Formal Aryne Polymerization: Use of [2.2.1]Oxabicyclic Alkenes as Aryne Equivalents

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S *Supporting Information*

ABSTRACT: Despite the high utility of aryne in organic synthesis, its polymerization has long been a significant challenge in polymer chemistry. A critical bottleneck in this process is the intrinsic instability of aryne and consequent short lifetime for polymerization. In order to circumvent the problem, we focus on a synthetic equivalent of aryne, [2.2.1]oxabicyclic alkene, as a monomer for polymerization. Palladium-catalyzed coordination—insertion polymerization of [2.2.1]oxabicyclic alkenes produced the corresponding polymers having an aliphatic main chain. Subsequent acid-promoted dehydration allowed the aliphatic main chain to be converted into an aromatic main chain to form poly(*o*-arylene)s. These sequential processes represent the first formal aryne polymerization, which offers an efficient method to synthesize a variety of poly(*o*-arylene)s in a chain-growth polymerization manner.

Owing to its unique structure and high reactivity, aryne—1,2-didehydroarene—serves as a useful intermediate in organic synthesis.[1] The increasing importance of arynes has been exemplified by the development of a broad range of synthetic applications, including polyaromatic compounds[2] and natural products.[3] Given that a representative mode of aryne reactivity is its ability to insert into polar and nonpolar σ-bonds,[4] it is quite natural for chemists to envisage that the successive, multiple insertion of arynes would form a polymer. However, the polymerization of aryne, leading to an efficient method to synthesize poly(*o*-arylene)s in a single-step procedure, has never been achieved because of difficulty in controlling the highly reactive aryne species (Scheme 1).[5,6]

Compared with poly(*p*-arylene)s[7] and poly(*m*-arylene)s,[8] poly(*o*-arylene)s have been a less studied class of π-conjugated compounds, which adopt helical conformation along their twisted main chains.[9] Since earlier studies into this molecular class,[10] most of the oligo- and poly(*o*-arylene)s reported to date

such as poly(*o*-phenylene)s[9,11] and poly(naphthalene-2,3-diyl)-s[12] have been synthesized based on the iterative (cross-)coupling strategy, which requires multistep procedures. For oligo- and poly(*o*-heteroarylene)s, two other synthetic approaches based on a polymerization strategy have been reported: one is step-growth polymerization by the cross-coupling reactions of bifunctional monomers, which only afforded oligo(quinoline-2,3-diyl)s with low degrees of polymerization (∼4) because of steric congestion along with their highly twisted backbones.[13] The other strategy involves the palladium- or nickel-catalyzed chain-growth polymerization of 1,2-diisocyanoarenes for the synthesis of poly(quinoxaline-2,3-diyl)s.[14] However, no example exists detailing the synthesis of hydrocarbon-based poly(*o*-arylene)s via polymerization. In our research, we focus on a synthetic equivalent of arynes, [2.2.1]oxabicyclic alkenes, as a monomer for polymerization[15] and disclose the formal chain-growth aryne polymerization based on palladium-catalyzed coordination—insertion polymerization of [2.2.1]oxabicyclic alkenes (**1**) followed by acid-promoted dehydration to synthesize a variety of poly(*o*-arylene)s (**3**) (Scheme 2).[16]

One of the potential side reactions in the coordination—insertion polymerization of [2.2.1]oxabicyclic alkene **1** (Scheme 3) is metal-catalyzed isomerization of **1** into 1-hydroxyarenes (**4**).[17] The polymerization may also be hampered by β-oxygen elimination from intermediates **5**, formed by the insertion of **1** into a metal-alkyl species (R-ML$_n$), to give ring-opened

