Unconventional Conjugated Polymers Derived from a Common Set of *trans*-Enediyne Monomers

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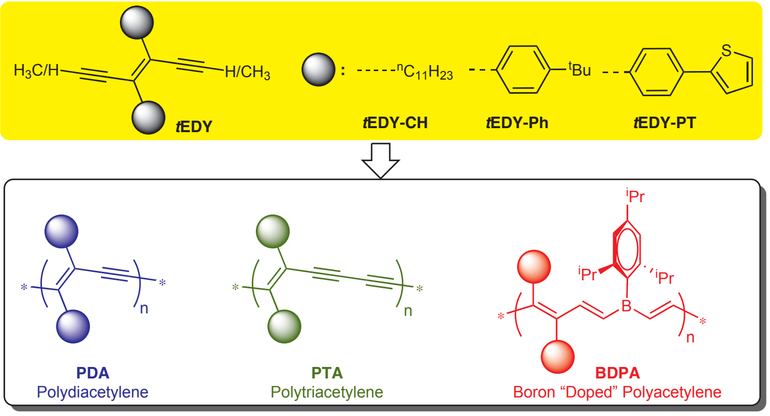

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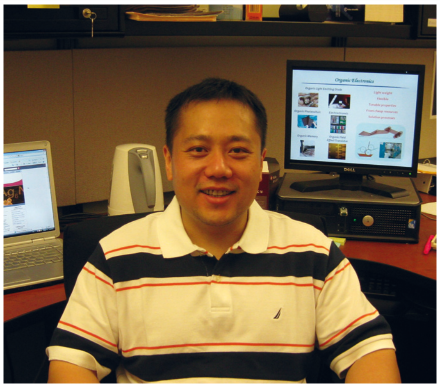
Abstract This account describes our recent efforts in the design and synthesis of several series of unconventional conjugated polymers derived from a common set of *trans*-enediyne (*t*EDY) monomers. The journey started with a failed attempt, through acyclic diene metathesis of triene monomers, to prepare soluble polyacetylenes (PAs) having cross-conjugated side-groups on alternate double bonds along the main chain. At this seemingly dead end of the project, we found that the *t*EDY intermediates leading to triene monomers could undergo alkyne metathesis to generate soluble polydiacetylenes (PDAs). Such acyclic enediyne metathesis represents the first example of a solution synthesis of PDAs, in contrast to the conventional topochemical methods. By applying Glaser–Hay-type reaction conditions with selected *t*EDY monomers, polytriacetylenes were smoothly obtained; these possessed aromatic units directly attached to the polymer main chains, which significantly affected the electronic properties of the polymers. Furthermore, through hydroboration of the *t*EDY monomers, 'boron-doped' polyacetylenes (BDPAs) were prepared that can be considered as PAs with every fourth double bond replaced with a boron atom. These BDPAs represent the first boron main-chain conjugated polymers lacking aromatic units along the backbone, potentially enhancing electronic delocalization along the main chain.

Key words conjugated polymers, enediynes, polyacetylenes, polydiacetylenes, polytriacetylenes, boron-containing polymers



Yang Qin was born and raised in Sichuan Province, a region of China famous for its spicy food and the giant panda. He studied chemistry and obtained a B.S. degree from Peking University in 2000, before coming to the USA, and in 2006, he obtained a Ph.D. degree in chemistry from Rutgers University at Newark. After two postdoctoral periods at the University of Minnesota, Twin Cities (2006–2009) and Brookhaven National Laboratory (2009–2010), respectively, he began his independent career as an assistant professor at the Department of Chemistry and Chemical Biology of the University of New Mexico, and was promoted to associate professor in 2017. The research in Yang's group is mainly focused on the design and synthesis of novel conjugated small molecules and polymers, and on their applications in thin-film optoelectronic devices, including OPVs. Besides chemistry, Yang's greatest passions are football (a.k.a. soccer in the USA) and cooking spicy food.

