ORIGINAL ARTICLE

Synthesis and low-temperature dehydrating imidation polymerization of 1,4-dihydro-1,4-diarsininetetracarboxylic acid dianhydride

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cis-1,4-Dihydro-1,4-dimethyl-1,4-diarsinine-2,3,5,6-tetracarboxylic acid dianhydride (*cis*-DHDADA) was quantitatively formed from *cis*-1,4-dihydro-1,4-dimethyl-2,3,5,6-tetrakis(*t*-butoxycarbonyl)-1,4-diarsinine (*cis*-DHDA*t*Bu) treated with formic acid as a Brønsted acid or with a cationic gold(I) catalyst as a Lewis acid. X-ray crystallography suggested that the six-membered ring in *cis*-DHDADA is in a boat conformation and is nearly flat, with the As–C=C bond angle of *cis*-DHDADA extending to 133°. The ultraviolet–visible absorption spectra of *cis*-DHDADA in CH_2Cl_2 showed a long-wavelength absorption maximum at 321 nm, which was redshifted compared with that of *cis*-DHDA*t*Bu. Polymerization of *cis*-DHDADA with 1,3-bis(4-aminophenoxy)benzene at 80 °C in *N,N*-dimethylacetoamide (DMAc) for 12 h yielded a soluble polyimide, with number-average and weight-average molecular weights estimated at 23 400 and 60 300, respectively. The polyimide was obtained even when the polymerization was conducted at 60 °C for 24 h.
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INTRODUCTION

The incorporation of metallic or metalloid elements, such as S, Se, PR, SiR_2, GeR_2 and BR, into polymer main chains appears to be a promising way of producing materials with useful properties.[1–5] For example, heteroatom-containing poly(phenylene)s, such as poly(phenyleneoxide), poly(phenylenesulfide) and polyaniline, are industrially important as engineering plastics and electrical materials. Heteroaromatic polymers, such as polythiophene and polypyrrole, have also been intensively investigated and widely applied. Among the various types of such polymers, much attention has been paid to heteroatom-containing polyimides in attempts to develop high-performance functional polymers, such as high-refractive-index polymers for optical applications, polymers resistant to atomic oxygen and ultraviolet radiation, as well as thermostable polymers.[6–10]

Organoarsenic compounds are currently being considered as ligands for transition metals because of their special properties;[11,12] however, fewer studies have been conducted with these than with their phosphorus analogs, because most organoarsenic compounds are prepared from arsenic chlorides or arsenic hydrides and require extreme caution in handling because of their volatility and toxicity. We previously reported the facile synthesis of a novel *cis*-1,4-diarsa-2,5-cyclohexadiene, that is, *cis*-1,4-dihydro-1,4-dimethyl-2,3,5,6-tetrakis(*t*-butoxycarbonyl)-1,4-diarsinine (*cis*-DHDA*t*Bu), which was synthesized by the radical reaction of pentamethylcyclopentaarsine

(cyclo-(MeAs)$_5$) and di-*t*-butyl acetylenedicarboxylate.[13,14] Their stability against air and moisture was high enough to allow handling in air. In this study, we found that *cis*-1,4-dihydro-1,4-dimethyl-1,4-diarsinine-2,3,5,6-tetracarboxylic acid dianhydride (*cis*-DHDADA) was quantitatively formed from *cis*-DHDA*t*Bu treated with formic acid as a Brønsted acid. We also found that dehydrating imidation polymerization of *cis*-DHDADA with diamines proceeded in a solution without catalysts even at 60 °C. This fact stands in sharp contrast to the synthesis of most polyimides that are processed in the form of their poly(amic acid) precursors and then thermally or chemically converted to imide structures. It should also be noted that this is the first reported polyimide containing arsenic atoms in the main chain.

EXPERIMENTAL PROCEDURE

Materials

Unless otherwise noted, all reagents and chemicals were purchased from commercial sources and used without further purification. *cis*-DHDA*t*Bu was synthesized as described in our previous report.[14] Gold(I) chloride and silver(I) trifluoromethanesulfonate were obtained from Sigma-Aldrich Chemical Co. (St Louis, MO, USA).