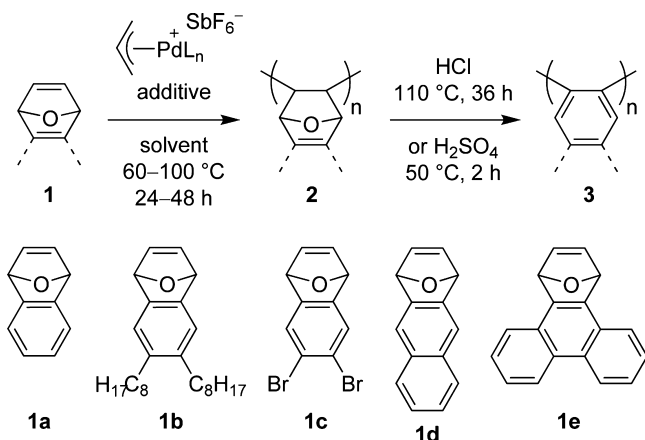## Scheme 1. A Challenge in Polymer Chemistry: Aryne Polymerization to Form Poly(*o*-arylene)
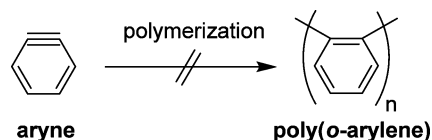
Scheme 2. Formal Aryne Polymerization: Synthesis of Poly(*o*-arylene)s and Potential Side Reactions
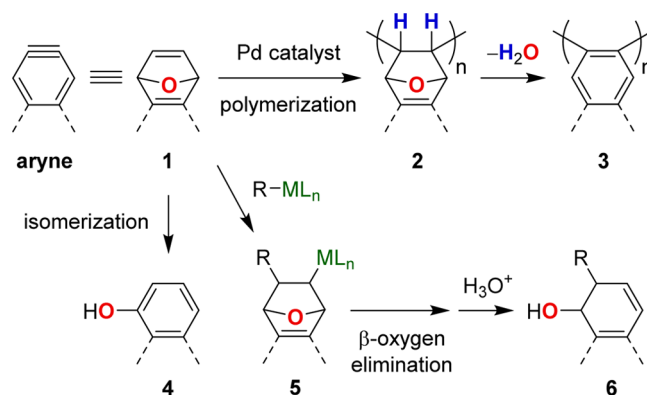
Scheme 3. Polymerization of [2.2.1]Oxabicyclic Alkenes (1) Followed by Dehydration to Form Poly(o-arylene)s (3)

products 6.[18] Inspired by Safir and Novak's reports on the palladium-catalyzed polymerization of 7-oxabicyclo[2.2.1]-hepta-2,5-diene-2,3-dicarboxylates,[15] we initially applied one of their methods to the polymerization of 1,4-dihydro-1,4-epoxynaphthalene (1a) as a 2,3-didehydronaphthalene equivalent, resulting in low yields of a polymer having a structure different from that of poly(1,2,3,4-tetrahydro-1,4-epoxynaphthalene-2,3-diyl) (2a).[19] In order to obtain polymer 2a, various transition-metal catalysts, ligands, and solvents were surveyed as summarized in Table 1.[20] The polymerization of 1a was

Table 1. Optimization of Conditions for the Polymerization of [2.2.1]Oxabicyclic Alkene 1a[a]

entry	solvent	ligand	2a (%)[b]	M_w[c]	M_w/M_n[c]	4a (%)[d]
1	toluene	–	11	5100	1.5	63
2	DCE	–	54[e]	4200	1.8	1
3	toluene/DCE	–	88[e]	9100	4.1	0
4	**toluene/ DCE**	**2,6-lutidine**	**80**	**5500**	**1.2**	**0**
5	toluene	2,6-lutidine	11	9700	1.5	79
6	DCE	2,6-lutidine	0[f]	–	–	0
7	toluene/DCE	PPh₃	79[e]	4700	2.4	0
8	toluene/DCE	2,2′-bipyridine	0	–	–	85

[a]Catalyst was prepared by mixing [PdCl(η³-allyl)]₂, ligand, and AgSbF₆ in an indicated solvent followed by filtration to remove AgCl. Polymerization of 1a (0.50 mmol) was performed at 60 °C for 16 h. DCE = 1,2-dichloroethane. [b]Determined after reprecipitation with methanol. [c]Determined by size-exclusion chromatography (SEC) analysis using THF as an eluent and polystyrene as an internal standard. Soluble fractions in THF were analyzed because of the low solubility of polymer 2a in organic solvents. [d]Yield determined by NMR analysis. [e]Partial dehydration proceeded. [f]Oligomer, which did not precipitate during precipitation process using methanol, was obtained.