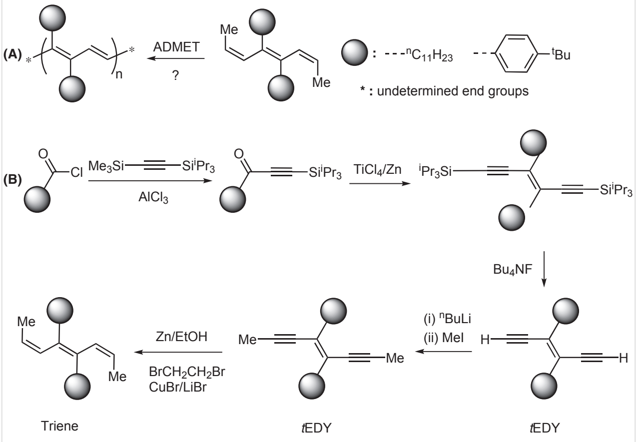
Since the discovery of metallic conductivity in doped polyacetylene (PA), conjugated polymers (CPs)[1] have become the subject of intense research in the field of organic electronics, including organic field-effect transistors,[2] organic light-emitting diodes (OLEDs),[3] organic photovoltaics (OPVs),[4] organic electrochromics,[5] and organic memory devices,[6] as well as solid-state lasers,[7] sensors,[8] actuators,[9] and corrosion-resistant coatings.[10] Each of these applications puts unique and stringent requirements on the properties of the materials used, including their solubility, bandgap, charge mobility, and environmental stability. Understanding the complex structure–property relationships of CPs and fine tuning the factors that affect device performance through tailor-made semiconducting materials have been the ongoing challenges in this field.

PA is the simplest prototype for CPs with a linear polyene backbone; the discovery of its high conductivity upon doping led to the award of the Nobel Prize to Hideki Shirakawa, Alan G. MacDiarmid, and Alan J. Heeger in 2000.[11] Due to their lack of side groups, pristine PAs are highly crystalline and insoluble materials, which has significantly limited their use in modern electronic devices.

There have been two main strategies for the synthesis of solution-processable PAs. The first is the so-called precursor route that takes advantage of the solubility of preformed polymers that can be later converted into pristine PAs.[12] The final conversion step to give PAs typically involves heating and elimination of small-molecule byproducts, which usually leads to defects from incomplete conversion, impurity inclusion, and volume shrinkage. The second approach is to prepare soluble PA derivatives with solubilizing side groups regularly attached to the polyene backbone. This strategy also permits fine tuning of the electronic properties and crystallinity of the resulting PAs.

The most studied and widely applied method for the synthesis of substituted PAs is the metal-catalyzed polymerization of alkynes.[13] These techniques use Ziegler–Natta-type catalysts that are generally air- and moisture-sensitive, and they are not compatible with monomers containing polar functional groups. As a result, the majority of PAs obtained through this method bear only phenyl or alkyl groups directly attached to the PA main chains. More importantly, PAs generated by using this method have substituents on every double bond along the polymer backbone, giving rise to steric hindrance that inevitably induces main-chain twisting and decreases the conjugation length. Research in this area has been mainly directed toward studies on the polymerization behavior of monomers having chiral or liquid-crystalline side chains and on the unusual optical properties induced by the secondary structures of the resulting polymers.[14] Another frequently applied strategy is the ring-opening metathesis polymerization of monosubstituted cyclooctatetraenes.[15] Recent developments in metathesis have led to air-stable catalyst systems that tolerate a wide variety of functional groups. However, substituted cyclooctatetraenes are difficult to synthesize, and PAs obtained from monosubstituted monomers have one side group for every four double bonds, which leads to only marginally improvements in solubility and provides similar electronic properties to those of pristine PAs.

These above examples show that having substituents on every double bond or every four double bonds along a PA backbone is not ideal in terms of maintaining main-chain planarity or in terms of providing tunability of solubility and electronic properties, respectively. We therefore hypothesized that if we could install two aromatic substituents on alternate double bonds along the PA main chain, as shown in Scheme 1(A), we would be able to achieve better solubility, electronic tunability, and main-chain coplanarity in a single polymer structure. The method that we chose to synthesize these targets was acyclic diene metathesis (ADMET) of triene monomers bearing two substituents at the central double bonds. As a variant of metathesis polymerization, ADMET[16] is a versatile method for the preparation of aliphatic polyenes with precisely placed side chains,[17] telechelic polymers with controlled molecular weights,[18] or conjugated poly(arylene vinylene)s.[19] The only one example of an ADMET synthesis of PAs is that reported by Wagener et al.,[20] who successfully polymerized unsubstituted conjugated oligoene monomers, such as hexa-2,4-diene, under ADMET conditions. Due to the lack of solubilizing side groups, the resulting PAs precipitated from the reaction mixtures, and only oligomers of six to ten repeat units were obtained. We therefore surmised that ADMET of substituted oligoene monomers, such as the triene shown in Scheme 1(A), might give soluble PAs with precisely placed substituents.



