INVITED REVIEW

Chain-growth polymerization enabling formation/introduction of arylene groups into polymer main chains

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Owing to the many advantages over step-growth polymerizations, chain-growth polymerization has been utilized in a variety of controlled polymer synthesis, including many important industrial processes. Chain-growth polymerization is generally used for alkenes and alkynes to form ‘aliphatic main chains’, such as alkylene and alkenylene units. In contrast, this method has rarely been applied to the construction of ‘aromatic main chains’ such as arylene units because of the poor variety of the corresponding aromatic monomers in polymer synthesis. Considering the increasing importance of arylene-containing polymers in academic and industrial societies, the development of controlled methods for the formation/introduction of arylene groups by chain-growth polymerization remains a challenging subject in polymer chemistry. In this review, the progress of chain-growth polymerization accompanied by formation/introduction of arylene groups into polymer main chains is reviewed.

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INTRODUCTION

The nature of polymers is largely determined by the structure of main chain. Thus polymers that contain arylene groups as the main chain are of high academic and industrial importance, because the arylene groups are responsible for various unique and interesting properties. The property of arylene-containing polymers is highly dependent on whether the main chain is fully conjugated or not. Arylene-containing conjugated polymers, including polyarylenes and poly(arylenevinylene)s, have attracted much attention owing to their applications as optoelectronic devices, such as organic field-effect transistor and organic light-emitting diode.^{1–4} On the other hand, a strong motivation to synthesize arylene-containing non-conjugated polymers is their applications as engineering plastics exhibiting thermally durable properties, as exemplified by polycarbonates, aromatic polyamides and poly(ether ether ketone)s.⁵ Therefore, the development of novel controlled methods for the synthesis of polymers containing arylene groups is an important subject in polymer chemistry.

Methods to synthesize polymers are generally classified into two categories: step-growth polymerization and chain-growth polymerization. The former polymerization method proceeds via stepwise intermolecular reactions of bifunctional or multifunctional monomers. Many naturally occurring polymers, such as polypeptides, polysaccharides and nucleic acids, and some synthetic polymers, such as polyesters and polyamides, are produced by step-growth polymerization. On the other hand, chain-growth polymerization proceeds via successive intermolecular reactions between monomers

and reactive sites on the polymer chain, with regeneration of the reactive sites at the end of each growth step.^{6,7} Hence, chain-growth polymerization methods offer many advantages over step-growth polymerization such as controlled molecular weights, narrow molecular-weight distributions and defined chain-end functional groups. Owing to these advantages, a variety of industrial processes for the production of synthetic polymers has been accomplished using the chain-growth polymerization method. Among them, the most representative examples are radical, anionic and cationic polymerizations of vinyl monomers, coordination–insertion polymerization of alkenes/alkynes and metathesis polymerizations. In general, almost all of these methods are applied to alkenes and alkynes to form ‘aliphatic main chains’, such as alkylene or alkenylene units. In contrast, the formation of ‘aromatic main chains’ such as arylene units by chain-growth polymerization remains a significant challenge in polymer synthesis. Over the past three decades, therefore, intensive efforts have been made by synthetic chemists to develop chain-growth polymerizations for forming polymers bearing arylene units in the main chain; this is the topic of the present review. It is worth noting that this review focuses on the introduction of arylene groups into the polymer main chain along with their formation and thus excludes polymerization of monomers bearing preformed intact arylene units, such as ring-opening metathesis polymerizations of arylene-containing monomers,⁸ catalyst-transfer condensation polymerizations^{9–18} and $S_{RN}1$ -type polycondensation reactions.¹⁹

Scheme 1 Polymerization of *p*-quinodimethane and its analogs.

p-ARYLENE UNITS

Polymerization of *p*-quinodimethanes and their analogs

Established monomers for formation/introduction of *p*-arylene units are *p*-quinodimethanes **1** and their analogs **2–5**, generated by formal replacement of one or two of the methylenic carbon atoms in **1** by oxygen or nitrogen functionality (Scheme 1). The polymerization of such monomers produces polymers bearing a main chain of $-(X\text{-arylene-}Y)_n-$, regardless of whether the polymerization occurred via step-growth or chain-growth mechanisms. As quinonoid polymerization has a long-established history and its scope and limitations have been described in great detail,^{20–25} this review is mainly focused on the general aspects and recent developments of the polymerization.