successfully catalyzed by a complex prepared from a π-allylpalladium chloride dimer ([PdCl(η³-allyl)]₂) and silver hexafluoroantimonate (AgSbF₆). For this polymerization, the choice of solvent was found to be essential. Whereas the use of toluene (entry 1) and 1,2-dichloroethane (DCE) (entry 2) as single solvent systems gave poor results, the combined use of toluene and DCE (1:1) drastically improved the yield of polymer to 88% (entry 3). In entries 2 and 3, however, the

chain propagation was accompanied by partial dehydration, leading to larger M_w/M_n ratios.[21] After screening of various ligands, 2,6-lutidine was found to produce polymer 2a in high yields and with a narrow molecular weight distribution (entry 4). The solvent effects discussed above were observed even in the presence of 2,6-lutidine; the use of toluene (entry 5) and DCE (entry 6) afforded lower yields and molecular weights of the polymer than those afforded by the mixed solvent system. The solvent effect is somewhat elaborate: toluene is needed presumably to stabilize the cationic palladium catalyst[22] and suppress β-oxygen elimination during chain propagation. A halogenated cosolvent such as DCE is required because of the low solubility of the cationic palladium catalyst in toluene.[23] The role of 2,6-lutidine is to suppress dehydration of the formed polymer 2a and isomerization of monomer 1 into 1-hydroxyarene 4 even under high-temperature conditions.[20] The other ligands we examined produced either a lower molecular weight polymer (entry 7) or no polymeric material (entry 8).

Using the optimized procedure, monomers 1a–1e having various substituents were polymerized on a large scale to form the corresponding polymers 2a–2e (Table 2). In all the entries, the formation of 1-hydroxyarenes 4 was not observed in the presence of 2,6-lutidine as a ligand. The polymerization of monomer 1b having alkyl chains afforded polymer 2b in 90% yield (entry 2), although the introduction of electron-donating groups generally enhanced its isomerization into 4.[17] Monomer 1c having electron-withdrawing bromo groups showed lower reactivity for the polymerization, requiring a higher reaction temperature of 80 °C and longer reaction time to afford polymer 2c in good yield (entry 3). The polymerization method could also be applied to monomers with longer π-conjugate systems such as 2,3-didehydroanthracene equivalent (1d) (entry 4) and 2,3-didehydrotriphenylene equivalent (1e) (entry 5), although the molecular weight of polymer 2e remained low, presumably due to steric congestion of 1e during the chain propagation.

Dehydration of polymers 2a–2e was accomplished by treatment with hydrogen chloride in 1,4-dioxane at 110 °C (entries 1, 2, 4, and 5) or with conc. sulfuric acid at 50 °C (entry 3) to afford the corresponding poly(o-arylene)s: poly(naphthalene-2,3-diyl)s 3a–3c, poly(anthracene-2,3-diyl) 3d, and poly(triphenylene-2,3-diyl) 3e (Table 2). The yields of the dehydration were generally high (85−97%) even after purification by reprecipitation. Complete dehydration was confirmed by matrix laser-assisted desorption/ionization time-of-flight (MALDI-TOF) mass analyses. The mass spectra of polymers 2a–2e showed ion signals with intervals of the repeating units (144, 368, 302, 194, and 244 Da for 2a–2e, respectively); after dehydration, the intervals were changed to smaller values by a difference of 18 Da (126, 350, 284, 176, and 226 Da, respectively), which correspond to the molecular weights of the dehydrated units in polymers 3a–3e.[24] In the case of poly(7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate)s, a retro Diels−Alder reaction accompanied by elimination of the corresponding furans is known to proceed under similar conditions.[15] In the present study, however, such a retro Diels−Alder reaction of polymer 2 was not observed, presumably due to the low eliminating ability of the resulting isobenzofuran.

