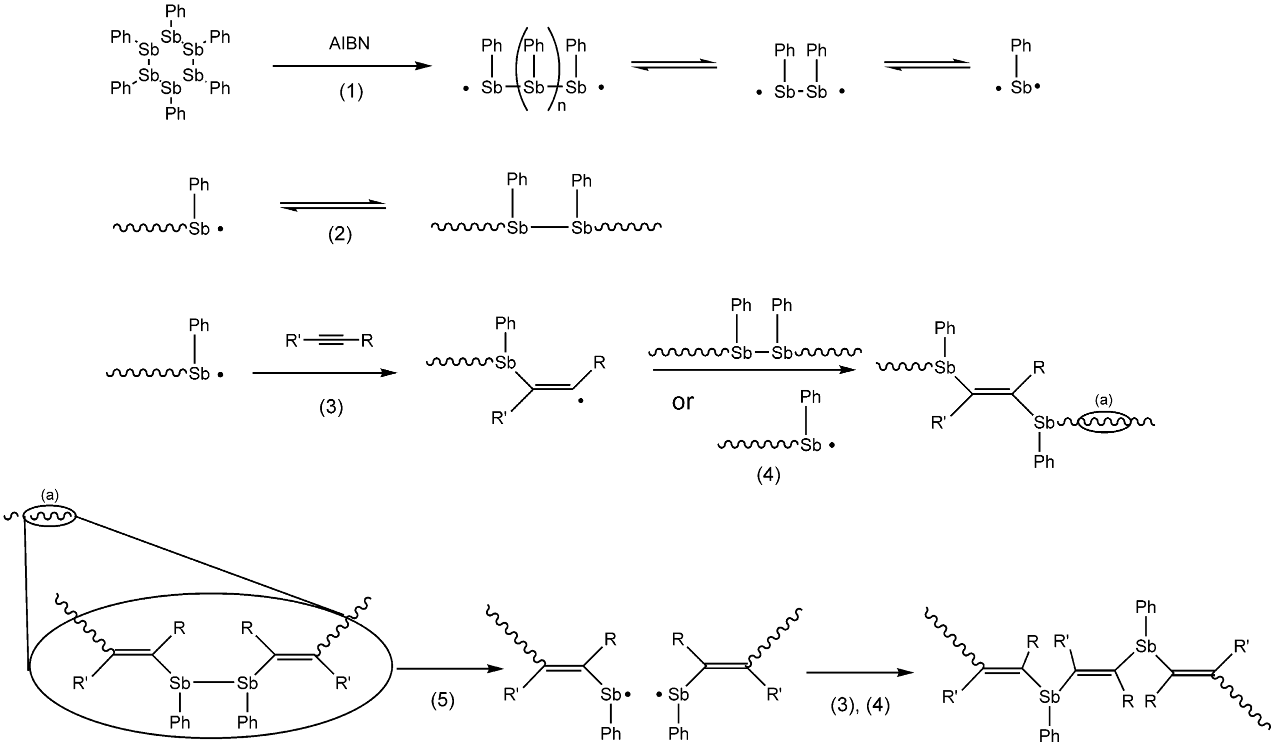
[a] Copolymerizations were carried out at 70 °C for 14.5 h. [b] Molar ratio of **1d** to *cyclo*-(PhSb)$_6$. [c] Determined by GPC (DMF with 0.1 M LiBr, polystyrene standards). [d] Isolated yield after reprecipitation from THF into diethyl ether. [e] Polymer fraction of the GPC trace. [f] Isolation of the polymer was not achieved due to contamination of large amount of **1d**.

The ^{1}H NMR spectra of the polymers **2a**−**2c** prepared by RCRAC of the monosubstituted acetylenic compounds (**1a**−**1c**) and *cyclo*-(PhSb)$_6$ showed broadening peaks in the aromatic area. In the case of **1c** and *cyclo*-(PhSb)$_6$, the ^{1}H NMR spectrum of the polymer showed a broadening peak at 8.6 ppm-6.0 ppm attributed to the aromatic protons and vinyl protons. Considering the integral ratio of the aromatic and vinyl protons and the protons of the methoxy group at around δ 3.7 ppm, the copolymer composition was approved to be nearly 1:1 structure of the antimony element and the vinylene unit.

