Macromolecules **2004,** *37,* 1271−1275 **1271**

Radical Copolymerization of Acetylenic Compounds with Phenyl-Substituted Cyclooligoarsine: Substituent Effect and Optical Properties

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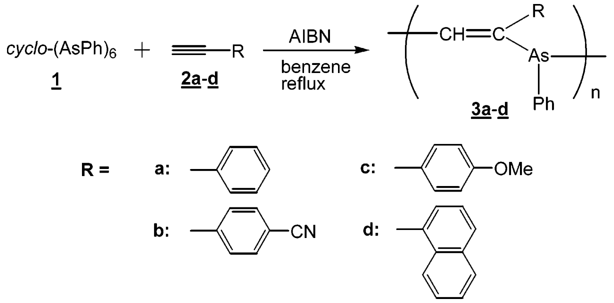
Received August 29, 2003; Revised Manuscript Received December 5, 2003

ABSTRACT: The radical reaction between hexaphenylcyclohexaarsine (**1**) and acetylenic compounds with various substituents (**2a**−**d**) using a catalytic amount of AIBN provided the corresponding alternating copolymer, poly(vinylene−arsine). The copolymers obtained were soluble in common organic solvents such as THF, chloroform, benzene, and toluene. From gel permeation chromatographic analysis (chloroform, PSt standards), the number-average molecular weights of the copolymers were found to be several thousands. Structural characterization of the copolymers was provided by ^{1}H and ^{13}C NMR spectroscopies. The measurement of the conversion rate of **2a**−**d** during the copolymerization by using gas chromatography gave an evidence to support the assumption that the formation of vinyl radicals by addition of arsenic radicals to acetylenic compounds was the rate-determining step in this copolymerization system. The copolymer obtained showed fluorescence properties which were influenced by the substituents of the acetylenic compounds.

Introduction

Polymers containing inorganic elements in the main chain structure are of current interest as a result of their unique properties.[1] For example, phosphorus-containing polymers have found a variety of important uses including flame retardants,[2] ionic conducting materials,[3] and easily separable supports for metal catalysts.[4] Recently, conjugated organophosphorus polymers were synthesized and showed interesting features such as significant extension of conjugation along the polymer backbone via the lone pair on P, fluorescent properties, and electron-donating character.[5] On the other hand, the organoarsenic chemistry has a long history that dates back to the synthesis and discovery in 1760 of the first organometallic compound, $Me_2AsAsMe_2$, by L. C. Cadet de Gassicourt.[6] The discovery of the medicinal action of organoarsenicals on syphilis in 1910 led to a rapid expansion of the work on arsenic derivatives. Since an alternative cure was developed in 1940s, less attention has been paid to chemotherapy roles and more to structures, stereochemistry, and donor properties of organoarsenic compounds. In the abundant accumulation of the organoarsenic chemistry, however, the incorporation of arsenic into polymer backbones has been limited.[7]

Scheme 1



The development of a new polymerization reaction makes it possible to create polymers having a unique structure which is difficult to construct by conventional procedures. As a part of our program to explore the synthesis and properties of inorganic and organometallic polymers,[5c,8] we recently reported the radical alternating copolymerization of arsenic homocycle (**1**) as arsenic atomic biradical equivalent with phenylacetylene (**2a**) to yield a first soluble organoarsenic polymer, poly(vinylene−arsine) (**3a**).[9] This was quite different from conventional radical alternating copolymerizations, which are achieved by donor−acceptor monomer pairs[10,11] In this paper, in addition to **2a**, we employed new comonomers—4-cyanophenylacetylene (**2b**), 4-methoxyphenylacetylene (**2c**), 1-naphthylacetylene (**2d**), and 1-hexyne (**2e**)—and investigated copolymerization behaviors of **2a**−**e** with hexaphenylcyclohexaarsine (**1**) to consider the copolymerization mechanism. In addition, we report here interesting optical properties of the copolymers obtained.