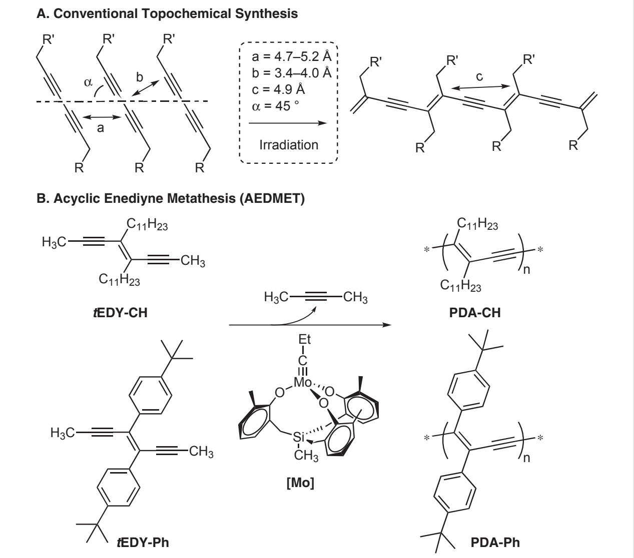
Scheme 1 Synthesis of substituted triene monomers and polyacetylenes through ADMET

The synthesis of the target triene monomers from alkanoyl or aroyl chlorides is shown in Scheme 1(B). The second step involved McMurry coupling reactions to give triisopropylsilyl (TIPS)-protected EDYs in which the central double bond had a 100% *trans* configuration as a result of the large size of the TIPS groups. After desilylation and methylation, the resulting methylated *t*EDY monomers were subjected to attempted hydrogenation by using Lindlar's catalysts, but this only resulted in quantitative recovery of the starting materials. However, reduction with activated Zn led to the desired triene monomers in high yields; in these products the terminal double bonds had an exclusive *cis* configuration, which has been shown to display faster ADMET kinetics in the case of the synthesis of poly(thienylene vinylenes).[19f] To our surprise, neither the alkyl- nor the phenyl-substituted triene monomers underwent a metathesis reaction in the presence of various catalysts based on ruthenium or molybdenum under a range of reaction conditions; the only change that we observed was the isomerization of the terminal double bonds to a *trans* configuration. We still do not fully understand this lack of reactivity of substituted trienes when compared with the successful

ADMET reactions of oligoenes, as demonstrated previously. This project seemingly had come to a dead end, but we soon realized that the *t*EDY intermediates might be used to construct CPs with unconventional main-chain structures.

Significant research efforts have been devoted to polydiacetylenes (PDAs), a classic group of conjugated polymers,[21] since the discovery of their solid-state synthesis in 1969.[22] PDAs are quasi-one-dimensional (1D) organic semiconductors that possess macroscopic long-range coherence as well as anisotropy.[23] Upon exposure to external stimuli, such as temperature,[24] solvents,[25] pressure,[26] light,[27] or specific biological analytes, these PDA materials undergo intriguing optical changes between blue, red, and yellow phases.[28] PDAs are consequently useful in a range of applications, including nonlinear optics,[29] organic conductors,[30] and, most commonly, as sensory materials.[31] Despite many examples, the inconvenient synthesis of PDAs has strongly impeded their practical applications, other than in sensors. PDAs reported to date have been prepared exclusively by a single type of reaction, the irradiation-initiated topochemical polymerization of diacetylene (DA) monomers in various forms, including crystals, films, gels, or micellar structures.[21a] Such reactions cannot occur efficiently unless the DA monomers can pack into periodic structures within very strict geometrical boundaries, as shown in Scheme 2(A).[32] Flexibility around the diacetylene moieties is also required to accommodate spatial rearrangement in which two sp-hybridized carbon atoms in every DA monomer switch to an sp^2 hybridization during the topochemical polymerization.[33] As a result, only a few types of DA monomers, typically having alkyl spacers between the DA cores and the functional side groups, can be successfully polymerized this way.[21] Electronic properties of the resulting PDAs are therefore intrinsic to the polyeneyne structures and are difficult to modify by changing substituents. There have been attempts at solid-state preparation of PDAs bearing directly attached aromatic moieties with the aim of tuning the electronic properties the PDA through side-chain conjugation. Among various tested systems, only a few DA monomers bearing substituted phenyl groups could be partially polymerized when assisted by supramolecular interactions from scrupulously selected side chains and substrates.[29b,34] Moreover, the resulting PDAs usually suffer from limited solubility, making integration into solution-fabricated electronic devices challenging.