The polymerization of *p*-quinodimethanes has attracted much attention as it affords poly(*p*-phenyleneethylenes) (idiomatically called 'poly(*p*-xylylene)').²² Unsubstituted *p*-quinodimethane (**1**; $R^1 = R^2 = H$) can be generated by a variety of methods, including the pyrolysis of *p*-xylene,²⁶ [2.2]paracyclophane²⁷ and monofunctional or bifunctional monomers XCH_2ArCH_2Y ($X, Y = \text{hydro, halogen, carboxy, ammonium, sulfonium and so on}$),²⁴ but the formed *p*-quinodimethane undergoes spontaneous polymerization without precise control via step-growth polymerization. The introduction of electronegative atoms or electron-withdrawing groups at the methylenic positions stabilizes the *p*-quinodimethane structure and enables their isolation and use in more controlled (co)polymerization, mainly by the radical mechanism.^{23–25} An interesting analog of *p*-quinodimethane is 10-methylene-9,10-dihydroanthryl-9-spiroarylcyclopropane **6**, in which one of the methylenic groups in 9,10-anthraquinodimethane is formally cyclopropylated. Cho and Song²⁸ reported, for the first time, that the polymerization of **6** was promoted by a radical initiator to produce poly(arylenevinylene) **7** (Scheme 2). The polymerization is driven by releasing the strain energy of the spiro structure and the subsequent aromatization of monomers. In the following papers, Mori and co-workers employed the reversible addition–fragmentation chain transfer method to this polymerization for synthesizing polymer **7** in a controlled manner.^{29–32}

p-Quinone methides have offered chemistry similar to that of *p*-quinodimethane. Although unsubstituted *p*-quinone methide (**2**; $R^3 = R^4 = H$) is an unstable species whose isolation is difficult, those with electron-withdrawing groups, such as cyano or

Scheme 2 Radical polymerization of 10-methylene-9,10-dihydroanthryl-9-spiroarylcyclopropanes.

alkoxycarbonyl groups, at the methylenic positions (R^4) can be isolated and polymerized mainly by anionic polymerization.^{24,25} Cho and Kim^{33,34} developed the polymerization of *p*-quinone methide analog **8**, in which the methylenic group is formally cyclopropylated. Monomer **8** was not polymerized by a radical initiator but polymerized in the presence of an anionic initiator to form polymer **9**. Based on the polymer structure, the polymerization was suggested to proceed via the nucleophilic attack of the anion intermediate to the more hindered carbon possessing the vinyl group, accompanied by ring opening of the cyclopropyl ring and aromatization (Scheme 3).^{33,34}

Other *p*-quinodimethane analogs have also been investigated as monomers for homopolymerization and copolymerization. *p*-Benzoquinone (**3**; $R^5 = R^6 = H$) is usually used as an inhibitor for radical polymerization, and thus it generally does not undergo radical homopolymerization. In contrast, *p*-benzoquinone bearing electron-withdrawing groups, for example, *p*-chloranil (**3**; $R^5 = R^6 = Cl$) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ; **3**; $R^5 = Cl, R^6 = CN$), are amenable to alternating copolymerization with styrene or other alkenes in the presence of a radical initiator.^{35,36} However, it was subsequently reported that DDQ was spontaneously copolymerized with styrene in the absence of an initiator,³⁷ suggesting ambiguity of the polymerization mechanism. *p*-Quinone methide imine bearing electron-withdrawing groups (**4**; $R^7 = R^8 = CN$)³⁸ was also homopolymerized and alternately copolymerized with styrene in the presence of 2,2'-azobis(isobutyronitrile) (AIBN) as a radical initiator. *p*-Quinone diimine **5** bearing substituents of $R^9 = SO_2Ph, CO_2Et$ and $COPh$ exhibited low reactivity for homopolymerization but alternately copolymerized with vinylarenes and vinyl ethers in the presence of AIBN as a radical initiator.^{39,40}