Results and Discussion

Synthesis and Characterization of Polymers. Copolymerization of **1** and **2a**−**d** was carried out in refluxing benzene using 2,2′-azobis(isobutyronitrile) (AIBN) as a radical initiator (Scheme 1). The copolymers obtained were purified by reprecipitation from benzene to *n*-hexane. The results of the copolymerization are summarized in Table 1. In the case that 1-hexyne (**2e**) was treated with **1** and AIBN in refluxing benzene, no high-molecular-weight material was obtained after stirring for 12 h. The structures of polymers **2a**−**d** were confirmed by ^{1}H and ^{13}C NMR spectra. The ^{1}H NMR spectrum of **2b** showed broadened peaks around 5.9−7.8 ppm which were assigned to aromatic protons and vinyl proton. The signal due to the acetylenic proton of the monomer **2b**[12] completely disappeared, indicating that the ethynyl group of **2b** was converted to vinyl groups in the main chain of copolymer **3b**. To confirm that the cyano group of **2b** has no reactivity toward **1** or AIBN, we treated a mixture of **1** and benzonitrile

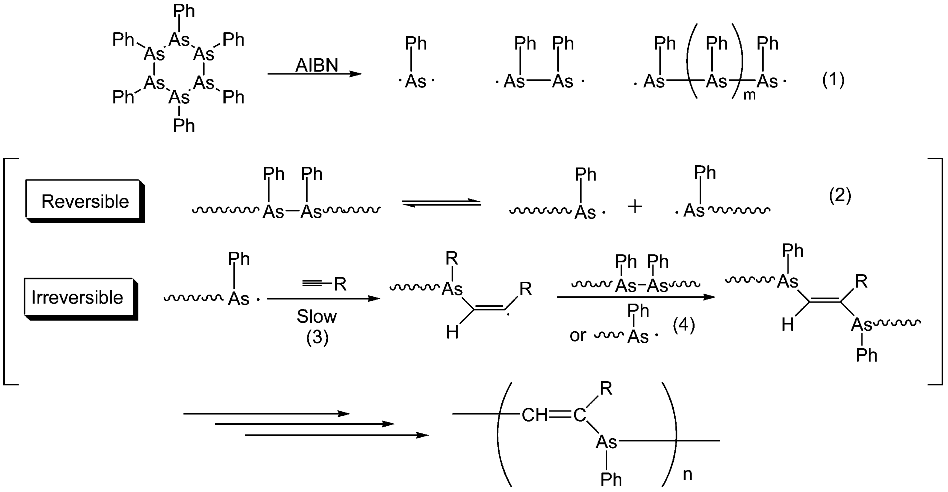
10.1021/ma035282c CCC: $27.50

Table 1. Syntheses and Optical Properties of Polymers 3a−e

run	**2**	M_w[a]	M_n[a]	M_w/M_n[a]	yield (%)[b]	DP[c]	emission λ_{max} (nm)[d]	excitation λ_{max} (nm)[d]
1	**2a**	5600	3900	1.4	35	15	437	375
2	**2b**	15100	8400	1.8	29	30	443, 466	394
3	**2c**	5100	3700	1.4	22	13	402	341
4	**2d**	9900	7600	1.3	33	25	350	315
5	**2e**	no polymer						

[a] GPC ($CHCl_3$). Polystyrene standards. [b] Isolated yields after reprecipitation into *n*-hexane. [c] Degree of polymerization. [d] Recorded in dilute $CHCl_3$ solutions at room temperature.

Scheme 2



with AIBN in refluxing benzene. After stirring for 12 h, benzonitrile remained intact according to gas chromatography. Consistently, the ^{13}C NMR spectrum of **3b** showed no peaks corresponding to the ethynyl group (around 81 ppm),[12] but the peaks of vinyl group at 136 (−***C***H=C−) and 158 ppm (−CH=***C***−). The molecular weight measurements were performed by gel permeation chromatography (GPC) in $CHCl_3$ eluent using a calibration curve of polystyrene standards (Table 1). The number-average molecular weight (M_n) of **3b** was estimated to be 8400, which corresponds to a degree of polymerization of 30, with $M_w/M_n = 1.8$. All the copolymers **3a**−**d** were soluble in common organic solvents such as THF, $CHCl_3$, benzene, and toluene. These polymers were stable to oxygen and water on exposure to air for several months.