Measurements

[1]H (300 MHz) and [13]C (100 MHz) nuclear magnetic resonance (NMR) spectra were recorded on a Bruker PDX-300 spectrometer (Bruker, Karlsruhe, Germany): the samples were analyzed in $CDCl_3$ or dimethyl sulfoxide-d$_6$

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(DMSO-d_6) using tetramethylsilane as an internal standard. Ultraviolet–visible spectra were obtained on a SHIMADZU UV-3600 spectrophotometer (Shimadzu, Kyoto, Japan) from samples in CH_2Cl_2 at room temperature. Elemental analyses were performed at the Microanalytical Center of Kyoto University. High-resolution mass spectra were obtained on a JEOL JMS700 spectrometer (JEOL, Tokyo, Japan). Gel permeation chromatography was performed on a TOSOH 8020 (TSK-gel α-M column) (Tosoh, Tokyo, Japan) using a N,N-dimethylformamide (DMF) solution containing 10-mM LiBr as an eluent after calibration with standard polystyrene. Fourier-transform-infrared (FT-IR) spectra were obtained on a Perkin Elmer 2000 spectrometer (PerkinElmer, Waltham, MA, USA). All procedures except annealing the polyimide were performed under nitrogen or argon atmospheres.

X-ray crystal structure analysis

X-ray diffraction patterns were collected on a Rigaku R-AXIS RAPID-F (Rigaku, Akishima, Japan) graphite-monochromated Mo Kα (λ=0.71075 Å) radiation diffractometer with an imaging plate. A symmetry-related absorption correction was carried out using the program ABSCOR.[15] The structures were solved by means of Patterson methods (Dirdif 99.2[16] and refined (SHELXL-97[17]) using Yadokari-XG.[18] The Oak Ridge Thermal Ellipsoid Plot (ORTEP)-III[19] program was used to generate the X-ray structural diagrams.

cis-DHDADA

Method 1. cis-DHDA*t*Bu (2.2 g, 3.4 mmol) was dissolved in formic acid (500 ml) and stirred at 120 °C for 24 h. The volatile components were removed under reduced pressure to yield a yellow residue. After the residue was extracted with $CHCl_3$ to yield a yellow solution, the solvent was removed to result in a yellow solid (yield: 93%).

Method 2. cis-DHDA*t*Bu (270 mg) was added to a mixture of gold(I) chloride (9.0 mg, 0.039 mmol) and silver(I) trifluoromethanesulfonate (10.0 mg, 0.039 mmol) in toluene (20.0 ml). After the mixture was stirred at 80 °C for 16 h, residual gold and silver were filtered out with a silica gel to result in a yellow solution. The solvent was removed to yield a yellow solid (yield: 85%).

FT-IR (KBr disk) at cm^{-1}: 1830, 1800 (C=O) and 1240 (C–O). ^{1}H-NMR (300 MHz, CDCl$_3$): δ 1.81 (6H, s). ^{13}C-NMR (100 MHz, CDCl$_3$): δ 162.99, 152.77 and 10.09. HR FAB–mass spectra (m/z): calculated for $C_{10}H_6O_6As_2$ and 371.8596; found, 372.8684. Anal. calculated for $C_{10}H_6O_6As_2$, C, 32.29; and H, 1.63. Found: C, 32.03; and H, 1.55.

Polymerization. A typical polymerization procedure was as follows: a mixture of cis-DHDADA (50 mg, 0.13 mmol) and 1,3-bis(4-aminophenoxy)benzene (BAB; 39 mg, 0.13 mmol) in N,N-dimethylacetoamide (DMAc) (0.5 ml) was stirred at 80 °C for 12 h to yield a yellow solution. The solution was added to methanol to result in a yellow precipitate.