Ring-opening metathesis polymerization of bicyclic alkenes as *p*-quinodimethane equivalents

Poly(*p*-arylenevinylene)s are an important π -conjugated polymer, which exhibits excellent material properties such as high electron conductivity when doped and photoluminescence and electroluminescence.^{41–43} In general, poly(*p*-arylenevinylene)s are prepared by step-growth polymerization via polycondensation.^{44–46} In this synthetic route, however, it is difficult to control molecular weights and polymer sequences. Grubbs and co-workers developed chain-growth polymerizations to synthesize poly(*p*-arylenevinylene)s via two-step processes. Molybdenum-catalyzed ring-opening metathesis polymerization (ROMP) of functionalized barrelene derivatives, biscarbonate **10**, afforded polymer **11**. The following elimination of carbon dioxide and methanol under thermal conditions led to the formation of poly(*p*-phenylenevinylene) **12** with high number average molecular weights (M_n) of 46 000–63 000 and low molecular weight distributions of 1.2–1.3 (Scheme 4a).⁴⁷ Similarly, the ROMP of alkylated benzobarrelenes **13** followed by oxidative dehydrogenation in the presence of DDQ was also developed to produce poly(naphthalene-1,4-diylvinylene)s **15** (Scheme 4b).^{48–50}

Scheme 3 Anionic polymerization of spiroquinones.

Scheme 4 Ring-opening metathesis polymerization of [2.2.2]bicyclic alkenes, (a) functionalized barrelene derivatives and (b) benzobarrelenes, followed by aromatization.

Scheme 5 Polymerization of *p*-didehydrobenzenes formed by the Bergman cyclization.

Scheme 6 Living anionic polymerization of cyclohexa-1,3-diene.

The presence of a fused benzene ring would be essential to promote dehydrogenation.

Polymerization of *p*-didehydroarene and their equivalents

The simplest candidate of monomers for efficient introduction of *p*-arylene units is *p*-didehydroarene (idiomatically called '*p*-aryne'), which was first generated by Jones and Bergman⁵¹ by pyrolysis of (*Z*)-hexa-3-en-1,5-diyne **16** ($R^1 = R^2 = H$) in 1972. Homopolymerization of *p*-didehydroarene is a potentially useful method because the resulting poly(*p*-phenylene) **18** has received considerable attention because of its high stability, electrical conductivity and optoelectronic properties.^{42,52,53} However, the intrinsic instability of *p*-didehydroarene⁵⁴ makes its use in polymerization difficult. The only known example includes the polymerization of 1,4-diradical intermediates **17** generated by the Bergman-type cyclization of enediyne-type compounds **16** (Scheme 5),^{55–57} but the details are not covered in this review because it is step-growth polymerization.

In order to achieve the controlled synthesis of poly(*p*-phenylene)s via chain-growth polymerization, chemists have focused on the polymerization of *p*-didehydrobenzene equivalents. The first attempts employed cyclohexa-1,3-diene **19** as a monomer. In reports in the 1950–1960s,^{58–61} the Ziegler-type catalysts were used to synthesize polycyclohexadienes, which contained a certain percentage of 1,2- and 1,3-cyclohexenylene units along with the desired 1,4-cyclohexenylene units. The subsequent aromatization by dehydrogenation or bromination/dehydrobromination afforded poor-quality poly(*p*-phenylene)s.^{58,59,61} In 1997, the living anionic polymerization of cyclohexa-1,3-diene **19** to form 1,4-regioregular polymers **20** was accomplished using the BuLi/amine system (Scheme 6).⁶² The ratio of 1,2- and 1,4-cyclohexenylene units in the polymer chain can be controlled up to almost perfect 1,4-selectivity by changing alkyl lithium and amine ligands.^{63–65} Subsequent dehydrogenation of the 1,4-regioregular polymer was accomplished using DDQ to form regioregular poly(*p*-phenylene) **21**.⁶⁶ The living anionic polymerization method could be applied to copolymerization to synthesize block,^{67–69} random,⁷⁰ quasi-alternating⁷¹ or C₆₀-graft^{72,73} copolymers, in which subsequent dehydrogenation produces *p*-phenylene groups in the copolymers.