Alkyne metathesis represents an emerging organic transformation that has attracted significant research interest and has been used in efficient syntheses of a variety of organic compounds and materials, including natural products, poly(*p*-aryleneethynylene)1D conductive polymers, shape-persistent 2D macrocycles, and rigid 3D molecular cages.[35] We hypothesized that our *t*EDY intermediates, leading to the triene monomers shown in Scheme 1, might be used in the construction of solution-processable PDAs through acyclic enedyne metathesis (AEDMET). If successful, our method should provide great flexibility in structural variations by attachment of different aromatic substituents to the *t*EDY monomers, leading to tunability in the physical and electronic properties of the resulting PDAs.



Scheme 2 Solid-state and solution synthesis of polydiacetylenes

As a proof-of-concept, we explored the feasibility of conducting AEDMET on *t*EDY monomers bearing alkyl and phenyl substituents, as shown in Scheme 2(B).[36] Conventional catalysts of the Mortreux[37] or Schrock[38] types all failed to initiate the polymerization of *t*EDY-CH and ***t*****EDY-Ph**, and only intact monomers were recovered after prolonged reaction times, even under forcing conditions. In marked contrast, the use of a recently developed molybdenum carbyne catalyst **[Mo]**,[39] resulted in the successful polymerization of ***t*****EDY-CH** and ***t*****EDY-Ph** to give **PDA-CH** and **PDA-Ph**, which were easily isolated by precipitation as red solids. The lack of reactivity of *t*EDY monomers toward the usual catalysts is presumably caused by chelation of the metal centers by the two triple bonds of the monomer molecule, preventing intermolecular condensation reactions. With the podand ligand in **[Mo]**,[40] the bottom binding site of Mo is blocked, which effectively prevents chelation from a single monomer and facilitates intermolecular alkyne metathesis.

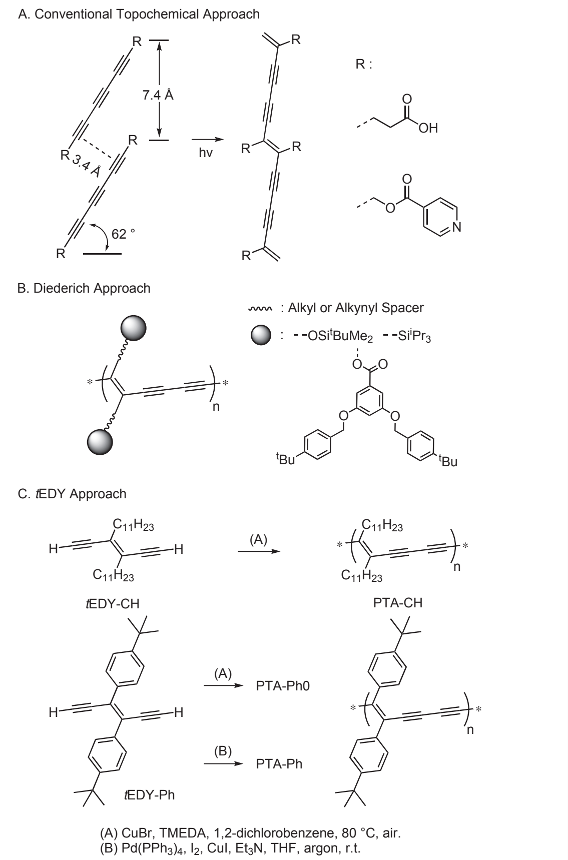
PDA-CH and **PDA-Ph** have distinct physical and electronic properties, as summarized in Table 1. **PDA-CH** is highly crystalline, as confirmed by differential scanning calorimetry (DSC) and X-ray diffraction (XRD) experiments, and it shows both solvatochromic and thermochromic yellow-to-red phase transitions. **PDA-Ph**, on the other hand, is completely amorphous, showing no thermochromic or solvatochromic behaviors. The steric bulkiness of the *tert*-butyl substituents on the phenyl side chains is considered to be responsible for preventing close packing and planarization of the polymer main chains. Interestingly, **PDA-Ph** appears red both in solutions and as thin films because it has a smaller bandgap than that of **PDA-CH**. This is caused by an electronic contribution from the aryl substituents, although the main-chain conformation is still in a 'yellow form'. Both polymers exhibit weak fluorescence, which is consistent with reports in the literature regarding yellow-chain PDAs.[41] As clearly shown by these preliminary results, we were able to control the crystallinity and the phase behaviors of PDA polymers by varying the size of the side chains; we were also able to adjust the electronic properties of the polymer through side-chain conjugation by direct attachment of aromatic substituents. Our current efforts in this subject involve the extension of the side chains to electronically more-active aromatic groups, including thiophene derivatives, which might exert a stronger influence on the electronic properties of the PDAs.