The structures of all polymers were confirmed by ¹H and ¹³C NMR analyses (Figure 1). In the ¹³C NMR spectrum of 2a shown in Figure 1a, broad signals were observed at 50(a) and 82(b) ppm, which are assignable to β and α carbons from the

Table 2. Polymerization of Various [2.2.1]Oxabicyclic Alkenes (1) Followed by Dehydration to Form Poly(o-arylene)s (3)

entry	monomer	polymerization step[a]					dehydration step[b]		
		temperature (°C)	time (h)	2 (%)[c]	$M_w{}^d$	$M_w/M_n{}^d$	3 (%)[c]	$M_w{}^d$	$M_w/M_n{}^d$
1	1a	60	24	86	5600[e]	1.2	94	3900	2.0
2	1b	60	36	90	9500	1.3	96	7000	1.5
3[f]	1c	80	48	76	3500	1.4	85	1200	1.9
4	1d	60	36	87	6500[e]	1.3	97	6300[e]	3.0
5	1e	100	36	86	700[e]	1.4	96	800	1.6

[a]Catalyst was prepared by mixing [PdCl(η^3-allyl)]$_2$, 2,6-lutidine, and AgSbF$_6$ in toluene/DCE followed by filtration to remove AgCl. Polymerization of 1 (10.0 mmol) was performed in toluene/DCE (40 mL). [b]A mixture of polymer 2 (1.0 mmol unit) and hydrogen chloride (4.0 M solution in dioxane; 10 mL) was stirred for 36 h at 110 °C, except for entry 3. [c]Yield was determined after precipitation with methanol. [d]Molecular weights determined by SEC analysis using THF as an eluent and polystyrene as an internal standard. [e]Soluble fractions in THF were analyzed because of the low solubility of polymer. See the Supporting Information for polymer solubility and SEC analyses using other solvents and conditions. [f]Dehydration was performed with conc. sulfuric acid (instead of hydrogen chloride) for 2 h at 50 °C.
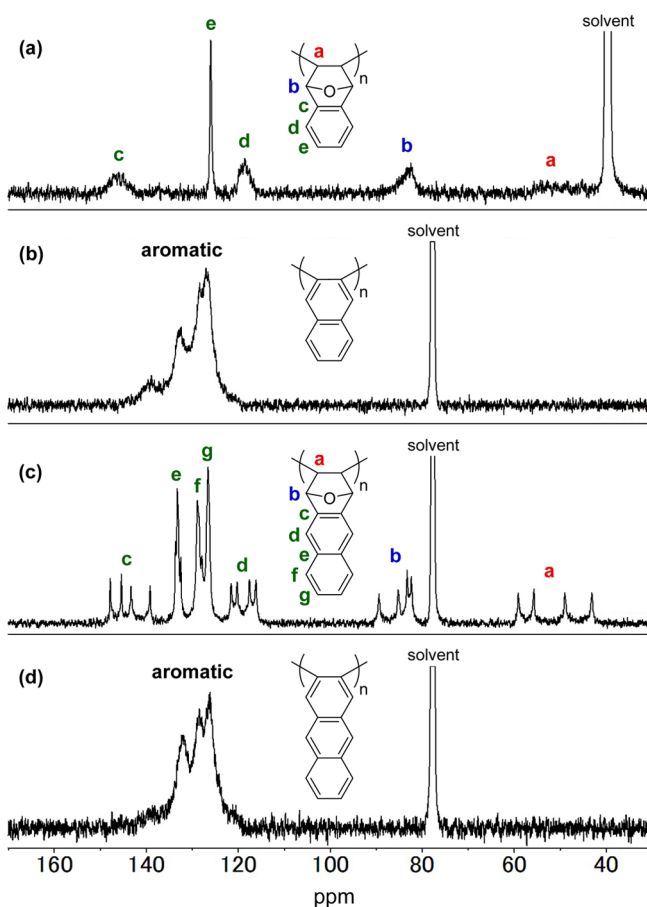

Figure 1. ^{13}C NMR spectra (101 MHz) and their assignments of (a) polymer 2a (DMSO-d_6, 100 °C), (b) polymer 3a (CDCl$_3$, rt), (c) polymer 2d (CDCl$_3$, rt), and (d) polymer 3d (CDCl$_3$, rt).

bridged oxygen atom, respectively. After dehydration (Figure 1b), these signals disappeared, with only aromatic signals at 120−145 ppm present in the spectrum of the dehydrated material. On the other hand, the ^{13}C NMR spectrum of polymer 2d (Figure 1c) exhibited more sharp signals than those of other poly(naphthalene-2,3-diyl)-type polymers 2a−2c. Four peaks were observed for each signal of a, b, c, and d in polymer 2d, which could be attributed to a triad sequences involving *meso−meso*, *meso−racemo*, *racemo−meso*, and *racemo−racemo* triads. This may be interpreted that the stereoregularity of polymers 2 was not controlled, but it is not a significant

problem because the information on stereoregularity disappears after dehydration.