In this regard, functionalized cyclohexa-1,3-dienes, including cyclohexa-3,5-diene-1,2-diyl dibenzoate (**22a**) and 5,6-bis(trimethylsiloxy) cyclohexa-3,5-diene (**22b**), are promising candidates for chain-growth polymerization to obtain poly(*p*-phenylene)s. Radical polymerization of **22a** produced the corresponding polymers, but the products

Scheme 7 (a) Radical polymerization of cyclohexa-3,5-diene-1,2-diyl dibenzoate and (b) nickel-catalyzed coordination-insertion polymerization of 5,6-bis(trimethylsiloxy)cyclohexa-1,3-diene to form poly(*p*-phenylene).

Scheme 8 Valence tautomerization of (a) *m*-quinodimethane and (b) *m*-quinone methide.

contained about 10–15% of 1,2-linkages along with 85–90% of 1,4-linkages (Scheme 7a).^{74–76} The non-regioregular polymers were converted to the corresponding poly(*p*-phenylene)s by thermal acid elimination, leading to the deterioration of molecular weights during the aromatization process.^{76,77} Following these reports, Grubbs and co-workers succeeded in obtaining the perfect regioregular polymers by using transition metal catalysis.^{77–79} The regioregular and stereoregular nickel-catalyzed polymerization of **22b** afforded polymer **23b** ($M_n = 20\,000$ – $50\,000$) containing only 1,4-linkages (Scheme 7b).⁷⁷ The following conversion of **23b** into acetate **23c** was needed before elimination of acetic acids for the production of poly(*p*-phenylene) **21**. When the aromatization of **23c** was induced under thermal conditions, the onset of chain degradation occurred before the onset of aromatization. Consequently, the assistance by Brønsted or Lewis-acid catalysis was essential for smooth elimination of acetic acids to produce poly(*p*-phenylene) **21** without significant decrease of molecular weight.⁷⁹

m-ARYLENE UNITS

Compared with the polymerization methods to form *p*-arylene units, fewer methods have been developed for the synthesis of *m*-arylene unit-containing polymers via chain-growth polymerization. This could be partly attributed to the absence of *m*-didehydroarene polymerization. *m*-Didehydroarene (idiomatically called '*m*-aryne')⁵⁴ has received less attention than the *p*- and *o*-analogs that have offered rich chemistry. Although *m*-didehydroarenes can be generated by various methods, including (flash vacuum) pyrolysis and photolysis,^{80–82} there are no literature reports of the polymerization of *m*-didehydroarenes.

In this sense, *m*-quinonoids are the only candidate available for formation/introduction of *m*-arylene units. Compared with *p*- and *o*-quinonoids, *m*-quinonoids are less stable because of their non-Kekulé structure. For example, *m*-quinodimethane is known to exist as a diradical species **24** rather than a closed tautomer structure such as **25** (Scheme 8a),⁸³ although its polymerization has not been reported. *m*-Quinone methide also has a non-Kekulé structure and thus can be isolated in the form of a valence tautomer, 6-methylenebicyclo[3.1.0]hex-3-en-2-one **27** (Scheme 8b), which was polymerized in a non-controlled manner by pyrolysis or photolysis to produce insoluble polymeric materials.⁸⁴ In that sense, the only example of chain-growth polymerization of *m*-quinonoids includes the polymerization of monomer **28**, a valence tautomer of *m*-naphthoquinone methide (Scheme 9).⁸⁵ Compound **28** was polymerized in the presence of AIBN as a radical initiator but not with cationic and anionic initiators. The polymerization was accompanied by the ring opening aromatization to obtain head-to-tail polymer **29** with M_n of 3200. Copolymerization of monomer **28** with methyl methacrylate was also accomplished using a radical initiator to produce the corresponding random copolymer **30** with M_n of 2200–70 000 depending on the content of methyl methacrylate.