The copolymerization of *cyclo*-(PhSb)$_6$ and **1d** was carried out in different solvents and feed ratios (Table 1). The polymer obtained in toluene has almost the same number-average molecular weight of **2d** as the polymer obtained in THF, and the polymer obtained in DMF gave a slightly lower number-average molecular weight. Although radical chain transfer to the solvent affects to the molecular weight in DMF, this RCRAC proceeds to produce the polymer with moderate yield and higher molecular weight. Although less radical chain transfer in toluene is expected than in THF, the obtained polymer has almost the same molecular weight. No obvious differences in the GPC and NMR analysis of the obtained polymer were observed even if changing the feed ratio of *cyclo*-(PhSb)$_6$ and **1d**. These results can be explained by the mechanism we proposed in the case of RCRAC of *cyclo*-(PhAs)$_6$ or *cyclo*-(MeAs)$_5$ and **1a**.[8] Since the vinyl radical reacts with the antimony−antimony bond or antimony radical immediately after production due to the instability, almost all of the propagating radicals in the copolymerization system are antimony radicals and the concentration of the vinyl radical is extremely low. Thus, the vinyl radical never reacts with another vinyl radical. When di-*tert*-butyl acetylenedicarboxylate was applied to this polymerization as an acetylenic comonomer, no polymer was obtained because of steric hindrance of the *tert*-butyl group.

Although RCRAC of *cyclo*-(PhSb)$_6$ and **1d** gave the polymer **2d**, no polymerization proceeded when hexaphenylcyclohexaarsine (*cyclo*-(PhAs)$_6$) was used in RCRAC system with **1d**. When the phenylacetylene derivatives (**1a**−**1c**) were used, the resulting arsenic polymers had larger number-average molecular weights and higher yields than the corresponding antimony polymers. These differences between the cases of *cyclo*-(PhAs)$_6$ and *cyclo*-(PhSb)$_6$ are derived from the reactivity of the corresponding radicals. We proposed that RCRAC proceeds via the following pathways (Scheme 4).[8] First, AIBN cleaved antimony−antimony bonds of the cyclic oligoarsine to produce antimony radicals (eq 1). The homolytic cleavage of the other antimony−antimony bonds proceeded spontaneously due to their instability by destruction of the quite stable six-membered ring structure (eq 2). In competition with this reaction, the antimony radical attacked the ethynyl group of the acetylenic compound to produce a vinyl radical (eq 3). Next, the vinyl radical reacted with the antimony−antimony bond or the antimony radical to

Scheme 4



produce a vinylene stibine structure (eq 4). Even if the antimony−antimony bond was left in the main chain (part a), antimony radicals are generated because of the easily cleavage of the antimony−antimony bond (eq 5). Then, generated antimony radicals attack the ethynyl group (eq 3) or react with the vinyl radical (eq 4). Repeating the cleavage of the antimony−antimony bond and addition to the ethynyl group results in the vinylene stibine structure with no antimony−antimony bond. We previously showed that the effects of conjugation or electron-withdrawing of the substituent of acetylenic monomer promoted RCRAC.[16] This result suggested that the arsenic radical preferred reacting with electron-accepting monomers due to the lone pair on the arsine atom. However, an excessive conjugative or electrostatic effect of the substitution of an acetylenic monomer such as **1d** decreased the reactivity of the vinyl radicals formed from the acetylenic compounds toward the arsenic radical due to increase stability of the vinyl radicals.