Table 1 Properties of PDAs (Thin Film Data in Parentheses)

	PDA-CH	PDA-Ph
M_n[a] (kDa)	15.6	10.2
Đ[b]	1.9	1.4
T_m (°C)	140	n.a.
Crystallinity	crystalline	amorphous
λ_{max} (nm)	430 (475)	500 (490)
E_g[c] (eV)	2.4 (2.2)	2.1 (2.1)
λ_{em} (nm)	520 (615)	575 (580)
Φ_f[d]	0.10%	0.09%

[a] Number-average molecular mass.
[b] Dispersity.
[c] Bandgap.
[d] Fluorescence quantum yield.

Compared with PDAs, polytriacetylenes (PTAs), which contain one more triple bond in every repeat unit, have received much less attention. Besides PAs and PDAs, PTAs are another classic example of nonaromatic main-chain CPs, and they have been regarded as intermediate molecular-wire like structures, potentially mimicking the carbon allotrope carbyne, which remains synthetically elusive.[42] PTAs exhibit good environmental stability, nonlinear optical properties, and unusual electronic properties; for example, the π-electrons along the PTA main chain are cylindrical in shape, which helps to maintain conjugation of the main chain, even when this is distorted by steric repulsion between adjacent substituents, in stark contrast to PAs and PDAs.[43] Synthetic examples of PTAs are relatively scarce. Lauher and co-workers investigated the solid-state synthesis of PTAs from crystals of 1,6-substituted triacetylene (TA) monomers as a natural extension of the solid-state preparation of PDAs, as shown in Scheme 3A.[42a,44] By means of supramolecular interactions, TA monomer single crystals were obtained and converted into PTA molecular wires upon irradiation. Because of the strict geometric requirement, similar to that in the topochemical synthesis of PDAs, this technique does not readily permit side-chain conjugation or functional-group variation in PTAs. Diederich and co-workers prepared various oligomeric and polymeric PTAs bearing functional groups attached to the main chain through either alkyl or alkyne spacers by means of Glaser–Hay-type coupling reactions, as shown in Scheme 3(B).[42b,43a,45] These materials exhibited unusually high thermal stabilities and interesting nonlinear optical properties.[46] However, PTAs having directly attached aromatic substituents, which can display higher degrees of electronic perturbations, have not been prepared and investigated.