o-ARYLENE UNITS

Polymerization of *o*-quinodimethanes

Polymerization of *o*-quinodimethanes^{24,86} is a powerful method to afford poly(*o*-phenyleneethylene). As *o*-quinodimethane is an unstable and non-isolable species, it is used after *in situ* generation from a suitable precursor. In a seminal paper, Errede⁸⁷ investigated the preparation and properties of *o*-quinodimethane **32** generated by flash vacuum pyrolysis of *o*-methylbenzyl(trimethyl)ammonium hydroxide, **31** (Scheme 10). The *in situ* generated compound **32** was trapped as the form of dibenzocyclooctadiene **33** and spirodimer **34** after quenching at low temperature.⁸⁷ Although compound **33** was thermally stable, spirodimer **34** was polymerized upon heating to form poly(*o*-phenyleneethylene) **35**.

Another representative precursor of *o*-quinodimethanes is benzocyclobutene.⁸⁸ Thermal isomerization of non-substituted benzocyclobutene into *o*-quinodimethane occurs above 200 °C, which would prohibit its use for controlled chain-growth polymerization. Chino and Endo⁸⁹ reported that the introduction of functional groups into the cyclobutene ring has a large influence on the isomerization temperature. For example, the introduction of an electron-donating methoxy group (**36a**; R = OMe) lowered the temperature to around 100 °C,⁸⁹ which is a suitable temperature to perform a variety of polymerization methods, including radical,^{90,91} cationic⁹² and anionic⁹² polymerizations, to afford polymer **38a** (Scheme 11). Subsequent treatment of polymer **38a** ($M_n = 5600$) with *p*-toluenesulfonic acid at 60 °C led to the formation of poly(*o*-phenylenevinylene) **39** with a slight decrease of molecular weight ($M_n = 3500$).^{90,91} The introduction of the electron-withdrawing cyano group also lowered the isomerization temperature to 120–150 °C, inducing radical polymerization to afford the corresponding polymers with molecular weights of $M_n = 1500$ – 4700 .^{93,94} In the case of the siloxy-substituted substrate **36b** (R = OSiMe₃), group-transfer polymerization of **36b** was shown to be available to afford polymer **38b** with low molecular weights of M_n up to 2000.⁹⁵

Polymerization of *o*-diisocyanarenes

A significant milestone in polymer synthesis via formation/introduction of *o*-arylene groups is the living polymerization of 1,2-diisocyanarenes to form poly(quinoxaline-2,3-diyl)s. In 1990,

Scheme 9 Homo- and copolymerization of a valence tautomer of *m*-naphthoquinone methide.

Scheme 10 Pyrolysis of *o*-methylbenzyl(trimethyl)ammonium hydroxide and polymerization of the formed spirodimer of *o*-quinodimethane.

Scheme 11 Polymerization of *o*-quinodimethane formed by pyrolysis of benzocyclobutenes.

Scheme 12 Metal-catalyzed living polymerization of diisocyanoarenes to form poly(quinoxaline-2,3-diyl)s.

Ito *et al.*⁹⁶ developed palladium-catalyzed polymerization of 1,2-diisocyanoarene **40** to produce poly(quinoxaline-2,3-diyl)s **41** (Scheme 12). The reaction proceeds by successive insertion of isocyanato groups into the metal–carbon bond of the catalyst (**40** → **A** → **B**). The stable (quinoxaliny)l palladium moiety **B** in the polymer chain end is essential for realizing living polymerization. As the poly(quinoxaline-2,3-diyl)s adopt a stable helical structure, it can be optically active if the polymerization proceeds with a preference for a single-handed helix. In 1992, the first enantioselective polymerization was accomplished to form optically active poly(quinoxaline-2,3-diyl)s possessing a single-helical helix.⁹⁷ Following these seminal reports, the chemistry based on helical poly(quinoxaline-2,3-diyl)s has been greatly expanded mainly by Suginome and co-workers for applications to asymmetric catalysis^{98–101} and chirality-switching materials.^{98,102–105}