The present results suggest that the arsenic radicals have more reactivity to the ethynyl groups than the antimony radicals and the antimony radicals have more reactivity toward the vinyl radicals. This reactivity difference is similar to that of group 16 elements. Sulfur radicals add to unsaturated bonds faster than selenic radicals[18] and the selenic radicals react with carbon radicals than the sulfur radicals.[19] In the case of RCRAC of *cyclo*-(PhSb)$_6$ with **1d**, the vinyl radical can react with the antimony radicals to proceed RCRAC. In the case of *cyclo*-(PhAs)$_6$ with **1d**, the resulting vinyl radical is too stable to react with the arsenic radicals.

The electronic structure of the polymer **2d** was studied by using UV−vis spectroscopy. The UV−vis absorption spectrum of the polymer **2d** in chloroform showed a small absorption at a visible region besides strong benzene-ring absorption at a UV region (Figure 5). The lower energy absorption edge was located around 440 nm. No emission was observed when **2d** was excited at 350 or 400 nm, while poly(vinylene arsine)s showed emission.[8,16,20] As the atomic number of the pnictogen increases, the s character of the lone pair is enhanced.[21] In the polymer **2d**, lone pairs are much more localized on the antimony element because of the stronger s-character. We assume that the interaction between the lone pair electron and the π electron of the vinylene unit decreases as compared with the case of the poly(vinylene arsine)s.[8,16,20]

Although no oxidation peak was observed in the cyclic voltammetric measurement of **2d**,[22] this polymer was oxidized by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). When DDQ was added to the $CHCl_3/CH_3CN$ solution of the polymer **2d**, the solution color turned dark red. The UV spectrum of the solution of **2d** and DDQ shows major maxima at 550 and 589 nm assignable to the anion radical of DDQ (Figure 6). The intensities at 550 and 589 nm were saturated at the amount of [DDQ]/[repeating unit of **2d**] = 0.4−0.5. This result showed that the half of the antimony atoms in the polymer can be oxidized under the present conditions. This may be due to an electrostatic repulsion of the adjacent oxidized antimony unit.

Conclusion

Novel organoantimony polymers were successfully synthesized by RCRAC of the cyclooligostibine with the electron-

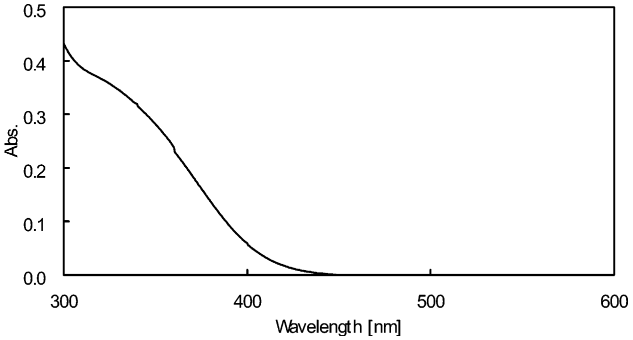


Figure 5. UV−vis absorption spectrum of **2d** (M_n = 4300, M_w = 6400) in $CHCl_3$ at room temperature.

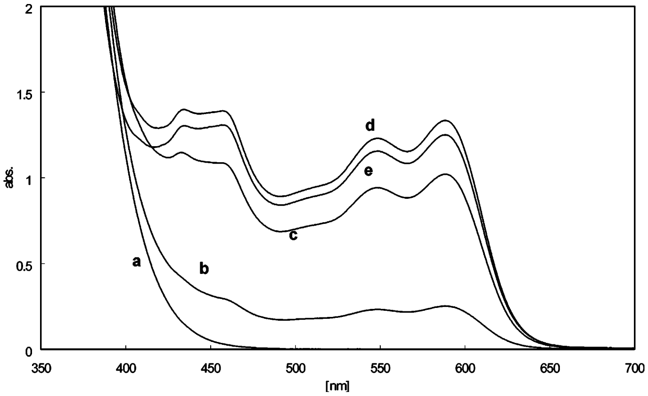


Figure 6. Dependence of the UV−vis absorption spectrum on the DDQ feed ratio against the antimony unit of **2d** (M_n = 4300, M_w = 6400). [DDQ]/[repeating unit of **2d**] = 0 (a), 0.1 (b), 0.3 (c), 0.5 (d), and 0.7 (e) at room temperature. [repeating unit of **2d**] = 2.34 mM.

