Radical Terpolymerization of Organoarsenic Homocycle, Phenylacetylene, and Vinyl or Butadienyl Monomers

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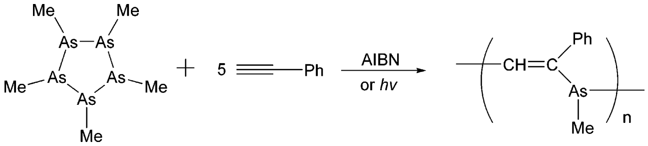
ABSTRACT: The free radical terpolymerization of pentamethylcyclopentaarsine (*cyclo*-(MA)$_5$), phenylacetylene (PA), and various vinyl monomers in toluene is described. The terpolymerization of *cyclo*-(MA)$_5$, PA, and styrene (St) in the molar ratio 1:5:5 with a catalytic amount of AIBN at 60 °C for 8 h provided a polymer in 38% yield after reprecipitation. The terpolymer was soluble in common organic solvents such as tetrahydrofuran, chloroform, benzene, and toluene. In the GPC analysis (chloroform, PSt standards), the terpolymer showed a single peak, and the number-average molecular weight was estimated to be 10 200. The structure of the terpolymer obtained was compared with those of poly(vinylene−arsine) and polystyrene by use of ^{1}H NMR and ^{13}C NMR and found to have two block units, [poly(MA-*alt*-PA)−poly(St)]. The integral ratio of the peak area in the ^{1}H NMR spectrum revealed the terpolymer composition, MA:PA:St = 1:0.99:0.56. The terpolymer showed fluorescence properties attributable to the n−π* transition in the poly(MA-*alt*-PA) block. The terpolymerization of *cyclo*-(MA)$_5$, PA, and St in various feed ratios was carried out in the presence of AIBN to yield the terpolymers which possessed poly(MA-*alt*-PA) and poly(St) blocks with various compositions. The terpolymer with the higher content of St unit exhibited a more blue-shifted emission peak. The radical terpolymerization of methyl methacrylate (MMA) with *cyclo*-(MA)$_5$ and PA also yielded the corresponding terpolymer with a poly(MA-*alt*-PA) unit and a poly(MMA) unit, while the terpolymerization employing vinyl acetate (VA) as a vinyl monomer produced poly(vinylene−arsine) with no VA segment. The radical reaction of 2,3-dimethyl-1,3-butadiene (DB) with *cyclo*-(AsMe)$_5$ and PA formed a different type of terpolymer which had alternating sequences of AsMe and PA or DB, e.g., [(MA-PA)−(MA-DB)]$_n$.

Introduction

When two monomers M$_1$ and M$_2$ are mixed together in the presence of a radical initiator, there are a number of different ways in which the monomers may combine. For the synthesis of the alternating copolymers, precise control of the propagating reaction is required, in which only the cross-reactions (M$_1$ → M$_2$ and M$_2$ → M$_1$) are repeated a number of times and no homopropagations (M$_1$ → M$_1$ and M$_2$ → M$_2$) take place. It is possible to divide the many systems of radical alternating copolymerizations reported so far into two broadly defined categories. One of them is the system with a combination of a strong electron acceptor such as maleic anhydride, *p*-quinodimethane derivatives, or sulfur dioxide, with an electron donor such as an olefin or vinyl ether.[1] Copolymerization then takes place with a terminal group control and/or through an intermediate comonomer complex, with, or sometimes without, the addition of a radical initiator. The other is the system where a copolymerization is carried out in the presence of a Lewis acid such as ZnCl$_2$ or AlEt$_n$Cl$_{3-n}$.[2] The Lewis acid acts by complexing with the electron acceptor and enhances its ability to interact with the electron donor. Many comonomer pairs, in which the relative strength of the electron donor or acceptor is insufficient, can achieve the alternating copolymerization by using a Lewis acid. Oxidation−reduction copolymerization of germylenes or stannylenes with *p*-benzoquinone derivatives is also an example of the radical alternating copolymerizations.[3]

Recently, we reported the synthesis of the novel organoarsenic polymer, poly(vinylene−arsine), by the ring-collapsed radical alternating copolymerization (RCRAC) of cyclooligoarsines, of which rings are built exclusively of arsenic atoms, with phenylacetylene (Scheme 1).[4] Poly(vinylene−arsine) is the first example of a soluble polymer containing arsenic atoms in the backbone with a well-defined structure. In this system, the radical alternating copolymerization was accomplished by a different mechanism from those mentioned above. One of the propagating radicals here is an arsenic radical which arises from the cleavage of the arsenic−arsenic bond of the arsenic homocycle. When the arsenic radical reacts with another arsenic radical, the diarsenic linkage is formed, which is unstable and tends to cause the homolysis reproducing the propagating arsenic radicals (Scheme 2a). Thus, the recombination reaction of the arsenic radicals is not a termination reaction of this copolymerization. The attack of the arsenic radical to the arsenic homocycle or the arsenic−arsenic bond also leads the labile As−As bond and a new propagating arsenic radical (Scheme 2b). In addition, the arsenic radicals never bring about disproportionation reactions. The other monomer, phenylacetylene, has the low homopolymerizability same as maleic anhydride and *p*-quinodimethane derivatives. The propagating ethynyl radical rarely attacks phenylacetylene (Scheme 2c). The recombination reaction of the ethynyl radicals seldom occurs, which is explained by the low concentration of the ethynyl radicals due to their high reactivity (Scheme 2d). Thus, the cross-reactions are repeated with the cleavage of As−As bonds to produce the alternating copolymer, poly(vinylene−arsine).