Discussion of the Copolymerization Mechanism. The reaction mechanism in Scheme 2 was proposed for the radical alternating copolymerization as discussed in the previous report.[9] First, AIBN cleaved arsenic−arsenic bonds of **1** to produce arsenic radicals. Second, the homolysis of the other arsenic−arsenic bonds proceeded spontaneously due to their instability by the destruction of the quite stable six-membered-ring structure. In competition with this reaction, an arsenic radical added to an acetylenic compound to give a vinyl radical. Next, a vinyl radical reacted immediately with an arsenic−arsenic bond or with an arsenic radical to form a new carbon−arsenic bond. Although the carbon−arsenic bond formation seems to result in losing a growing radical and no chain growth proceeds anymore, the labile As−As bonds in the product caused homolysis easily to produce a new arsine radical, and the chain growth could restart. In this manner, repeating production of the arsine radical by the As−As bond cleavage and its addition to the acetylenic compound leads to a polymer with a simple main-chain structure, poly(vinylene−arsine). Since the vinyl radicals are more instable and reactive than the arsenic radicals, formation of the vinyl radicals (eq 3) should be relatively slower than creation of the arsine radical (eq 2) and of a carbon−arsenic bond (eq 4). One of the propagating radicals in this copolymerization system is the vinyl radical, which might not cause recombination due to the low concentration. The vinyl radical might not react with the acetylenic compound to produce a new vinyl radical because of its instability but reacts with an arsenic radical or an arsenic−arsenic bond. The other propagating radical is the arsenic radical which cannot cause disproportionation as a termination reaction. A recombination of the arsenic radical generates an As−As bond which is easily cleaved under the benzene refluxing condition to reproduce the propagating arsenic radicals.

Radical reaction of 1-hexyne (**2e**) with **1** provided no high molecular weight materials (Table 1), suggesting that the alkyl-substituted vinyl radical was too unstable to be formed. The aromatic stabilization of the vinyl radical is essential for the copolymerization. We speculate that the more effectively aromatic stabilization acts on the vinyl radical, the more smoothly the copolymerization progresses. Here are shown the examination of the rates of conversion of monomers **2a**−**d** during the copolymerization with **1**. The radical copolymerization of **2a**−**d** with **1** was carried out in the presence of *n*-alkane as a reference material to monitor the amount of consumption of monomers **2a**−**d** by using gas chromatography (GC). In each experiment, the same concentrations of AIBN (0.006 mol/L), **1** (0.060 mol/L), acetylenic compound (0.36 mol/L), and *n*-alkane (0.04 g/L) were used in benzene at 78 °C. The moment of feeding AIBN to the mixture of **1** and acetylenic compounds **2a**−**d** in refluxing benzene was defined as initiating point (0 min) of the copolymerization. All of the experiments were performed three times, and the average values are presented with error bars in Figure 1. In every copolymerization, the consumption of acety-

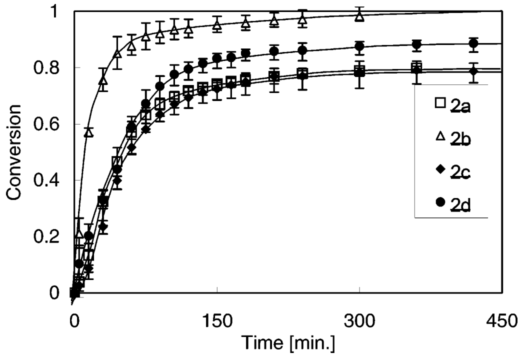


Figure 1. Time−conversion plots of **2a**−**d** during the copolymerization with **1**.