PI-1: 51% yield, FT-IR (KBr disk) at cm^{-1}: 1760, 1703 (C=O) and 1382 (C–N). ^{1}H-NMR (300 MHz, DMSO-d_6): δ 7.42 (d, 4H), 7.18 (d, 4H), 7.87–6.75 (m, 4H) and 1.63 (s, 3H). ^{13}C-NMR (100 MHz, DMSO-d_6): δ 169.16, 158.17, 156.03, 149.43, 131.85, 128.78, 127.49, 119.49, 114.42, 109.94 and 10.80.

PI-2: 57% yield, FT-IR (KBr disk) at cm^{-1}: 1760, 1695 (C=O) and 1386 (C–N). ^{1}H-NMR (300 MHz, CDCl$_3$): δ 7.38 (d, 2H), 7.15 (d, 2H) and 1.81 (s, 3H). ^{13}C-NMR (100 MHz, CDCl$_3$): δ 168.57, 156.29, 149.93, 127.37, 126.78, 119.58 and 10.90.

RESULTS AND DISCUSSION

Synthesis of cis-DHDADA

We found that cis-DHDADA was quantitatively formed from cis-DHDA*t*Bu treated with formic acid as a Brønsted acid. When cis-DHDA*t*Bu was dissolved in formic acid and stirred at 120 °C, the reaction mixture turned yellow within 5 min. After the removal of formic acid under reduced pressure and extraction with $CHCl_3$, the solvent was removed to yield a yellow solid. In the FT-IR spectrum, the product showed characteristic C=O vibrations at 1830 and 1800 cm^{-1}, indicating the formation of an anhydride structure. The ^{1}H- and ^{13}C-NMR, FAB–MASS spectrometry and elemental
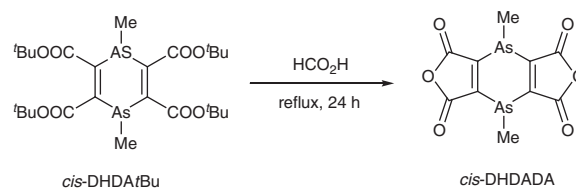
Scheme 1 Synthesis of cis-DHDADA from cis-DHDA*t*Bu.

Figure 1 ORTEP drawing of cis-1,4-dihydro-1,4-dimethyl-1,4-diarsinine-2,3,5,6-tetracarboxylic acid dianhydride with thermal ellipsoids shown at the 50% probability level. The hydrogen atoms are omitted for clarity.

analysis data all supported the formation of cis-DHDADA. Although *t*-butyl esters are known to be readily cleaved by moderately acidic hydrolysis, the anhydride structure was obtained in the present case (Scheme 1).

The same cis-DHDADA was also obtained from cis-DHDA*t*Bu using the cationic gold(I) catalyst as a Lewis acid, which was prepared *in situ* from gold(I) chloride and silver(I) trifluoromethanesulfonate. The structure of cis-DHDADA was estimated from the FT-IR, ^{1}H- and ^{13}C-NMR, and FAB–MASS spectrometry results. The gold(I) catalyst may interact not only with the carbonyl but also with the arsenic groups of cis-DHDA*t*Bu to reduce electrons near the carbonyl carbons. cis-DHDADA was simply purified by filtering out residual gold and silver. cis-1,4-Dihydro-1,4-dimethyl-2,3,5,6-tetrakis(methoxycarbonyl)-1,4-diarsinine, the methyl ester analog of cis-DHDA*t*Bu, hardly reacted when Brønsted acid was used to obtain cis-DHDADA, because the methoxy group has fewer electrons than the *t*-butoxy group. cis-DHDADA, however, was obtained from cis-1,4-dihydro-1,4-dimethyl-2,3,5,6-tetrakis(methoxycarbonyl)-1,4-diarsinine using the cationic gold(I) catalyst.