Scheme 1



In this paper, we provide various vinyl monomers coexistent for this unique radical copolymerization system

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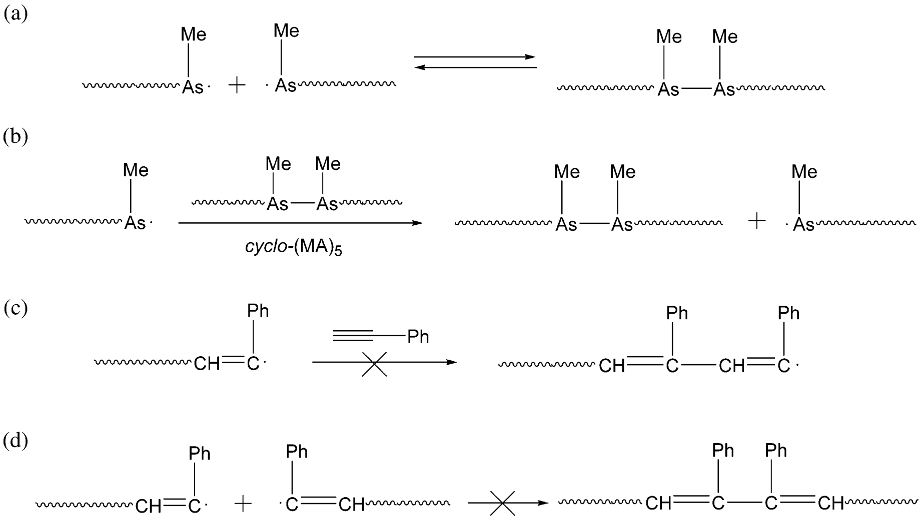
Scheme 2



of the arsenic homocycle and phenylacetylene. Recently, free radical terpolymerizations of electron-rich monomers with electron-accepting monomers, which result in terpolymers with alternating sequences of the donor and acceptor monomers, were studied intensively in view of the scientific position.[5] Here we describe the radical terpolymerization of the arsenic homocycle, phenylacetylene, and a vinyl monomer in the presence of a radical initiator. The obtained polymer was a terpolymer which possessed two block segments of poly(vinylene−arsine) and the vinyl polymer. To our knowledge, this is the first example of a terpolymer with the structure of [poly(M_1-*alt*-M_2)−poly(M_3)] synthesized by a simple radical terpolymerization of M_1, M_2, and M_3. The relationship of the terpolymer composition and optical properties was also a subject of this study. In addition, the radical terpolymerization using 2,3-dimethyl-1,3-butadiene instead of vinyl monomers was investigated.

Experimental Section

Materials. Unless otherwise noted, all reagents and chemicals were purchased from Wako Pure Chemical Industries, Ltd. Dehydrated toluene (water < 30 ppm) was bubbled with a stream of nitrogen before use. Dehydrated *n*-hexane (water <30 ppm) was used without further purification. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. Styrene (St), methyl methacrylate (MMA), and vinyl acetate (VA) were distilled under reduced pressure before use. Phenylacetylene (PA) and 2,3-dimethyl-1,3-butadiene (DB) were purchased from Aldrich and purified by distillation under reduced pressure. Pentamethylcyclopentaarsine (*cyclo*-$(MA)_5$) was synthesized using a literature procedure.[6]

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). UV−vis spectra were measured on a JASCO V-530 spectrometer, and samples were analyzed in $CHCl_3$ at room temperature. Fluorescence emission spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer, and samples were analyzed in $CHCl_3$ at room temperature. Gel permeation chromatography 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.

Polymerization. Terpolymerization of *cyclo*-(MA)$_5$, PA, and St with AIBN as a Radical Initiator. To a solution of *cyclo*-$(MA)_5$ (0.569 g, 1.27 mmol) and St (0.658 g, 6.33 mmol) in toluene (2.0 mL) was added a solution of PA (0.646 g, 6.33 mmol) and AIBN (0.030 g, 0.18 mmol) in toluene (0.5 mL) at room temperature. The mixture was immediately heated at 60 °C and stirred. The flask for PA and AIBN was rinsed with toluene (0.5 mL), and the resulting toluene solution was added to the reaction mixture. After stirring for 8 h at 60 °C, the mixture was cooled at room temperature and then poured into *n*-hexane to precipitate a polymeric material, which was purified twice by reprecipitation from toluene to *n*-hexane. After freeze-drying for 10 h, the polymer was obtained as a light yellow powder (0.726 g, 38% yield). ^{1}H NMR (δ, ppm): 6.95−7.50 (ArH_m and ArH_p of PA, ArH_m and ArH_p of St), 6.70−6.95 (ArH_o of PA), 6.40−6.70 (ArH_o of St), 6.05−6.40 ((*E*)- and (*Z*)-C═C*H*), 1.70−2.00 ($-CH_2-$), 1.25−1.70 (−CH−), 1.05−1.20 ($-CH_3$ from AIBN), 0.50−1.05 ($-CH_3$). ^{13}C NMR (δ, ppm): 158.8, 152.5 ((*E*)- and (*Z*)-*C* ═CH), 145.1 (CH_2-CH-C_{Ar} of St), 141.4 ($CH{=}C-C_{Ar}$ of PA), 139.2, 138.2 ((*E*)- and (*Z*)-C═C*H*), 127−130 ($C_{Ar}H_m$ and $C_{Ar}H_p$ of PA, $C_{Ar}H_m$ and $C_{Ar}H_p$ of St), 126.7 ($C_{Ar}H_o$ of PA), 125.6 ($C_{Ar}H_o$ of St), 41−46 ($-CH_2-$), 40.4 (−CH−), 10.2 ($-CH_3$).