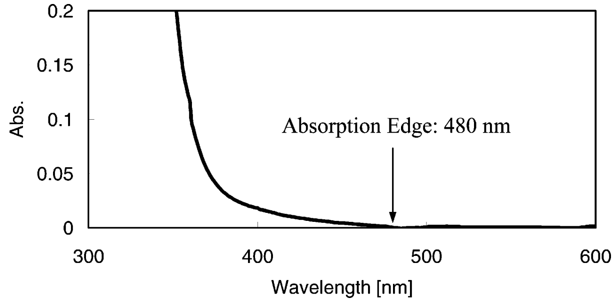


Figure 2. UV−vis absorption spectrum of **2b** in $CHCl_3$ at room temperature.

lenic monomers **2a**−**d** was induced smoothly by addition of AIBN and almost ceased in 4 h. In the case of using cyano-substituted phenylacetylene **2b**, the polymerization proceeded to reach nearly quantitative conversion. The rate increased in the order **2c** < **2a** < **2d** < **2b**. The copolymerization of **1** with **2b** or **2d** was faster than that with **2a** because the aromatic stabilization of the vinyl radical by 4-cyanophenyl or naphthyl group is stronger than that by phenyl group. The copolymerization of **1** with **2c** was slightly slower than that with **2a**, suggesting that electrostatic effect of the substituent might affect the reaction between arsenic radical and carbon−carbon triple bond. The arsenic radical may prefer to react with electron-accepting monomers rather than electron-donating monomers due to the lone pair on the arsenic atom. Both conjugative and electrostatic effects of the 4-cyanophenyl group made the fastest consumption of **2b** during the copolymerization with **1** among the acetylenic monomers employed here. The GC analyses suggest that the less activation energy of reaction 3 (formation of the vinyl radical) results in the more rapid progress of the total copolymerization. These results are consistent with our speculation and therefore support the mechanism of the copolymerization as proposed above.

Optical Properties of Polymers 3a−d. The electronic structures of polymers **3a**−**d** were studied by UV−vis spectroscopy. Figure 2 shows an absorption spectrum of **3b** recorded in chloroform at room temperature. Not only strong absorption in the UV region derived from $\pi-\pi^*$ transition of the benzene ring but also small absorption in the visible region was observed. The absorption edge located at around 480 nm. We assume that $n-\pi^*$ transition in the main chain brought about the lower energy absorption as seen in poly(phenylene−phosphine)s.[5d]

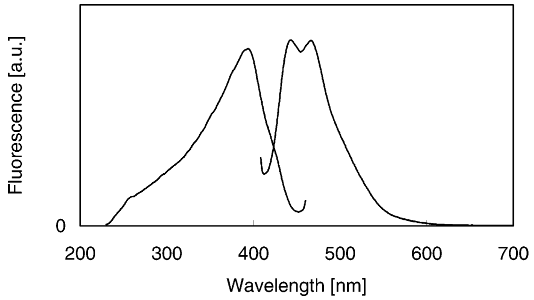
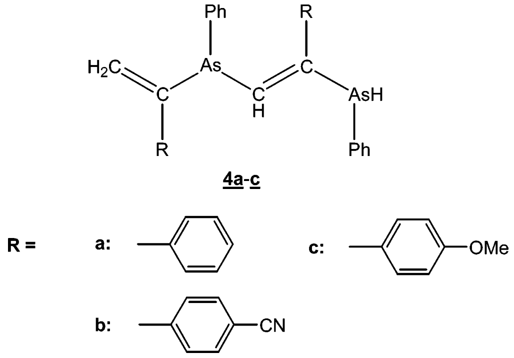


Figure 3. (a) Fluorescence spectrum of **3b** excited at 394 nm. (b) Excitation spectrum of **3b** emitted at 466 nm. Both measurements were carried out in $CHCl_3$ at room temperature.