The stereochemical structure of cis-DHDADA in the crystal form was determined by X-ray crystallography. The crystallographic data suggest that the six-membered ring was in a boat conformation and was nearly flat (Figure 1). A selection of bond lengths and angles for the crystals is summarized in Tables 1 and 2. Although the usual bond angle at the sp^2-hybridized carbon is 120° and the As–C=C bond angle of cis-DHDA*t*Bu was 121°,[14] that of cis-DHDADA extended to 133°. In our previous report, the As–C=C bond angle of the chair conformer of trans-DHDA*t*Bu extended to 129°.[14] In a similar phosphorus compound, the P–C=C angles extend to only 122°.[20] The flexibility of the bond angles around the arsenic center is an inherent property in the organoarsenic compounds. The average As–C bond length was 1.939 Å, which was shorter than that of cis-DHDA*t*Bu (1.971 Å). This indicates an increase in the π-bonding character of the As–C bonds in the six-membered ring. The interior angles around the arsenic atoms of the six-membered ring were reduced (to 93.2°) compared with those in cis-DHDA*t*Bu (at 95.0°). The repulsion of the paired electrons around the arsenic atoms may have decreased because of their delocalization in the six-membered ring.

Table 1 Selected crystallographic data and refinement parameters

	cis-DHDADA
Empirical formula	$C_{10}H_6As_2O_6$
Formula weight	371.99
Crystal system	Monoclinic
Space group	$P21$
a (Å)	7.379(4)
b (Å)	7.971(4)
c (Å)	10.272(5)
α (deg)	90
β (deg)	103.55(3)
γ (deg)	90
V (Å^3)	587.3(5)
Z	2
D_{calcd} (g cm^{-3})	2.103
μ (mm^{-1})	5.705
T (K)	116
Reflections collected	5111
Independent reflections (R_{int})	2494 (0.0840)
Observed reflections ($I > 2\sigma(I)$)	1805
Parameters	165
T_{max}/T_{min}	0.5993/0.5993
Residual density (eÅ^{-3})	0.874/−0.697
R_1	0.0573
wR_2	0.1337
GooF	0.974

Abbreviation: cis-DHDADA, cis-1,4-dihydro-1,4-dimethyl-1,4-diarsinine-2,3,5,6-tetracarboxylic acid dianhydride; GooF, goodness of fit.

Table 2 Selected distances (Å) and angles (deg) of cis-DHDADA

As(1)-As(2)	3.961 (2)		
C(9)-C(16)	1.347 (15)	R	1.324 (16)
As(1)-C(9)	1.932 (11)	As(2)-C(16)	1.936 (12)
As(1)-C(14)	1.937 (12)	As(2)-C(11)	1.950 (12)
C(9)-As(1)-C(14)	93.5 (4)	C(16)-As(2)-C(11)	92.9 (5)
C(16)-C(9)-As(1)	131.5 (8)	C(14)-C(11)-As(2)	132.3 (9)
C(11)-C(14)-As(1)	133.2 (9)	C(9)-C(16)-As(2)	133.6 (8)
C(14)-C(11)-C(12)	106.4 (11)	C(11)-C(14)-C(10)	109.1 (11)
C(9)-C(16)-C(18)	107.5 (10)	C(16)-C(9)-C(17)	107.6 (10)

Abbreviation: cis-DHDADA, cis-1,4-dihydro-1,4-dimethyl-1,4-diarsinine-2,3,5,6-tetracarboxylic acid dianhydride.

The ultraviolet–visible absorption spectra of cis-DHDADA in CH$_2$Cl$_2$ showed a long-wavelength absorption maximum at 321 nm (6400 M^{-1} cm^{-1}), which was redshifted compared with that of cis-DHDAtBu at 272 nm (11000 M^{-1} cm^{-1}) (Figure 2). The conjugation system of the nearly flat six-membered ring of cis-DHDADA affected the absorption. When cis-DHDAtBu was dissolved in formic acid and stirred at 120 °C, the reaction mixture turned yellow within 5 min, as described above. This indicates that cis-DHDADA was formed in the solution. The conjugation stabilization might be the main reason for the facile formation of the dianhydride structure.