Polymerization of 3,3-diarylcyclopropenes via 1,4-rhodium migration

Shintani *et al.*¹⁰⁶ reported a new mode of metal-catalyzed polymerization to form novel *o*-arylene-containing polymers. The rhodium-

Scheme 13 Rhodium-catalyzed polymerization of 3,3-diarylcyclopropene via 1,4-rhodium migration.

Scheme 14 Benzyne polymerizations: (a) copolymerization of benzyne and pyridine and (b) homopolymerization of arynes.

catalyzed polymerization of 3,3-diarylcyclopropenes **42** proceeded through the insertion of **42** into a rhodium–carbon bond and a subsequent 1,4-rhodium migration (**C**→**D**) to produce poly(cyclopropylene-*o*-phenylene)s **43** with M_n of 8000–27 000 (Scheme 13).¹⁰⁶ Although the selectivity of 1,4-rhodium migration was not perfect, the ratio of cyclopropylene-*o*-phenylene unit **I** to cyclopropylene unit **II** was improved up to 91:9 by optimizing the rhodium catalyst, polymerization initiator and concentration. In the sequence of the polymerization, aryl groups are transformed into arylene groups via *in situ* 1,4-rhodium migration, which allows access to a unique main-chain structure that is difficult to construct by conventional polymerization methods.

Polymerization of arynes (*o*-didehydroarenes)

The simplest ideal monomer for efficient introduction of *o*-arylene units is an aryne—*o*-didehydroarene—formed by abstraction of two neighboring hydrogen atoms from an arene compound. Since their first synthetic report in 1902,^{107,108} arynes have served as useful intermediates in organic synthesis for >100 years.^{109–112} Despite their significant utility, arynes had been an elusive monomer for polymerization until recently. If aryne could be (co)polymerized, it would allow the direct synthesis of *o*-arylene-containing polymers such as poly(*o*-arylene)s. In contrast to extensively studied *p*- and *m*-connected analogs, poly(*o*-arylene)s have been the least studied

Scheme 15 [2.2.1]Oxabicyclic alkenes as an aryne equivalent: polymerization and possible side reactions.

class of π -conjugated compounds, which adopt helical conformation along their twisted main chains.

The first attempt to polymerize benzyne was reported by Ihara *et al.*¹¹³ in 2005. They tried to polymerize benzyne **45**, prepared by the reaction of *o*-silylphenyl triflate **44** with cesium fluoride, by using a wide range of initiators under various conditions, but all the attempts resulted in no polymerization. Instead, they found that the copolymerization of benzyne with pyridine proceeded to give the corresponding alternating copolymer **46** (Scheme 14a). Ten years later, in 2015, Mikami and Uchiyama reported the first copper-catalyzed homopolymerization of benzynes (Scheme 14b).¹¹⁴ Benzyne monomers **48** were prepared by reaction of *o*-silylaryl triflate **47** with fluoride anion. The use of copper(I) catalysts was effective to promote the polymerization into poly(*o*-phenylene)s **49** with M_n of 2400–13 800. In particular, when Lipshutz cuprate ($\text{Bu}_2\text{Cu}(\text{CN})\text{Li}_2$) or copper cyanide (CuCN) was used, matrix-assisted laser desorption ionization time-of-flight mass analysis revealed that the obtained polymer has a cyano group (CN) as an initiation chain end. Based on the results, the authors claimed that the polymerization was initiated by addition of cyanide anion (^-CN) to a benzyne and proceeded via successive insertion of benzynes in a chain-growth manner.