deficient acetylene derivative. In the case of dimethyl acetylenedicarboxylate (**1d**), RCRAC provided the polymer whose number-average molecular weight was 4300. Comparing the results of RCRAC of *cyclo*-(PhAs)$_6$ and *cyclo*-(PhSb)$_6$, the arsenic radicals had more reactivity to the ethynyl groups and the antimony radicals had more reactivity toward the vinyl radicals. The present results demonstrate that RCRAC provides general methodology to synthesize heteroatom-including poly(vinylene)s.

Experimental Section

Materials. Tetrahydrofuran (THF) and diethyl ether were dried over Na and distilled before use. Dehydrated toluene and *N*, *N*-dimethylformamide (DMF) were used without further purification. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. Phenylacetylene (**1a**), and dimethyl acetylenedicarboxylate (**1d**) were distilled before use. 4-Cyanophenylacetylene (**1b**) and 4-methoxyphenylacetylene (**1c**) were synthesized using a literature procedure.[23] Hexaphenylcyclohexaarsine (*cyclo*-(PhAs)$_6$) was prepared according to ref 24.

Equipment. ^{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) analysis was carried out on a Tosoh 8020 instrument with a TSK-gel Alpha 3000 column for an *N*, *N*-dimethylformamide solution containing 10 mM LiBr as an eluent at 40 °C after calibration with standard polystyrene samples. The optimized geometries of the dimer models were calculated by Fujitsu WinMopac 3.0 with the AM1 Hamiltonians.

MALDI−TOF−MS was performed on a PerSeptive Biosystems Voyager DE-STR equipped with 2-m linear and 3-m reflector flight tubes and a 337 nm nitrogen laser (pulse width, 3 ns), along with a delayed extraction capability. This experiment was carried out at an accelerating potential of 20 kV in a linear mode. Mass spectra from 128 laser shots were accumulated summed to produce a final spectrum. Angiotensin I (human; MW = 1296.5) (BACHEM) and insulin (bovine pancreas 28.3; MW = 5733.50) (Nakalai) were used as internal standards to calibrate the mass scale. Sample for MALDI−TOF−MS analysis was prepared by mixing the polymer, a matrix (1,8-dihydroxy-9(10*H*)-anthracenone; dithranol), and a cationizing agent (sodium trifluoroacetate) in THF. The mixture was deposited onto the gold-coated sample plate and dried in air at room temperature.

Hexaphenylcyclohexastibine (*cyclo*-(PhSb)$_6$).[25] Preparation of *cyclo*-(PhSb)$_6$ was referred to a literature procedure.[11] A solution of 1.0 g (5.29 mmol) of bis(cyclopentadienyl)cobalt(II) in 50 mL of THF was added dropwise in the dark to the solution of 2.14 g (7.93 mmol) of dichlorophenylstibine in 50 mL of THF. Stirring the mixture for 0.5 h resulted in the formation of a red solution and a yellow solid. The solution was separated by decantation and cooled to −50 °C. After several days, 0.18 g of *cyclo*-(PhSb)$_6$ was formed as an orange solid (yield 17.7%). Anal. Found: C, 36.0; H, 2.5. Calcd for $C_{36}H_{30}Sb_6$: C, 36.2; H, 2.5.

Polymerization. A typical experimental procedure is as follows. After deaeration in a sealed tube, a THF solution of a catalytic amount of 2,2′-azobis(isobutyronitrile) (AIBN) (3 mol %), *cyclo*-(PhSb)$_6$ and an acetylenic monomer was heated. In the case of **1d**, after stirring the reaction mixture for 15 h at 70 °C, the solution was poured into diethyl ether under argon to yield poly(vinylene stibine) (**2d**).