Polymerization

The polymerization of cis-DHDADA with BAB was conducted at 80 °C in DMAc for 12 h (Scheme 2). The polymerization proceeded in a homogeneous solution, which was subsequently added to methanol to yield a yellow precipitate. The obtained polymer (PI-1) was soluble in organic solvents, including DMAc, DMF and
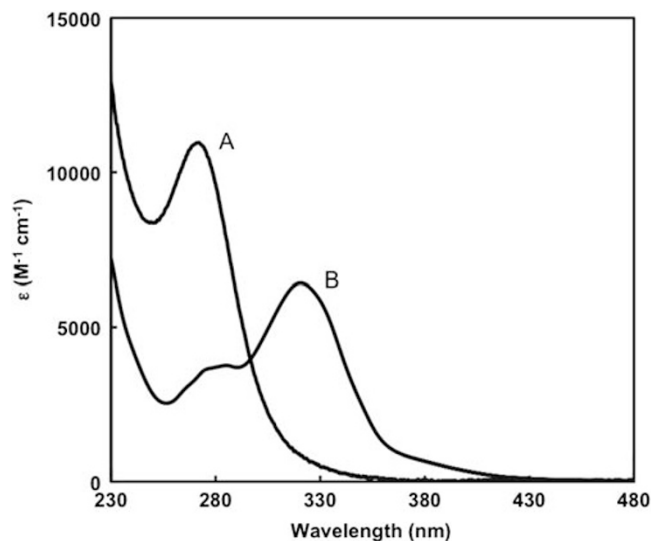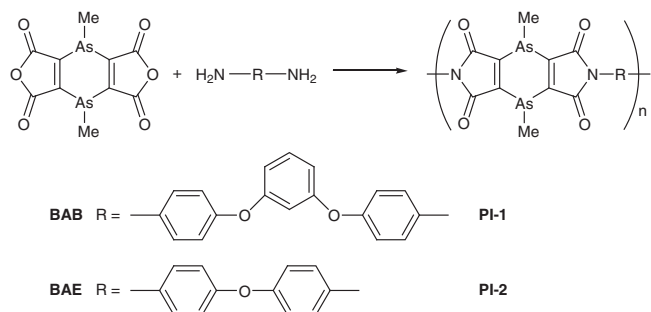

Figure 2 Ultraviolet–visible absorption spectra of cis-1,4-dihydro-1,4-dimethyl-2,3,5,6-tetrakis(t-butoxycarbonyl)-1,4-diarsinine (A) and cis-1,4-dihydro-1,4-dimethyl-1,4-diarsinine-2,3,5,6-tetracarboxylic acid dianhydride (B) in CH$_2$Cl$_2$.

BAB R = ... PI-1

BAE R = ... PI-2

Scheme 2 Polymerization of cis-DHDADA with BAB or BAE.

DMSO, and partially soluble in CHCl$_3$, CH$_2$Cl$_2$, CH$_3$CN and tetrahydrofuran (THF). From gel permeation chromatography analysis (DMF 0.1 mM LiBr, PSt standards), the number-average and weight-average molecular weights of PI-1 were estimated to be 23 400 and 60 300, respectively. The obtained polymer was identified by FT-IR and NMR. The FT-IR analysis showed peaks unique to the imide structure at 1373 cm^{-1} (C–N stretching) and at 1715 and 1760 cm^{-1} (C=O stretching). The NMR spectra are in agreement with the proposed structure. The ^{1}H-NMR spectrum showed one sharp resonance for As–Me at 1.64 p.p.m., which was shifted downfield compared with that of cis-DHDADA (Figure 3a). The peak-area ratio of the aromatic (6.7–7.5 p.p.m.) and methyl moieties confirmed the polyimide structure. Analysis of PI-1 by ^{13}C-NMR spectroscopy in DMSO-d$_6$ showed only one sharp resonance for the methyl carbon at 10.8 p.p.m., suggesting that the arsenic in the polymer existed in a pure form and no oxidized arsenic was present (Figure 3b). The polyimide showed a 10% weight loss at 329 °C under air.