Terpolymerization of *cyclo*-(MA)$_5$, PA, and MMA. In toluene (3.0 mL in total), *cyclo*-$(MA)_5$ (0.561 g, 1.25 mmol), MMA (0.625 g, 6.24 mmol), PA (0.637 g, 6.24 mmol), and AIBN (0.030 g, 0.18 mmol) were employed. The terpolymerization and purification were carried out as described above, and the corresponding polymer was obtained (1.02 g, 56% yield). ^{1}H NMR (δ, ppm): 7.08−7.58 (ArH_m, ArH_p), 6.82 (ArH_o), 6.05−6.55 ((*E*)- and (*Z*)-C═C*H*), 3.60 ($-OCH_3$), 1.80−2.20 ($C-CH_3$), 1.2−1.6 ($-CH_3$ from AIBN), 1.03 ($-CH_2-$), 0.84 ($As-CH_3$).

Terpolymerization of *cyclo*-(MA)$_5$, PA, and DB. In toluene (3.0 mL in total), *cyclo*-$(MA)_5$ (0.561 g, 1.25 mmol), PA (0.637 g, 6.23 mmol), DB (0.512 g, 6.23 mmol), and AIBN (0.030 g, 0.18 mmol) were employed. The terpolymerization and purification were carried out as described above, and the corresponding polymer was obtained (0.578 g, 34% yield). ^{1}H NMR (δ, ppm): 7.05−7.60 (ArH_m and ArH_p), 6.65−7.05 (ArH_o), 6.05−6.60 ((*E*)- and (*Z*)-C═C*H*), 2.02 ($-CH_2-$), 1.25−1.70 (−CH−), 1.65 (C−CH_3), 0.78 (As−CH_3). ^{13}C NMR (δ, ppm): 148.2. 145.8 ((*E*)- and (*Z*)-*C*═CH), 141.6 ($CH{=}C-C_{Ar}$), 139.4, 138.4 ((*E*)- and (*Z*)-C═C*H*), 126−131 ($C_{Ar}H_o$, $C_{Ar}H_m$, and $C_{Ar}H_p$ of PA, −*C*Me═*C*Me−), 33.1 ($-CH_2-$), 18.5 (C−CH_3), 10.2 ($As-CH_3$).

Results and Discussion

Terpolymerization of *cyclo*-(MA)$_5$ with PA and St. The radical terpolymerization of *cyclo*-$(MA)_5$ with PA and St in the feed ratio 1:5:5 was conducted in toluene at 60 °C in the presence of a catalytic amount of AIBN (Scheme 3, R_1 = H, R_2 = Ph). After stirring for

Scheme 3

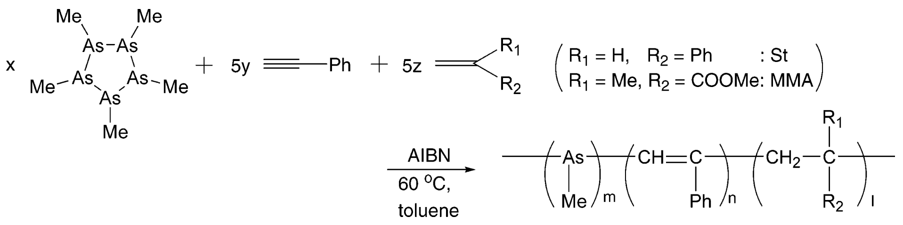


Table 1. Results of Terpolymerization of *cyclo*-(Ma)$_5$, PA, and St in Various Feed Ratios or at Various Temperatures

run	x:y:z[a]	temp (°C)	M_w[b]	M_n[b]	M_w/ M_n[b]	yield (%)[c]	m:n:l[d]
1	1:1:1	60	13 900	10 200	1.4	38	1:0.99:0.56
2	1:1:0.11	60	13 800	9 800	1.4	45	1:1.00:0.06
3	1:1:0.33	60	11 000	9 300	1.2	39	1:1.00:0.10
4	1:1:0.67	60	11 000	7 700	1.4	37	1:1.00:0.25
5	1:1:3	60	15 100	11 100	1.4	44	1:1.02:2.58
6	1:1:9	60	24 800	15 500	1.6	41	1:1.05:6.35
7	1:0.33:1	60				0	
8	1:0.67:1	60	7 300	6 300	1.2	28	1:1.01:0.13
9	1:2:1	60	12 400	10 000	1.2	29	1:1.09:0.10
10	0.25:1:1	60	14 900	11 000	1.3	13	1:1.09:0.26
11	0.5:1:1	60	14 500	11 400	1.3	22	1:1.04:0.14
12	2:1:1	60	8 200	7 300	1.1	5	1:1.00:0.00
13	1:1:1	45	19 400	14 900	1.3	37	1:1.05:0.00
14	1:1:1	75	11 100	8 400	1.3	41	1:1.04:0.70
15	1:1:1	90	13 000	9 700	1.4	37	1:1.00:0.51