Polymerization of aryne equivalents (formal aryne polymerization)

As stated in previous section, aryne was a difficult monomer to polymerize and still remains so. In order to expand the utility and variety of aryne polymerization chemistry, we saw the need for development of novel polymerization methods that can utilize more stable and controllable monomers. In our research, therefore, we focus on a synthetic equivalent of arynes, [2.2.1]oxabicyclic alkenes **50**, as monomers for polymerization. [2.2.1]Oxabicyclic alkenes have been employed as useful building blocks and intermediates in organic synthesis, especially for efficient construction of various synthetically useful carbocycles and heterocycles, which are not accessible by

Scheme 16 Formal aryne polymerization using [2.2.1]oxabicyclic alkenes as an aryne equivalent to form poly(*o*-arylene)s.

Scheme 17 Formal aryne/carbon monoxide alternating copolymerization to form aromatic polyketones/polyketals.

other conventional methods.^{115–118} However, the monomers have rarely been used as a monomer for polymerization.^{119–122} As shown in Scheme 15, polymerization of **50**, if successful, affords the corresponding polymer **51**, which can be converted to *o*-arylene units **52** by subsequent dehydration. Importantly, in the whole process, monomer **50** functions as an aryne equivalent, enabling the formation/introduction of *o*-arylene groups in the main chain of polymers. A potential side reaction in the coordination–insertion polymerization of **50** is the metal-catalyzed isomerization of **50** into 1-hydroxyarenes **53**.^{123,124} The polymerization may also be hampered by β -oxygen elimination from intermediates **54**, formed by the insertion of **50** into a metal-alkyl species ($R-ML_n$), to give ring-opened products **55**.^{115–118}

First, we developed homopolymerization of aryne equivalents **50**.¹²⁵ In order to achieve polymerization, a wide range of transition-metal catalysts, ligands and solvents were screened using monomer **50a**.

As a result, the polymerization was found to be successfully catalyzed by a cationic palladium complex $(\eta^3\text{-allyl})Pd^+SbF_6^-$ stabilized by 2,6-lutidine (Scheme 16). An important role of 2,6-lutidine is to suppress monomer isomerization even under high-temperature conditions: In the absence of 2,6-lutidine, the monomer tends to be rapidly isomerized into 1-hydroxyarene **53**. In addition, the use of combined solvents, toluene and 1,2-dichloroethane was also essential to improve the polymer yield and molecular weight. Toluene is needed to stabilize the cationic palladium catalyst¹²⁶ and suppress β -oxygen elimination from **54** during chain propagation. A halogenated co-solvent, 1,2-dichloroethane, is required to dissolve the cationic palladium catalyst. The following dehydration of polymer **56** was accomplished by treatment with hydrogen chloride or concentrated sulfuric acid to afford the corresponding poly(*o*-arylene)s **57**. The present two-step method was demonstrated to synthesize poly(naphthalene-2,3-diyl)s, which bear hydro groups **57a** ($M_w = 3900$), electron-donating alkyl groups **57b** ($M_w = 7000$) and electron-withdrawing bromo group **57e** ($M_w = 1200$), in good yields. The method could also be applied to monomers with longer π -conjugate systems in order to synthesize poly(anthracene-2,3-diyl) **57f** ($M_w = 6300$) and poly(triphenylene-2,3-diyl) **57g** ($M_w = 800$).

The advantage of the present ‘formal aryne polymerization’ method is that the aryne equivalents could be used for copolymerization as they are a stable monomer, unlike an unstable aryne. Thus we targeted the copolymerization with carbon monoxide, which leads to the formation of aromatic polyketones/polyketals.¹²⁷ Aromatic polyketones,^{128,129} bearing the main chain consisting of arylene and carbonyl groups, have received much attention because of their potential applications as superengineering plastics.^{130–132} However, the range of accessible aromatic polyketones has been limited, and all the methods rely on step-growth condensation polymerization,^{128–134} rather than chain-growth polymerization. Thus we focused on the transition-metal-catalyzed alternating copolymerization of alkenes and carbon monoxide, which produces aliphatic polyketones bearing saturated aliphatic main chains.^{135–138} Although the methods have never been applied to an ‘aromatic comonomer’ such as aryne, we envisioned that the use of aryne equivalents would achieve the synthesis of aromatic polyketones with alternating *o*-arylene and carbonyl linkages.