The polymerization of cis-DHDADA with bis(p-aminophenyl) ether was conducted at 90 °C in DMAc for 12 h (Scheme 2). The solution was added to methanol to yield a yellow precipitate. The obtained polymer (PI-2) was partially soluble in DMSO and DMF, and insoluble in CHCl$_3$, CH$_2$Cl$_2$, CH$_3$CN and THF.
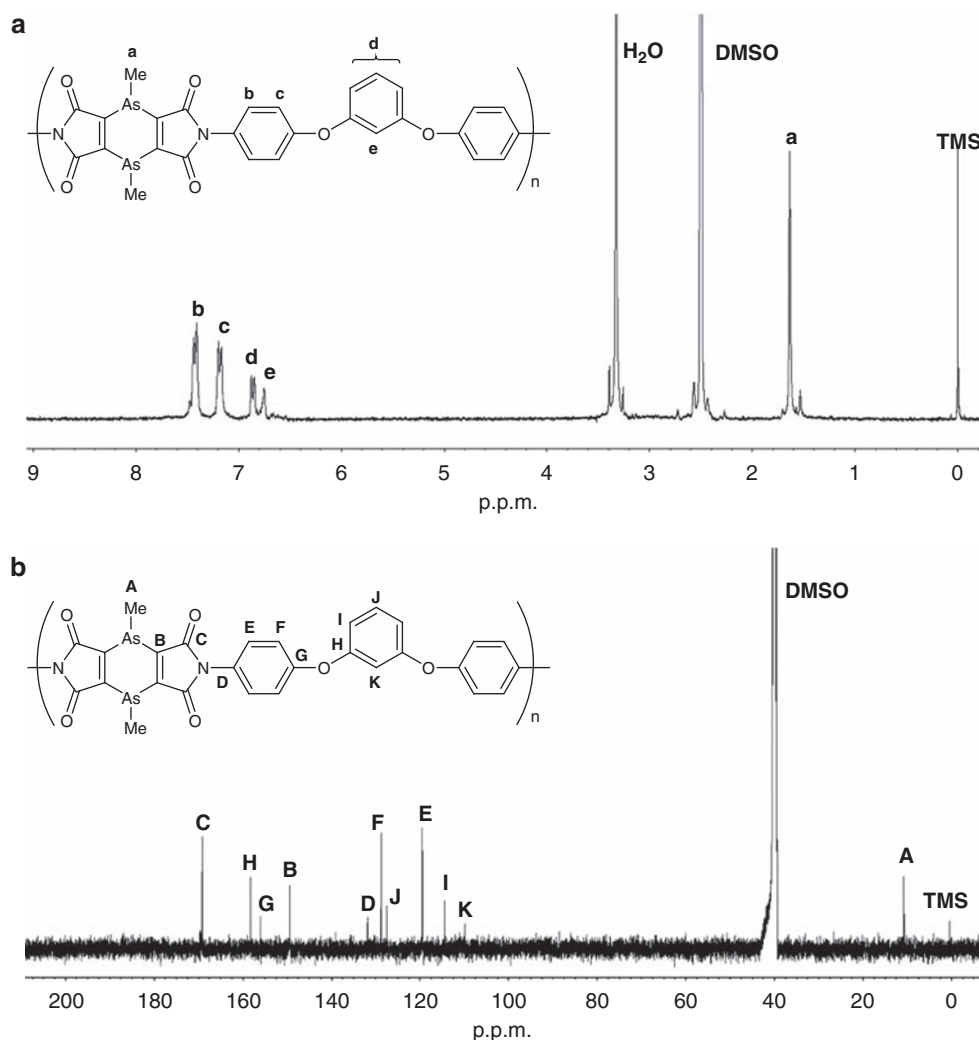
Figure 3 (a) ^{1}H- and (b) ^{13}C-nuclear magnetic resonance spectra of PI-1 in DMSO-d$_6$.

From a gel permeation chromatography analysis (DMF 0.1 mM LiBr, PSt standards), the number-average and weight-average molecular weights of the soluble part of PI-2 were estimated to be 5800 and 11 300, respectively. The FT-IR analysis showed peaks unique to the imide structure at 1382 cm^{-1} (C–N stretching), 1703 and 1760 cm^{-1} (C=O stretching). A soluble part of PI-2 in DMSO was identified by ^{1}H-NMR, which is in agreement with the proposed structure. The ^{1}H-NMR spectrum showed one sharp resonance for As–Me at 1.66 p.p.m.