[a] Molar ratio of the fed monomers. [b] Estimated by GPC analysis in chloroform on the basis of polystyrene standards. [c] Isolated yield after reprecipitation from toluene to hexane, (weight of the obtained polymer)/(total weight of the monomers). [d] Estimated by ^{1}H NMR.

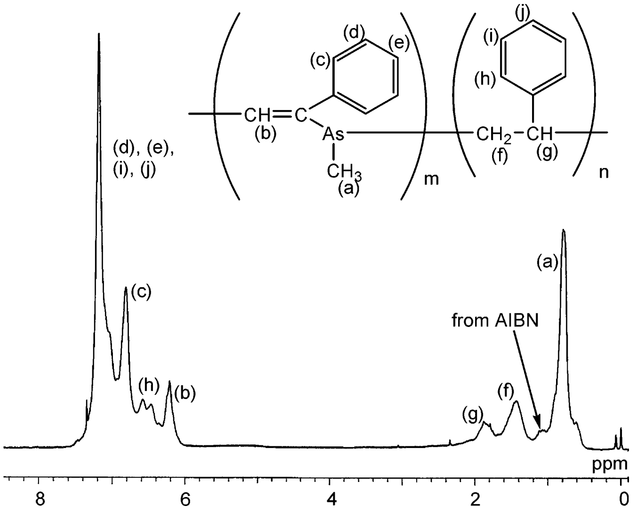


Figure 1. ^{1}H NMR spectrum of **1** recorded in $CDCl_3$.

8 h, the reaction mixture was cooled to room temperature and then added to *n*-hexane to precipitate a polymer. The polymer obtained was purified by reprecipitation from toluene to *n*-hexane twice and freeze-dried for 10 h to yield the polymer **1** as a light yellow powder in 38% yield. The resulting polymer **1** was highly soluble in common organic solvents including THF, $CHCl_3$, toluene, etc., and easily cast on a glass plate to give a film. The GPC ($CHCl_3$) trace of **1** showed a single peak. The number-average molecular weight of **1**, determined by GPC ($CHCl_3$) using polystyrene standard, was 10 200 (Table 1, run 1) with polydispersity index of 1.4.

Characterization by ^{1}H and ^{13}C NMR Spectra. Figures 1 and 2 show the ^{1}H and ^{13}C NMR spectra of **1** recorded in $CDCl_3$ at room temperature. Both of the spectra exhibit the peaks attributable to polystyrene in addition to the peaks from poly(vinylene−arsine). No obvious peaks were observed other than those peaks. These observations suggest that the terpolymer **1** was composed of two block segments of poly(vinylene−arsine) and polystyrene (Chart 1, $R_1 = H$, $R_2 = Ph$). In the ^{1}H NMR spectrum, two main groups of the peaks associated with chemical shifts at 1.0−2.2 and 6.1−7.5 ppm can be attributed to the aliphatic groups and the aromatic and vinyl protons, respectively. The assignments of these peaks are given in Figure 1. The integral ratio of these peaks revealed that the composition of **1** was methylarsine (MA):PA:St = 1:0.99:0.56. The molar quantities of MA and PA unit in the terpolymer were almost equal, which also ensured the structure in Chart 1. The content of the St unit in the terpolymer was smaller than the monomer feed ratio of St. The ^{13}C NMR spectrum (Figure 2) of **1** shows peaks at 152−159 and 138−140 ppm attributable to the vinyl carbons. Each area has two peaks derived from the cis and trans isomers. Only one sharp resonance for AsCH_3, of which the assignment was supported by the DEPT spectrum, is observed at 10.2 ppm in Figure 2, suggesting that the copolymerization of *cyclo*-(MA)$_5$ with PA proceeded highly alternatingly to produce the poly(vinylene−arsine) segment.

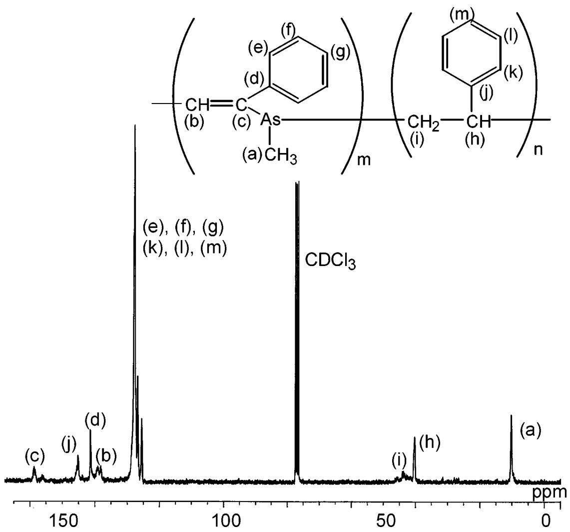
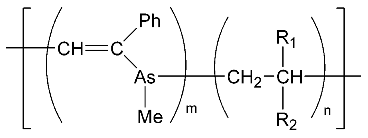


Figure 2. ^{13}C NMR spectrum of **1** recorded in $CDCl_3$.