Scheme 3 Polytriacetylene synthesis

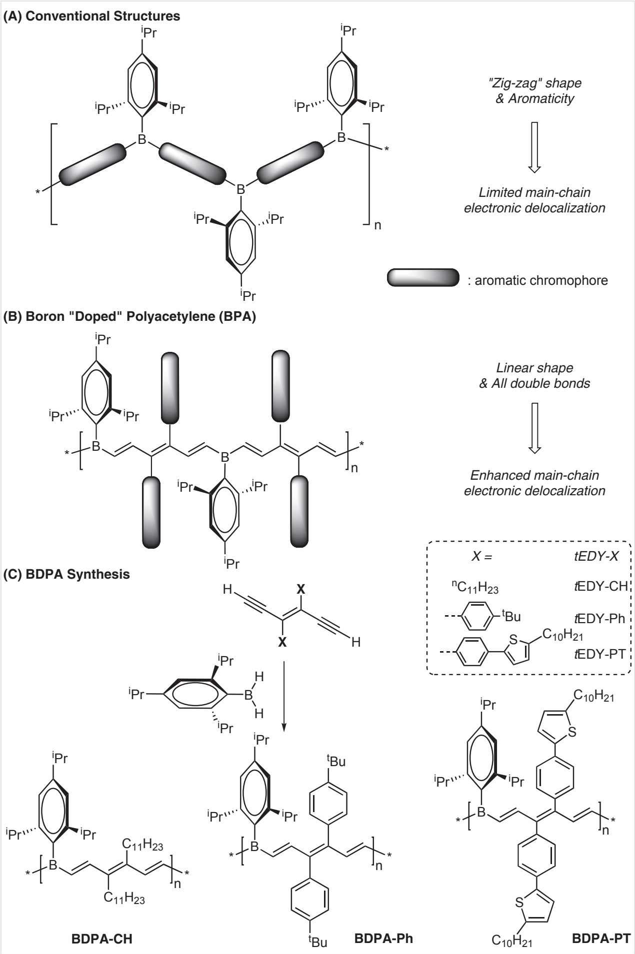
Our synthesis of *t*EDY permitted the installation of aromatic side groups directly on the central double bond, and the resulting monomers possessing terminal alkyne moieties that we hoped would undergo alkyne coupling reactions, expectedly leading to PTAs having directly attached conjugated side chains. We therefore subjected the ***t*EDY-CH** and ***t*EDY-Ph** monomers to standard Glaser–Hay coupling reaction conditions, as shown in Scheme 3(C), and the physical and electronic properties of resulting polymers are summarized in Table 2.[47] **PTA-CH** of high molecular weight was smoothly obtained, whereas under similar reaction conditions, ***t*EDY-Ph** only gave **PTA-Ph0** of low molecular weight. NMR studies of **PTA-Ph0** revealed several broad and unidentifiable signals. Because the Glaser–Hay coupling reactions involve acetylenic radicals as reaction intermediates, we suspect that the phenyl conjugation effects in ***t*EDY-Ph** somehow affected the reactivity/stability of such intermediates, leading to unwanted side reactions. We are currently investigating the origins and possible mechanisms of these observations. Instead, by applying palladium-catalyzed alkyne-coupling reaction conditions in the presence of CuI and I_2,[48] **PTA-Ph** was smoothly obtained with high molecular weight as a dark-purple solid. As in the case of PDAs, **PTA-CH** was shown by DSC and XRD studies to be significantly more crystalline than **PTA-Ph**. As expected, the electronic properties of the PTAs were affected by side-chain conjugation, as shown by the red-shifted absorption and emission spectra of **PTA-Ph**, in both solution and as a thin film, compared with those of **PTA-CH**. The fluorescence quantum yield of **PTA-CH** is about one order of magnitude greater than that of **PTA-Ph** or those of PDAs, confirming the influence of side-chain conjugation on exciton-decay dynamics. We also carried out fluorescence-quenching experiments with poly(3-hexylthiophene) (P3HT), a widely studied CP in organic electronic devices, with our newly prepared PTAs as quenchers. Both PTAs effectively quenched the fluorescence of P3HT; this was assigned to an electron-transfer mechanism because there was little overlap between the absorption spectra of the PTAs and the emission spectra of P3HT that would have permitted energy transfer to occur. The Stern–Volmer constants of **PTA-CH** and **PTA-Ph** were 1.4×10^5 M^{-1} and 4.9×10^4 M^{-1}, respectively, and the difference in these is probably caused by the steric effects of the bulky substituents in **PTA-Ph** slowing the electron-transfer reaction rates.