The polymerization of *cis*-DHDADA with BAB was conducted at 60 °C in DMAc for 12 h. The ^{1}H-NMR and FT-IR analyses indicated that the polymer structure was a mixture of the imide and amide acid units. In addition to the As–Me resonance for the imide unit, two sets of As–Me signals corresponding to the amide acid were observed. The amide acid has two isomeric structures, that is, the *meta*- and *para*-isomers. The peaks corresponding to *meta*- and *para*-isomeric structures can be separated. For the *para*-isomer, the chemical shift of As–Me should appear as a singlet peak. Conversely, for the *meta*-isomer, two peaks assigned to As–Me in different chemical environments should be expected. The ^{1}H-NMR spectrum at the methyl region shows the peaks corresponding to the *meta*- and *para*-isomers of the amide acid unit and the imide unit (Figure 4).

We conducted the polymerizations at different temperatures and at different times. The results are summarized in Table 3. The polyimide was obtained even when the polymerization was conducted at 60 °C for 24 h and the molecular weight increased with an increase in the polymerization time to 48 h. The polyimide structure was also formed at room temperature. However, the ratio of the imide unit against the amide acid unit was not improved even when the polymerization was conducted at room temperature for 96 h. The solubility of the polymer decreased when both reaction temperature and time were increased (Scheme 3).

CONCLUSIONS

We found that *cis*-DHDADA was quantitatively formed from *cis*-DHDAtBu when treated with formic acid as a Brønsted acid or the cationic gold(I) catalyst as a Lewis acid. The X-ray crystallography suggested that the six-membered ring in *cis*-DHDADA is in a nearly flat boat conformation and that the As–C=C bond angle of *cis*-DHDADA extends to 133°. The ultraviolet–visible absorption spectra of *cis*-DHDADA in CH$_2$Cl$_2$ showed a long-wavelength absorption maximum at 321 nm, which was redshifted compared with that of *cis*-DHDAtBu. The conjugation stabilization may be the main reason for the formation of the dianhydride structure.
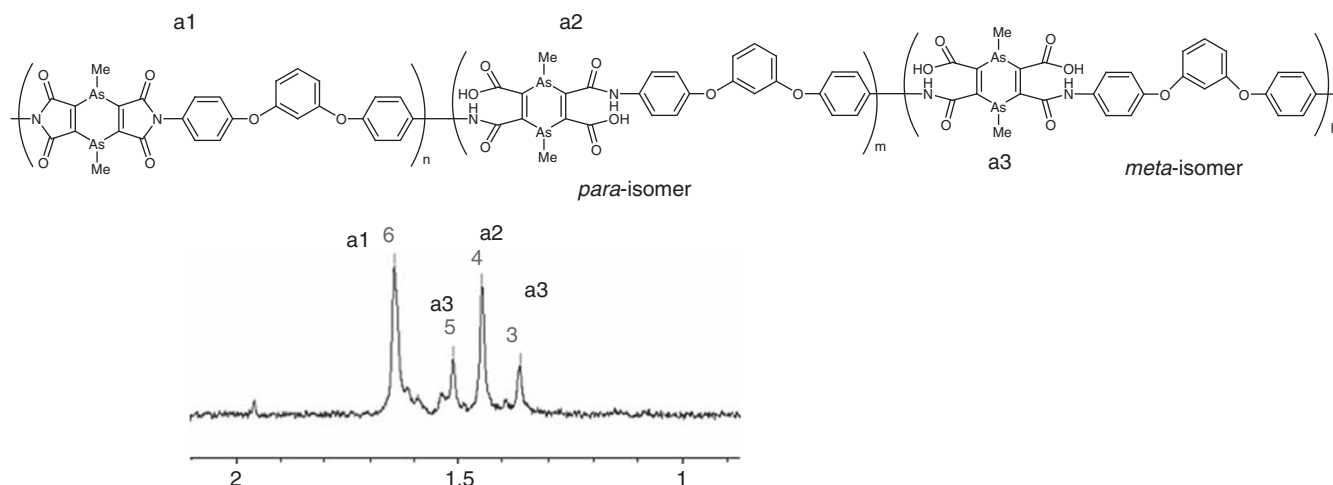
Figure 4 The aliphatic region of the [1]H-nuclear magnetic resonance spectrum of the polymer obtained from the polymerization of *cis*-1,4-dihydro-1,4-dimethyl-1,4-diarsinine-2,3,5,6-tetracarboxylic acid dianhydride with 1,3-bis(4-aminophenoxy)benzene conducted at 60 °C in DMAc for 12 h (run 3 in Table 2).