Chart 1



Copolymerization of Two Monomers out of *cyclo*-(MA)$_5$, PA, and St. To investigate the reactivity of *cyclo*-(MA)$_5$, PA, and St to each other, we treated two monomers out of the three in the presence of a catalytic amount of AIBN at 60 °C. As mentioned previously, the radical reaction between *cyclo*-$(MA)_5$ and PA produced the alternating copolymer, poly(vinylene−arsine).[4] The treatment of *cyclo*-$(MA)_5$ with St resulted in the formation of purple-black precipitate which was insoluble in all solvents. Since the precipitate was insoluble and fuming in the air, we have suspended the full characterization of the mixture. It can, however, be presumed from the appearance that the precipitate was linear poly(methylarsine) which stacked with each other to form a ladder structure.[7] No polystyrene or copolymer containing the styrene unit was obtained. Though it remains to be seen whether radical species from AIBN reacted with *cyclo*-$(MA)_5$ or St, *cyclo*-$(MA)_5$ inhibited the radical polymerization of St. Stirring a mixture of the equimolar amount of PA and St with a catalytic amount of AIBN in toluene at 60 °C brought about a polymeric material. After reprecipitation from toluene to methanol (yield 9%), the molecular weight of the copolymer was estimated by GPC ($CHCl_3$, polystyrene standard) and found to be low ($M_n = 1800$, with polydispersity index of 1.3). This result suggests that the homopropagation of St was inhibited by PA which had low homopolymerizability under this condition.

Mechanism of the Terpolymerization. In the terpolymerization system of *cyclo*-$(MA)_5$ with PA and St, the following elementary reactions can be proposed in the initiation and chain-growth reactions:

initiation

$$R^{\bullet} + (MA)_5 \rightarrow {}^{\bullet}MA^{\bullet},\ {}^{\bullet}MA{-}MA^{\bullet},\ {}^{\bullet}MA{-}(MA)_n{-}MA^{\bullet} \qquad (1)$$

$$R^{\bullet} + PA \rightarrow R{-}PA^{\bullet} \qquad (2)$$

$$R^{\bullet} + St \rightarrow R{-}St^{\bullet} \qquad (3)$$

propagation

$$\sim MA^{\bullet} + MA \rightarrow \sim MA{-}MA^{\bullet} \qquad (4)$$

$$\sim MA^{\bullet} + PA \rightarrow \sim MA\ {-}PA^{\bullet} \qquad (5)$$

$$\sim MA^{\bullet} + St \rightarrow \sim MA{-}St^{\bullet} \qquad (6)$$

$$\sim PA^{\bullet} + MA \rightarrow \sim PA{-}MA^{\bullet} \qquad (7)$$

$$\sim PA^{\bullet} + PA \rightarrow \sim PA{-}PA^{\bullet} \qquad (8)$$

$$\sim PA^{\bullet} + St \rightarrow \sim PA{-}St^{\bullet} \qquad (9)$$

$$\sim St^{\bullet} + MA \rightarrow \sim St{-}MA^{\bullet} \qquad (10)$$

$$\sim St^{\bullet} + PA \rightarrow \sim St{-}PA^{\bullet} \qquad (11)$$

$$\sim St^{\bullet} + St \rightarrow \sim St{-}St^{\bullet} \qquad (12)$$

Among the three initiation reactions, (2) is improbable due to the low reactivity of PA with the carbon radical from AIBN.[4] Thus, the initiations of the terpolymerization are competitive reactions of (1) and (3). The ^1H NMR spectrum of **1** (Figure 1) showed the peaks due to the terminal AIBN, which did not appear in that of poly(vinylene−arsine) but in that of polystyrene. This result also ensures that the initialization reaction of the terpolymerization includes the attack of radicals from AIBN on St monomer.

The propagation reactions of (5) and (7) proceed readily as well as (12), which was evidenced in the previous report.[4] Since the arsenic−arsenic bond is unstable and easily cleaved to reproduce the arsenic radicals, reaction 4 is excluded from the chain growth. Though the elementary reactions of (6), (8), (9), (10), and (11) can be included in the propagation reactions of the terpolymerization, the frequencies of them are much lower than those of the other chain-growth reactions, which is presumed by the results of the binary copolymerizations described above. This is also supported experimentally by the ^1H and ^{13}C NMR spectra which suggest the structure of the terpolymer with two block segments, poly(MA-*alt*-PA) and poly(St). The reactions of (6), (9), (10), and (11) with low frequencies make the connecting point of the two blocks. The possibility of these reactions in the terpolymerization will be discussed in the next section.