Chart 1



Polymers **3a**−**d** showed fluorescent properties. The fluorescence and excitation spectra of a dilute chloroform solution of **3b** measured at room temperature are shown in Figure 3 as a typical representative example. The emission was observed in the visible blue-purple region with a peak at 443 and 466 nm. The emission peak maximum was independent of the concentration of polymer **3b**. In the excitation spectrum of **3b** monitored at 470 nm, the absorption was not observed in the shorter wavelength region but in the longer wavelength region with a peak at 394 nm. This means that the absorption of **3b** in the higher energy region and the absorption in the lower energy region originated from the different absorbing species: $\pi-\pi^*$ and $n-\pi^*$ transition. The emission of **3b** results from only the absorption of the latter transition. Table 1 also summarizes emission and excitation spectral data. Each emission peak maximum of **3a**−**c** was red-shifted in the order **3c** < **3a** < **3b**, which coincides with the order of strength of electron-withdrawing properties of the substituents. This indicates that the donor−acceptor (arsenic atom with a lone pair and vinylene unit with electron-accepting group) repeating units made the band gap narrower and resulted in the lower energy of the emission. The optical properties of poly(vinylene−arsine)s were tuned by changing the substituents of the acetylenic compounds. In the case of **3d**, the naphthyl group itself has a fluorescent property which is stronger than that derived from the $n-\pi^*$ transition in the main chain of the polymer, and therefore the emission peak due to the main chain was hidden. The absorption peaks in the excitation spectra of **3a**−**d** showed the same order as the emission peaks because of the same reason discussed above.

Calculation of HOMO and LUMO of dimer models (**4a**−**c**) of **3a**−**c** (Chart 1) was carried out using the CNDO/S Hamiltonians. The arsenic atom of **4a** bears large electron density of lone pair at HOMO, while no electron density of lone pair is observed at LUMO (Figure 4). LUMO of **4a** shows electron density of π^* of styrene unit. These results support the assumption that

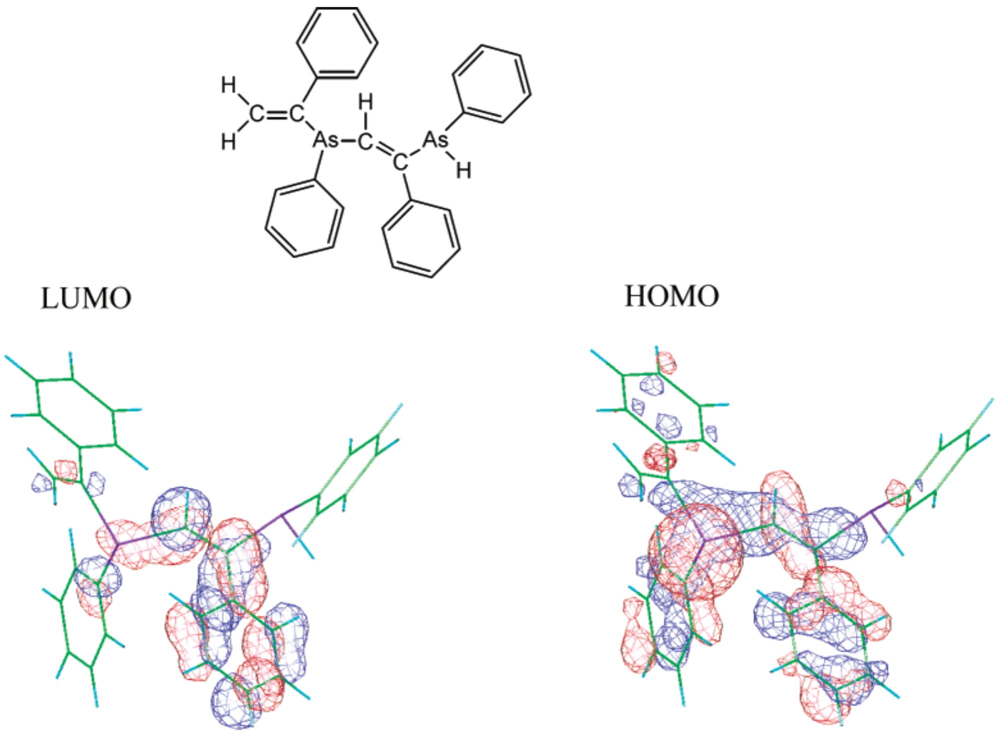


Figure 4. HOMO and LUMO density surface of **4a**.