Scheme 18 Formal aryne/ethylene copolymerization to form *o*-arylene-containing polyethylenes.

Extensive catalyst screening for polymerization of [2.2.1]oxabicyclic alkenes **50a** revealed that the use of palladium/phosphine–sulfonate catalysts^{136–138} was effective to produce polymers **58** in terms of polymer yield and molecular weights (Scheme 17). The optimum reaction conditions enabled the synthesis of various copolymers **58** from 2,3-didehydronaphthalene equivalents bearing hydro groups **50a**, electron-donating groups **50b** and **50c** and electron-withdrawing groups **50d** as well as 2,3-didehydroanthracene equivalent **50f**. The obtained polymers have a mixed structure of polyketone form **58_{ktn}** and polyketal form **58_{ktd}**, in which the ratio of **58_{ktn}**/**58_{ktd}** depends on the monomer used. Subsequent dehydration reactions of **58a–c** and **58f** were accomplished by the treatment of polymers with hydrogen chloride to obtain aromatic polyketone/polyketals **59**. Although polymers **59a** and **59f** were insoluble in common organic solvents, polymers **58b** and **58c** showed good solubility, which enabled to determine their molecular weights to be M_n of 4000–4800. The resulting copolymers **59** were amorphous solids, which exhibited high 5%-weight-loss temperatures at 281–317 °C.

Finally, we focused our attention on the formal aryne copolymerization with ethylene, which produces *o*-arylene-containing polyethylenes. The introduction of functional groups or different comonomers into linear polyethylenes is effective for the modification of both surface and materials properties.¹³⁶ Toward the end, a range of comonomers, including polar monomers^{136–139} and carbon monoxide,¹³⁵ have thus far been incorporated, but the use of aryne or its congeners for the introduction of *o*-arylene linkage has been unexplored. Thus we employed our formal aryne polymerization strategy for the copolymerization with ethylene (Scheme 18).¹⁴⁰

Copolymerization of aryne equivalents **50** and ethylene, followed by acid-induced dehydration, was found to proceed to generate the corresponding copolymers **61** containing *o*-arylene units in the main chain when palladium/alkylphosphine–sulfonate complexes^{141–143} were used as a catalyst. In particular, the use of a phosphine–sulfonate ligand bearing bulky methyl groups on the phosphorus atoms was essential to produce copolymers with high M_n of up to 18 200. It is worth noting that other transition metal catalysts that are capable of

promoting ethylene/polar monomer copolymerization, such as palladium/ α -diimine,^{144,145} nickel/imine–phenolate¹⁴⁶ and palladium/bisphosphine–monoxide,¹⁴⁷ produced no polymer. Nuclear magnetic resonance analysis of the obtained copolymers **61** revealed that the copolymers have a linear polyethylene backbone without detectable alkyl branching and that the introduced arene units were attached mainly to the main chain as an *o*-arylene group and partly to the chain end as an aryl group. The copolymers exhibited linear low-density polyethylene-like thermal properties as determined by differential scanning calorimetric measurements.

CONCLUSION

Despite significant advances in polymer synthesis, the introduction of arylene units relies largely on step-growth polymerization, and it is still difficult to achieve controlled synthesis of arylene-containing polymers based on chain-growth polymerization. A serious bottleneck is the limited variety of monomers that enable the introduction of arylene units, that is, chemists need to use unstable and uncontrollable monomers, such as quinonoids and didehydroarenes. Hence, many of the successful (co)polymerizations enabling the formation/introduction of arylene groups in the main chain of polymers in a chain-growth manner resulted from the use of stable surrogates or valence tautomers of the otherwise unstable monomers. Although the molecular weights of the resulting polymers were relatively low, the methods in this review offer the versatile and useful methods for the synthesis of various arylene-containing polymers via chain-growth polymerization.

CONFLICT OF INTEREST

The author declares no conflict of interest.

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