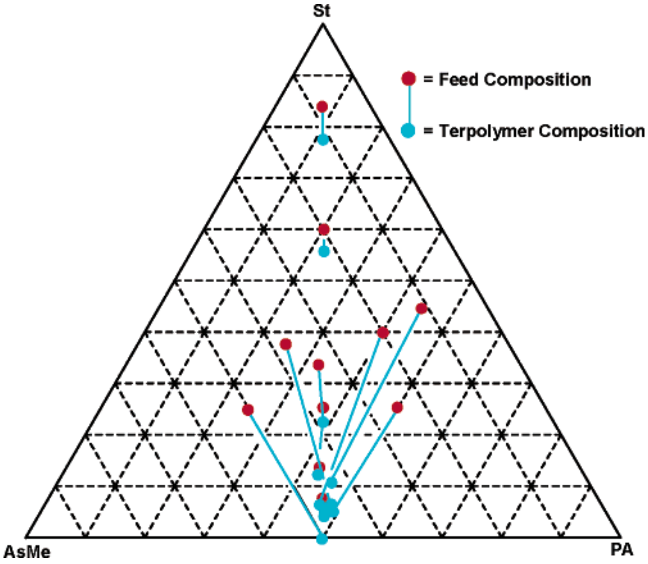


Figure 3. Monomer−terpolymer composition diagram: (red circles) for monomer feed ratio and (blue circles) for terpolymer composition.

Terpolymerization of *cyclo*-$(MA)_5$ with PA and St in Various Monomer Feed Ratios or at Various Temperatures. The radical terpolymerization of *cyclo*-$(MA)_5$ with PA and St using AIBN was carried out in various monomer feed ratios. The results of molecular weights, yields, and terpolymer compositions of the resulting polymers are listed in Table 1. In the Slocombe plot (Figure 3) based on the results in Table 1, the feed composition (red circle) and the terpolymer composition (blue circle) are shown. As can be seen, all blue circles are nearly on the perpendicular line which represents the equimolar amount of the MA and PA units. The ^1H and ^{13}C NMR spectra of the obtained polymers exhibited the peaks of poly(vinylene−arsine) unit and polystyrene unit, suggesting that the terpolymer had the two block segments. In every case the blue circle is located below the corresponding red circle, indicating that the content of St unit in the terpolymer was less than the feed ratio of St. In run 7 where the feed ratio was MA:PA:St = 1:0.33:1, no copolymer or terpolymer but purple-black precipitate was obtained. As in the reaction of *cyclo*-$(MA)_5$ and St, MA acted as a polymerization inhibitor. Similarly to this, the radical reaction in run 12 (feed ratio MA:PA:St = 2:1:1) yielded the alternating copolymer of MA and PA with no St unit in low yield. The terpolymerization in run 9 (feed ratio MA:PA:St = 1:2:1) gave the terpolymer with low content of St unit (terpolymer composition MA:PA:St = 1:1.01:0.13) in comparison with run 1. Under the condition where an excess amount of PA was employed, the chain transfer

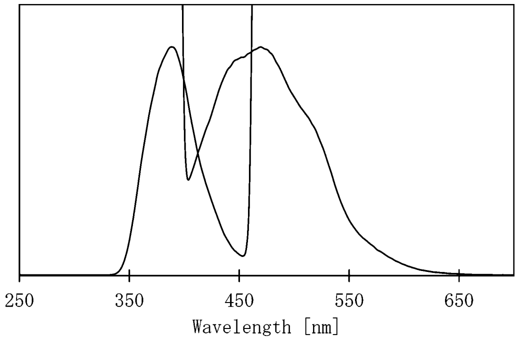


Figure 4. Emission ((a), excited at 388 nm) and excitation ((b), emitted at 470 nm) spectra of **1** recorded in chloroform at room temperature.

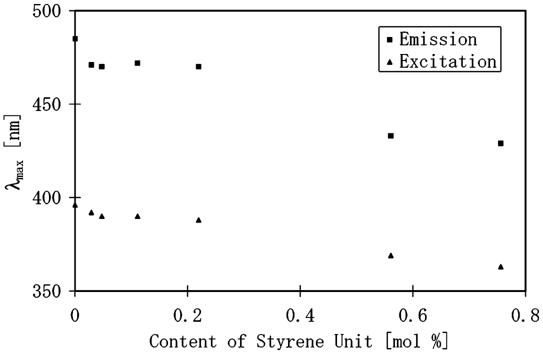


Figure 5. Effect of content of St unit in the terpolymer obtained in runs 1−6 on λ_{max} in emission (■) and excitation (▲) spectra.

of polymer St radical with PA monomer (propagation (11)) was caused more often than in run 1.

The terpolymerization of MA with PA and St in the feed ratio 1:1:1 was performed at various temperatures (runs 1 and 13−15). The radical reaction above 60 °C (runs 1, 14, and 15) produced the terpolymer composed of two block segments. The reaction at 45 °C (run 13), in contrast, resulted in the poly(vinylene−arsine) with no St unit. It turned out that the initiation reaction 1 proceeded in preference to (3), and the chain transfer of MA and PA radical to St (propagation (6) and (9)) was excluded at this temperature.