the lower energy absorption is attributable to n$-\pi^*$ transition in the main chain of the polymer. The HOMO−LUMO band gaps of the dimers increase in the order **5b** < **5a** < **5c**. The cyano groups of **5b** enhance the electron-withdrawing ability of the π-electron system and lower the level of LUMO. The electron-donating methoxy groups of **5c** brought about the much higher LUMO level compared to that of **5a** or **5b**. The substituent group of the acetylenic compounds influenced the LUMO levels of the dimers more than HOMO levels. These results are consistent with the emission or excitation spectral data of polymers **3a**−**c** (Table 1) where the higher electron-accepting ability leads to the more red-shifted emission or absorption peak.

Conclusion

We have synthesized the organoarsenic polymers, poly(vinylene−arsine)s, by the radical copolymerization of hexaphenylcyclohexaarsine (**1**) with acetylenic compounds with various substituents (**2a**−**d**). The analyses of the conversion rate of the acetylenic monomers during the copolymerization supported the reaction mechanism we proposed before. The poly(vinylene−arsine)s obtained showed the unique optical properties which were tunable by changing the substituent of the acetylenic compound. Further studies on the reactivities of organoarsenic homocycles with a variety of comonomers including common vinyl monomers are in progress.

Experimental Section

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). UV−vis spectra were measured on a JASCO V-530 spectrometer, and the 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. GC analyses were carried out on a SHIMADZU GC-12A using helium gas as a carrier gas. Fourier transform infrared (FT-IR) spectra were obtained on a Perkin-Elmer 2000 spectrometer. Geometry optimization was performed using the MOPAC2000 program with the AM1 Hamiltonians.[13] Calculations for HOMO and LUMO levels were carried out using the Fujitsu MOS-F program packages[14] with CNDO/S Hamiltonians.

Materials. Benzene was dried over CaH_2, distilled, and bubbled with a stream of nitrogen before use. 2,2′-Azobis-(isobutyronitrile) (AIBN) was recrystallized from methanol. Phenylacetylene (**2a**) was distilled under reduced pressure. 1-Hexyne (**2e**) was distilled from $NaBH_4$. *n*-Dodecane and *n*-pentadecane were obtained commercially and used without further purification. Hexaphenylcyclohexaarsine (**1**),[15] 4-cyanophenylacetylene (**2b**),[16,17] 4-methoxyphenylacetylene (**2c**),[16,18] and 1-naphthylacetylene (**2d**)[16,19] were synthesized using literature procedures.

Polymerization. A typical experimental procedure is as follows. Under a nitrogen atmosphere, a benzene solution (0.4 mL) of a catalytic amount of 2,2′-azobis(isobutyronitrile) (0.005 g, 0.030 mmol) was added to a refluxing benzene solution (4.6 mL) of **2b** (0.229 g, 1.8 mmol) and hexaphenylhexacycloarsine (**1**) (0.273 g, 0.3 mmol). The mixture was stirred for 10 h and then poured into *n*-hexane to precipitate the product. After three times reprecipitation from benzene into *n*-hexane, the product was freeze-dried for 10 h and the corresponding polymer **3b** was obtained as a light-yellow powder. Yield: 0.145 g, 29%.