MALDI-TOF mass analyses provided useful information for elucidation of the chain ends. For polymer 2a, only the allyl group (−CH$_2$CH═CH$_2$) was detected as an initiation chain end, and for other polymers 2b−2d, two initiation chain ends—allyl and hydrogen (−H) groups—were observed. The 1-hydroxynaphthalene-2-yl group was detected as a termination chain end for polymers 2a−2d. Based on the mass analyses, we propose the plausible mechanism shown in Scheme 4. The

Scheme 4. Plausible Mechanism of the Polymerization
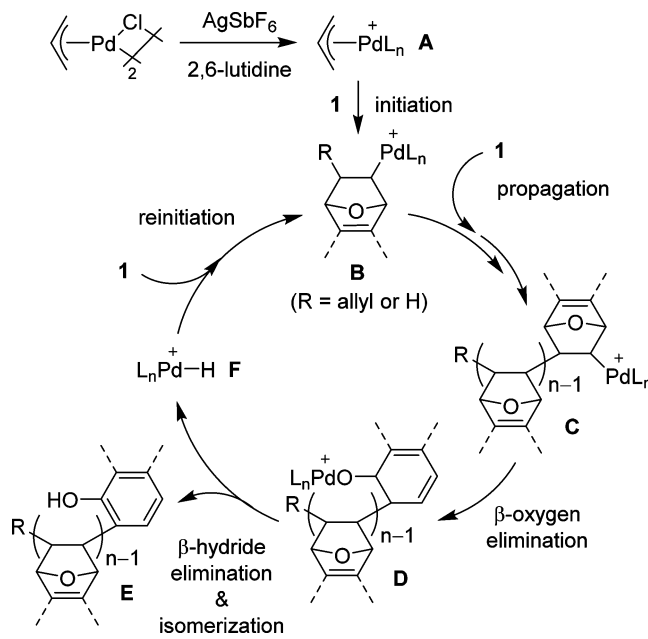
polymerization is initiated by insertion of monomer 1 into π-allylpalladium species A to form alkylpalladium species B. After successive insertion of 1 to propagate the main chain, termination occurs by β-oxygen elimination from C to D followed by β-hydride elimination into product E. The formed palladium−hydride complex F reinitiates the chain propagation by reacting with monomer 1. During these processes, the toluene solvent would regulate the Lewis acidity of the cationic palladium catalyst and suppress side reactions such as β-oxygen elimination.

In summary, we have developed a novel method for the synthesis of poly(o-arylene)s using [2.2.1]oxabicyclic alkenes as

aryne equivalents. Palladium-catalyzed coordination−insertion polymerization of [2.2.1]oxabicyclic alkenes (**1**) produced the corresponding polymers **2** having an aliphatic main chain. Subsequent acid-promoted dehydration allowed the aliphatic main chain to be converted into an aromatic main chain to form polymers **3**. These sequential processes enable formal aryne polymerization, providing a new method to prepare poly(*o*-arylene)s which are otherwise difficult to synthesize.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(19) See the SI for details.

(20) Complete data set for the optimization of polymerization condition is described in the SI.

(21) The larger molecular weight distribution is attributed to higher solubility of polymer **3a** than polymer **2a**. See the SI for the solubility of polymers.

(22) For example, see: Walter, M. D.; Moorhouse, R. A.; Urbin, S. A.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **2009**, *131*, 9055.

(23) Use of a halogenated solvent as a single solvent system led to the formation of low molecular weight oligo- or polymers because it promotes β-oxygen elimination during the polymerization process and the subsequent chain transfer reaction.

(24) Ion signals in the MALDI-TOF mass spectra of polymer **3** were broader than those of polymer **2**. This could be attributed to low ionizable nature of polymer **3**, leading to low signal-to-noise ratios.