Optical Properties of the Terpolymers. In accordance with the fact that the terpolymer possesses the poly(vinylene−arsine) unit in the backbone, the terpolymer showed optical properties which are analogous to those of the poly(vinylene−arsine).[4] The solution of the terpolymer **1** in chloroform exhibited not only the strong absorption in the region < 360 nm derived from $\pi-\pi^*$ transition but also the weak absorption in the region > 360 nm. The absorption edge was located at around 500 nm. We attribute the latter lower energy absorption to the $n-\pi^*$ transition in the poly(vinylene−arsine) block. The dilute chloroform solution of **1** exhibited the emission with a maximum peak at 470 nm by irradiation at 470 nm (Figure 4). The excitation spectrum of **1** emitted at 470 nm showed a peak at 388 nm but no absorption in the region < 340 nm (Figure 4). This result suggests that the emission of **1** arises from only the $n-\pi^*$ transition in the poly(vinylene−arsine) segment. Figure 5 presents the emission or excitation peaks as a function of the content of St unit in the terpolymer (runs 1−6). The data reveal that the increase of St unit in the terpolymer causes blue shift of the peaks in both emission and excitation spectra. Though it remains to be seen how long the effective conjugation length of poly(vinylene−arsine) is, the terpolymer with high ratio of St unit has shorter chain of poly(vinylene−arsine) than the effective conjugation length.

Radical Terpolymerization of *cyclo*-$(MA)_5$, PA, and Other Vinyl or Butadienyl Monomers. We performed the radical terpolymerization of *cyclo*-$(MA)_5$, PA, and methyl methacrylate (MMA) in the feed ratio MA:PA:MMA = 1:1:1 (Scheme 3, R_1 = Me, R_2 = COOMe). After the reprecipitation, a polymer was obtained as a light yellow powder (yield 56%). The polymer showed a single peak in the GPC trace, and the number-average molecular weight using polystyrene standard was 12 500 with the polydispersity index of 1.5. By characterization with ^1H and ^{13}C NMR spectra, the resulting polymer was terpolymer with two block segments, poly(vinylene−arsine) and poly(MMA). The peak area ratio in the ^1H NMR spectrum revealed that the composition of the two blocks was 1:0.48. On the other hand, the radical reaction of *cyclo*-$(MA)_5$ with PA and vinyl acetate (VA) under the same conditions yielded poly(vinylene−arsine). No poly(VA) or copolymer containing VA unit was obtained, whereas VA can be homopolymerized in toluene at 60 °C with a catalytic amount of AIBN. Since VA has no substitution group with resonance effect, the reactivity of the vinyl group of VA is low compared to that of St or MMA. Thus, no initiation reaction of AIBN with VA or chain-transfer reaction to VA took place.

We also employed 2,3-dimethyl-1,3-butadiene (DB) as a monomer instead of the vinyl monomer and carried out the radical terpolymerization with *cyclo*-$(MA)_5$ and PA using AIBN in toluene at 55 °C (Scheme 4). After the reprecipitation a polymeric material (**2**) was obtained as a white powder in 34% yield. The resulting polymer showed a single peak in the GPC trace. The GPC analysis using polystyrene standards estimated the number-average molecular weight of **2** to be 6900 with polydispersity index of 1.8 (Table 2, run 16). Figure 6 shows the ^1H NMR spectrum of **2**.[8] In addition to the peaks due to the aromatic and vinyl protons and the methyl group attached to the arsenic atom, two peaks are observed in the aliphatic region of the spectrum. The ^{13}C NMR spectrum of **2** (Figure 7) also exhibits a few aliphatic peaks besides the peaks identical to poly(vinylene−arsine). One of the additional peaks is assigned to $AsCH_3$ next to the butadienyl unit.[8] From the peak area ratio in the ^1H NMR spectrum, the terpolymer composition of **2** is calculated to be MA:PA:DB = 1:0.91:0.10 (Table 2, run 17). In contrast to **1**, the content of MA in the terpolymer was not same as that of PA but almost same as the sum of the content of PA and DB. The radical terpolymerization in run 15, where twice the molar amount of DB as that of PA was employed, produced the terpolymer with the composition MA:PA:DB = 1:0.84:0.14 (Table 2, run 17). The terpolymer obtained here also contained about 50 mol % of MA unit. From these results we assume that the terpolymer possess the structure with alternating sequences of MA unit and PA or DB unit (Chart 2) in a similar manner with the complex-radical terpolymerization of acceptor−donor−acceptor or donor−acceptor−donor monomer systems.[5] Whereas the radical reaction of MA with St yielded the poly(MA) with the ladder structure, the reaction of MA and DB with heat or under the irradiation of an incandescent lamp produced a cyclic diarsine compound, 1,2,4,5-tetramethyltetrahy-

Scheme 4

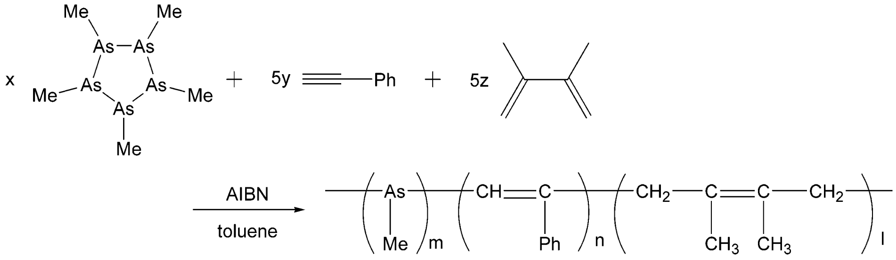


Table 2. Results of Terpolymerization of *cyclo*-(MA)$_5$, PA, and DB in Various Feed Ratios

run	x:y:z^a	temp (°C)	$M_w{}^b$	$M_n{}^b$	$M_w/M_n{}^b$	yield (%)^c	m:n:l^d
16	1:1:1	55	12700	6900	1.8	34	1:0.91:0.10
17	1:1:2	55	9000	5900	1.5	27	1:0.84:0.14
18	1:1:3	55				trace	