3b. ^{1}H NMR (δ in $CDCl_3$, ppm): 5.8−6.7 [C=C*H*], 6.7−8.0 [Ar−*H*]. ^{13}C NMR (δ in $CDCl_3$, ppm): 109.8−110.1 [C_{Ar}−CN], 117.4 [*C*N], 126.5 [C_{Ar}−C_{Ar}−C=C], 127.0−129.4 [C_{Ar}−As, m-C_{Ar}−As], 130.6−132.5 [p-C_{Ar}−As, C_{Ar}−C_{Ar}−CN], 132.8−140.0 [*C*H=C, o-C_{Ar}−As], 143.9 [C_{Ar}−C=C], 156.0−159.0 [*C*=CH]. IR (cm^{-1}): 2228 [−CN].

3c. ^{1}H NMR (δ in $CDCl_3$, ppm): 3.4−3.9 [C*H*$_3$O], 6.2−6.4 [C=C*H*], 6.4−7.9 [Ar−*H*]. ^{13}C NMR (δ in $CDCl_3$, ppm): 55.3 [*C*H$_3$O], 113.2 [C_{Ar}−C_{Ar}−OCH$_3$], 128.5 [C_{Ar}−C=C, C_{Ar}−C_{Ar}−C=C], 129.1 [*C*H=C], 130.8 [o-C_{Ar}−As], 132.0−133.5 [m-C_{Ar}−As, p-C_{Ar}−As], 140.6−141.1 [C_{Ar}−As], 158.5−158.8 [*C*=CH], 159.8−160.0 [C_{Ar}−OCH$_3$]. Yield: 22%.

3d. ^{1}H NMR (δ in $CDCl_3$, ppm): 5.6−6.2 [C=C*H*], 6.2−8.1 [Ar−*H*]. ^{13}C NMR (δ in $CDCl_3$, ppm): 123.5−124.1 [3-C_{Nap}], 124.1−125.2 [2-C_{Nap}, 6-C_{Nap}, 7-C_{Nap}], 125.6−126.6 [4-C_{Nap}], 126.9−127.3 [5-C_{Nap},8-C_{Nap}], 128.9−129.7 [ ], 130.1−133.4 [o-C_{Ar}−As, m-C_{Ar}−As, p-C_{Ar}−As], 136.0−138.0 [*C*H═C], 137.2−138.2 [ ], 138.2−139.7 [1-C_{Nap}], 139.8−140.6 [C_{Ar}−As], 157.4−158.5 [*C*═CH]. Yield: 33%.

Measurement of the Rate of Monomer Consumption. In the presence of 0.2 L/L of *n*-dodecane (**2a**−**c**) or *n*-pentadecane (**2d**), the copolymerization was carried out under the same conditions as described above. During the copolymerization, the amount of **2a**−**d** relative to that of *n*-alkane was monitored by using gas chromatography.

References and Notes

(1) (a) Rehahn, M. *Acta Polym.* **1998**, *49*, 201. (b) Manners, I. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1602. (c) Nguyen, P.; Gomez-Elipe, P.; Manners, I. *Chem. Rev.* **1999**, *99*, 1515.

(2) (a) *Flame Retardancy of Polymeric Materials*; Kuryla, W. C., Papa, A. J., Eds.; Marcel Dekker: New York, 1973; Vols. 1−5. (b) Ghassemi, H.; McGrath, J. E. *Polymer* **1998**, *38*, 3139.

(3) Allcock, H. R.; Olmeijer, D. L.; O'Connor, S. J. M. *Macromolecules* **1998**, *31*, 753.

(4) (a) Leadbeater, N. E.; Marco, M. *Chem. Rev.* **2002**, *102*, 3217. (b) Kanbara, T.; Takase, S.; Izumi, K.; Kagaya, S.; Hasegawa, K. *Macromolecules* **2000**, *33*, 657.