2d. ^{1}H NMR (δ in CDCl$_3$, ppm): 8.0−6.5 (Ar-*H*), 4.0−2.0 (CO$_2$C*H*$_3$). ^{13}C NMR (δ in CDCl$_3$, ppm): 171−168 (*C*O$_2$CH$_3$), 145−142 (Sb−*C*=*C*), 137−132 (C_{Ar}−Sb, *m*-C_{Ar}−Sb), 130−127 (*o*,*p*-C_{Ar}−Sb), 53−50 (CO$_2$*C*H$_3$). Anal. Found: C, 41.2; H, 3.3. Calcd for $[C_6H_6O_4(C_6H_5Sb)_{1.0}\,]_m$: C, 42.3; H, 3.3.

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References and Notes

(1) (a) Manners, I. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1603−1621. (b) Rehahn, M. *Acta Polym.* **1998**, *49*, 201−224. (b) Archer, R. D. *Inorganic and Organometallic Polymers*; Wiley-VCH: New York, 2001. (c) Allcock, H. R. *Adv. Mater.* **1994**, *6*, 106−115. (d) Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers*; Prentice Hall: Upper Saddle River, NJ, 1992.

(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) (a) Notles, J. G.; Kerk, G. J. M. van der **1961**, *80*, 623−631. (b) Neumann, W. P.; Schneider, B. *Ann. Chem.* **1967**, *707*, 20−25.

(4) Carraher, C. E., Jr.; Dammeier, R. L. *Makromol. Chem.* **1970**, *135*, 107−112.

(5) Carraher, C. E. Jr.; Scherubel, G. A. *J. Polym. Soc.* **1971**, *A-1* (9), 983−989.

(6) For example, (a) Kobayashi, S.; Cao, S. *Chem. Lett.* **1993**, *22*, 1385−1388. (b) Carraher, C. E., Jr.; Winter, D. O. *Makromol. Chem.* **1971**, *141*, 259−264.

(7) (a) Ikeda, Y.; Ozaki, M.; Arakawa, T. *J. Chem. Soc., Chem. Commun.* **1983**, *24*, 1518−1519. (b) Ikeda, Y.; Ozaki, M.; Arakawa, T.; Takahashi, A.; Kambara, S. *Polym. Commun.* **1984**, *25*, 79−80. (c) Ikeda, Y.; Ozaki, M.; Arakawa, T. *Mol. Cryst. Liq. Cryst.* **1985**, *118*, 431−434.

(8) Naka, K.; Umeyama, T.; Chujo, Y. *J. Am. Chem. Soc.* **2002**, *124*, 6600−6603.

(9) (a) Ateş, M.; Breunig, H. J.; Ebert, K. H.; Gülec, S.; Kaller, R.; Dräger, M. *Organometallics* **1992**, *11*, 145−150. (b) Breunig, H. J.; Ghesner, I.; Loak, E. *Organometallics* **2001**, *20*, 1360−1364.

(10) For example: (a) Breunig, H. J.; Ebert, K. H.; Gülec, S.; Probst, J.*Chem. Ber.* **1995**, *128*, 559−603. (b) Breunig, H. J.; Soltani-Neshan, A. *J. Organomet. Chem.* **1984**, *262*, C27−C29. (c) Mourad, Y.; Mugnier, Y.; Breunig, H. J.; Ateş, M. *J. Organomet. Chem.* **1991**, *406*, 323−329.

(11) For example: (a) Karak, N.; Maiti, S. *J. Polym. Mater.* **1996**, *13*, 179−190. (b) Carraher, C. E., Jr.; Hedlund, L. J. *J. Macromol. Soc. Chem.* **1980**, *A14* (5), 713−728. (c) Carraher, C. E., Jr.; Naas, M. D.; Giron, D. J.; Cerutis, D. R. *J. Macromol. Sci.—Chem.* **1983**, *A19* (8&9), 1101−1120. (d) Carraher, C. E. Jr.; Blaxall, H. S. *Angew. Makromol. Chem.* **1979**, *83*, 37−45. (e) Karak, N.; Maiti, S. *J. Polym. Mater.* **1997**, *14*, 71−78.