[a] Molar ratio of the fed monomers. [b] Estimated by GPC analysis in chloroform on the basis of polystyrene standards. [c] Isolated yield after reprecipitation from toluene to hexane, (weight of the obtained polymer)/(total weight of the monomers). [d] Estimated by ^{1}H NMR.

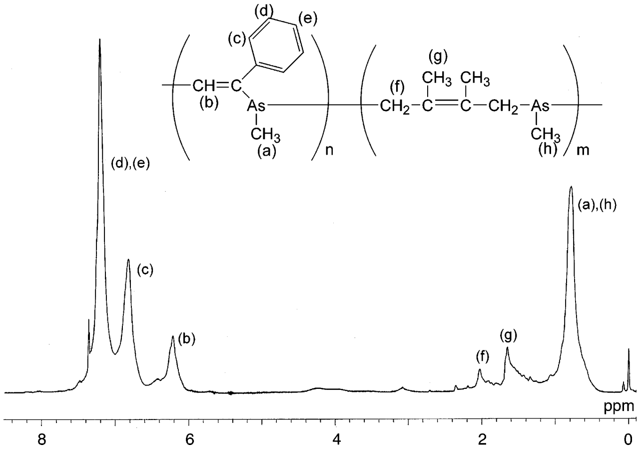


Figure 6. ^{1}H NMR spectrum of **2** recorded in CDCl$_3$.

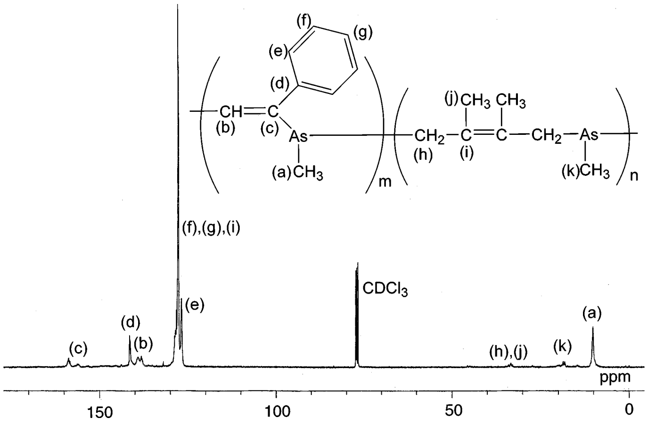
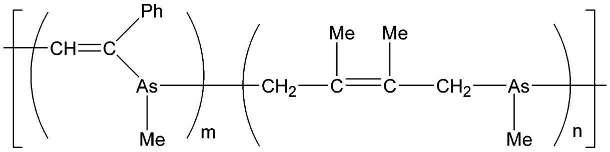


Figure 7. ^{13}C NMR spectrum of **2** recorded in CDCl$_3$.

Chart 2



drodiarsine.[9] The treatment of the cyclic compound with PA in the presence of AIBN or irradiation of the incandescent lamp produced no polymeric material. It turns out, therefore, that the terpolymerization of MA with PA and DB proceeded without the cyclization. It can be presumed that the "alternating terpolymerization" of MA, PA, and DB was achieved by the preferential reactivity of PA and DB polymer radical to MA and that of MA polymer radical to PA and DB. The terpolymerization in the feed ratio MA:PA:DB = 1:1:3 resulted in no polymeric material (Table 2, run 18) since the high concentration of butadienyl radical caused easily the recombination reaction to terminate the polymerization.

Summary

We describe here a radical terpolymerization of *cyclo*-(MA)$_5$, PA, and a vinyl monomer. In the case of employing St or MMA as a vinyl monomer, a terpolymer with poly(vinylene−arsine) and poly(St) or poly(MMA) segments in the backbone was obtained. The terpolymer was formed by chain-transfer-type reactions of polymer MA or PA radical with the vinyl monomer and of polymer vinyl radical with MA or PA. Though the ratio of the chain-transfer reactions is unclear, this terpolymerization system is unique in the respect that it gave a terpolymer with two kinds of blocks by the simple treatment of three kinds of monomers. One of the blocks is an alternating copolymer, and the other is a homopolymer. The obtained terpolymer showed fluorescent properties due to the poly(vinylene−arsine) block, and the emission peak could be tuned by varying the monomer feed ratio. The radical reaction of *cyclo*-(MA)$_5$ with PA and DB, in contrast, produced the random copolymer with MA−PA and MA−DB units.

Although the further investigations on the mechanism such as kinetic studies of elementary reactions are needed, these terpolymerizations are useful for the synthesis of organoarsenic polymers with various functional groups.

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