(5) (a) Mao, S. S. H.; Tilley, T. D. *Macromolecules* **1997**, *30*, 5566. (b) Hay, C.; Fischmeister, C.; Hissler, M.; Toupet, L.; Reau, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 1812. (c) Morisaki, Y.; Aiki, Y.; Chujo, Y. *Macromolecules* **2003**, *36*, 2594. (d) Lucht, B. L.; Onge, N. O. S. *Chem. Commun.* **2000**, 2097. (e) Smith, R. C.; Chen, X.; Protasiewicz, J. D. *Inorg. Chem.* **2003**, *42*, 5468.

(6) Krannich, L. K.; Watkins, C. L. In *Encyclopedia of Inorganic Chemistry;* King, R. B., Ed.; John Wiley & Sons: Chichester, England, 1994; Vol. 1, p 200, and references therein.

(7) (a) Kraft, M. Y. *Dokl. Akad. Nauk SSSR* **1960**, *131*, 1342. (b) Kallenbach, L. R.; Irgolic, K. J.; Zingaro, R. A. *Eur. Polym. J.* **1970**, *6*, 479. (b) Carraher, C. E.; Moon, W. G. *Eur. Polym. J.* **1976**, *12*, 329.

(8) (a) Chujo. Y.; Tomita, I.; Hashiguchi, Y.; Saegusa, T. *Macromolecules* **1991**, *24*, 345. (b) Matsumi, N.; Naka, K.; Chujo, Y. *J. Am. Chem. Soc.* **1998**, *120*, 5112. (c) Naka, K.; Uemura, T.; Chujo, Y. *Macromolecules* **1998**, *31*, 7570. (d) Naka, K.; Uemura, T.; Chujo, Y. *J. Am. Chem. Soc.* **2001**, *123*, 6209. (e) Konishi, G.; Naka, K. Chujo, Y. *J. Inorg. Organomet. Polym.* **1999**, *9*, 179.

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

(10) For example: (a) Walling, C.; Mayo, F. R. *Discuss. Faraday Soc.* **1947**, *2*, 295. (b) Tsuchida, E.; Tomono, T. *Makromol. Chem.* **1971**, *141*, 265. (c) Dogson, K.; Ebdon, J. R. *Eur. Polym. J.* **1977**, *13*, 791. (d) Iwatsuki, S.; Itoh, T.; Horiuchi, K. *Macromolecules* **1978**, *3*, 497.

(11) Many combinations of vinyl monomers in which the relative strength of the electron donor or acceptor is insufficient have been found suitable for the preparation of the alternating copolymers with the aid of Lewis acids. See for example: (a) Hirooka, M.; Yabuuchi, H.; Morita, S.; Kawasumi, S.; Nakaguchi, K. *J. Polym. Sci., Polym. Lett.* **1967**, *5*, 47. (b) Hirooka, M.; Yabuuchi, H.; Iseki, J.; Nakai, Y. *J. Polym. Sci., Part A-1* **1968**, *6*, 1381. (c) Gaylord, N. G.; Takahashi, A. *J. Polym. Sci., Polym. Lett.* **1969**, *7*, 443. (d) Yabumoto, S.; Ishii, K.; Arita, K. *J. Polym. Sci., Part A-1* **1969**, *7*, 1577.

(12) Dawson, D. A.; Reynolds, W. F. *Can. J. Chem.* **1975**, *53*, 373.

(13) MOPAC2000 ver. 1.0, Fujitsu Ltd, Tokyo, Japan, 1999.

(14) Matsuura, A. MOS-F 4.2C, Fujitsu, Ltd, Tokyo, Japan, 2000.

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

(16) Takahashi, S.; Sonogashira, K.; Higahara, N. *Synthesis* **1980**, 627.

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

(18) Overmeire, I. V.; Boldin, S. A.; Venkataraman, K.; Zisling, R.; Jonghe, S. D.; Calenbergh, S. V.; Keukeleire, D. D.; Futerman, A. H.; Herdewijn, P. *J. Med. Chem.* **2000**, *43*, 4189.

(19) John, J. A.; Tour, J. M. *Tetrahedron* **1997**, *53*, 15515.

MA035282C