(12) Adrova, N. A.; Koton, M. M.; Prokhorova, L. K. *Vysokomol. Soedin.* **1964**, 9−10.

(13) See the references of, for example: (a) Champness, N. R.; Levason, W. *Coord. Chem. Rev.* **1994**, *133*, 115−127. (b) Freedman, L. D.; Doak, G. O. *J. Organomet. Chem.* **1991**, *404*, 49−85. (c) Freedman, L. D.; Doak, G. O. *J. Organomet. Chem.* **1992**, *442*, 1−60. (d) Freedman, L. D.; Doak, G. O. *J. Organomet. Chem.* **1995**, *486*, 1−20.

(14) See the references in: *Gmelin handbook of inorganic chemistry, Sb organoantimony compounds part 1*; Springer: Berlin and New York,

1981. For example: Challenger, F.; Pritchard, F.; Jinks, R. A. *J. Chem. Soc.* **1924**, *125*, 864−875.

(15) (a) Nunn, M.; Sowerby, D. B.; Wesolec, D. M. *J. Organomet. Chem.* **1983**, *251*, C45−C46. (b) Breunig, H. J.; Ebert, K. H.; Probst, J.; Mourad, Y.; Mugnier, Y. *J. Organomet. Chem.* **1996**, *514*, 149−152.

(16) Umeyama, T.; Naka, K.; Nakahashi, A.; Chujo, Y. *Macromolecules* **2004**, *37*, 1271−1275.

(17) Because of a poor solubility of *cyclo*-$(SbPh)_6$ in THF, the reaction mixture was initially heterogeneous. In the copolymerization of *cyclo*-$(SbPh)_6$ with the monosubstututed acetylenic monomers (**1a**−**1c**), the mixture became homogeneous and then the white precipitates appeared in the reaction mixture. The reason for the homogeneous solution may be due to a ring collapsing of *cyclo*-$(SbPh)_6$ by AIBN, which was observed the case of RCRAC of *cyclo*-$(AsPh)_6$. When **1d** was used as an acetylenic comonomer, no precipitate was observed after the reaction. The white precipitates was assumed to be decomposed products derived from *cyclo*-$(SbPh)_6$.

(18) Russell, G. A.; Tashtoush, H. *J. Am. Chem. Soc.* **1983**, *105*, 1398−1399.

(19) Ito, O. *J. Am. Chem. Soc.* **1983**, *105*, 850−853.

(20) Umeyama, T.; Naka, K.; Bravo, M. D.; Nakahashi, A.; Chujo, Y. *Polym. Bull. (Berlin)* **2004**, *52*, 191.

(21) Nagase, S. *The Chemistry of Organic Arsenic, Antimony, and Bismuth Compounds*; Patai, S., Ed.; John Wiley and Sons: New York, 1994; p 5.

(22) No peak was observed in a solution phase and even in a film state under following condition. In a CH_2Cl_2 solution of 0.1M $[CH_3(CH_2)_3]_4N-PF_6$ as a supporting electrolyte, the concentration of the polymer was the same order as in the case of the UV measurements, and a thin film of the polymer on an indium−tin-oxide electrode. Platinum wire auxiliary electrode and Ag/AgCl RE-5 reference electrode were used in the CV measurement.

(23) (a) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Higahara, N. *Synthesis* **1980**, *8*, 627−630. (b) Moroni, M.; Lemoigne, J.; Luzzati, S.; *Macromolecules* **1994**, *27*, 562−571.

(24) Reesor, J. W. B.; Wright, G. F. *J. Org. Chem.* **1957**, *22*, 382−385.

(25) Breunig, H. J.; Häberle, K.; Dräger, M.; Severengiz, T.; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 72−73.

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