Table 3 Results of polymerization

| Run	Diamine	Temperature, °C	Time, h	Yield, %[a]	x[b]	M_n[c]	M_w[c]	M_w/M_n[c]
1	BAB	RT	48	40	0.25			
2	BAB	60	12	43	0.44			
3	BAB	60	24	50	0.99	700	15800	22.6
4	BAB	60	48	56	1	9800	58900	6.01
5	BAB	80	5	37	0.42			
6	BAB	80	12	51	1	11200	45500	4.06
7	BAB	90	12	76	1	23400	60300	2.58
8	BAB	100	12	66	1	2100	8900	4.24
9	BAE	90	12	57	1[d]	5800[d]	11300[d]	1.94

Abbreviations: BAB, 1,3-bis(4-aminophenoxy)benzene; BAE, bis(*p*-aminophenyl) ether; GPC, gel permeation chromatography; NMR, nuclear magnetic resonance; RT, room temperature.
[a]Isolated yield after reprecipitation into CHCl₃.
[b]By ^{1}H-NMR.
[c]By GPC (10 mM LiBr in DMF). Polystyrene standard.
[d]DMF soluble part.
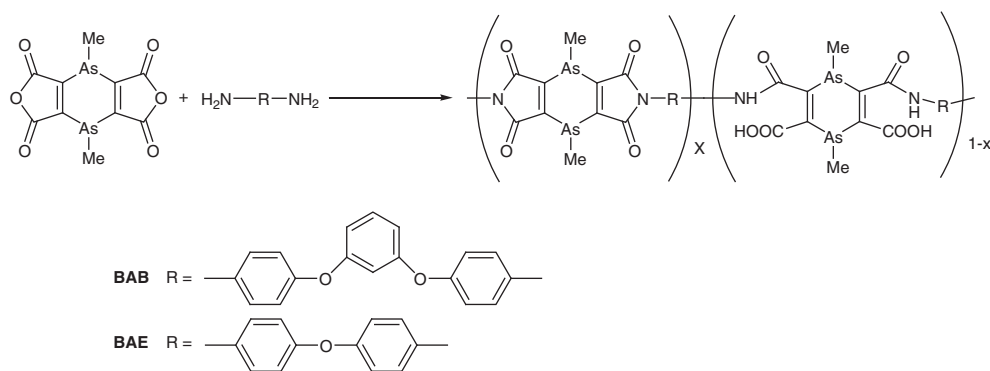
Scheme 3 Polymerization of *cis*-DHDADA with BAB or BAE at different temperatures and at different times.

Polymerization of *cis*-DHDADA with BAB at 80 °C in DMAc for 12 h yielded the soluble polyimide, with number-average and weight-average molecular weights estimated at 23 400 and 60 300, respectively. The polyimide was obtained even when polymerization was conducted at 60 °C for 24 h. The polymerization at 60 °C for 12 h yielded a polymer composed of both imide and amide acid units. Generally, the polymerization of dianhydrides with diamines forms poly(amic acid)s in solutions. Dehydrating imidation polymerization of the *cis*-DHDADA with diamines, however, proceeded in a solution without catalysts even at 60 °C. Because of the flexibility of the bond angles

around the arsenic center in the novel organoarsenic compound, conjugation stabilization may be the main driving force for the facile formation of the imide structure even at 60 °C in solution. In addition, this is the first reported polyimide containing arsenic atoms in the main chains. An investigation of further details of the properties of the polymers is currently underway.

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