Table 2 Properties of PTAs (thin film data in parentheses)

	PTA-CH	PTA-Ph0	PTA-Ph
M_n (kDa)	24.4	2.9	35.2
Đ	2.1	3.3	2.8
λ_{max} (nm)	440 (510)	–	493 (535)
E_g (eV)	2.3 (2.3)	–	2.1 (1.9)
Φ_f	1.4%	–	0.1%

The PTAs derived from our *t*EDY monomers represent the first examples of PTAs bearing aromatic groups directly attached to the main chain. Our method can be expanded to various functionalized monomers and polymers to permit fine tuning of physical and electronic properties, as well as for flexible electronic applications, an area in which PTAs have rarely been studied before.

Boron atoms typically adopt trigonal planar geometries in compounds, and they possess an empty p orbital. This unique characteristics has led to a wide range of applications for boron-containing materials, especially in Lewis-acid-based catalysis, ceramic materials, and boron neutron capture therapy.[49] The incorporation of electron-deficient boron centers into polymeric structures is particularly intriguing, as it provides an opportunity for taking advantage of the facile and reversible formation of Lewis donor–acceptor bonds for the further manipulation and functionalization of the resulting polymers,[50] for example, in polymer-supported Lewis acids,[51] polymeric metal-chelating ligands,[52] luminescent materials,[53] preceramics,[54] sensors,[55] or supramolecular materials.[56] We are especially interested in CPs that contain boron atoms within their main chains as parts of the conjugation systems. The electronic properties of the resulting polymers can be modulated through the empty p orbitals on boron, and by interactions with Lewis-basic analytes. As pioneered by the groups of Chujo and Jäkle, main-chain boron-containing CPs are typically prepared by hydroboration of aromatic dialkynes with sterically hindered boranes, by exchange reactions involving boron halides and organometallic reagents, or by cross-coupling reactions of boron-containing conjugated monomers.[57] Some representative structures of CPs containing tricoordinated boron centers in their main chains are shown in Scheme 4(A); these feature alternating boron and aromatic units along the polymer backbone. The trigonal planar geometry of boron centers and the linear aromatic chromophores result in zig-zag-shaped main chains; this, together with the confinement effects of aromatic units, can decrease the tendency to electronic delocalization along the main chain. In fact, existing CPs containing tricoordinated boron centers in their main chains are exclusively wide-bandgap materials, except for a few examples containing oligothiophenes as the aromatic units.[58] We suggested a 'boron-doped' polyacetylene (BDPA) design, as shown in Scheme 4(B), which can be regarded as polyacetylenes (PAs) with every fourth double bond replaced by a boron atom. We surmised that these polymer structures might be obtained by hydroboration of our *t*EDY monomers. In this design, all the atoms in the backbone possess trigonal planar geometries, and we therefore expected the main chain to be linear and to show enhanced electronic delocalization. In addition, by varying the double bond substituents cross-conjugated with the main chain, we might be able to fine tune the physical and electronic properties of the BDPAs without perturbing their linearity.



Scheme 4 Main-chain boron-containing conjugated polymers

The boron centers in boron main-chain polymers are trivalent and are susceptible to hydrolysis, owing to the presence of empty p orbitals on boron that can interact strongly with Lewis bases such as water. As a result, adequate steric protection around these boron centers is crucial if the polymers are to be air stable. Both mesitylborane ($MesBH_2$) and (2,4,6-triisopropylphenyl)borane ($TripylBH_2$) have been extensively applied in the synthesis of boron-main-chain polymers through hydroboration reactions, and most of the existing examples with either borane are claimed to be stable. We therefore began our project by using $TripylBH_2$ to provide a greater degree of steric protection for the boron centers in the target BDPA polymers.

As shown in Scheme 4(C), we have prepared three BDPAs containing side chains with different electronic properties through hydroboration reactions of $TripylBH_2$ with *t*EDY monomers bearing appropriate substituents. The physical and electronic properties of the products are summarized in Table 3.[59] The absorption and emission maxima of these BDPAs showed a gradual red-shift as the side chains was changed from an alkyl group to an aryl group and then to a thienylphenyl group. Density-functional theory calculations (B3LYP, 6-31G*) showed that the HOMO and LUMO orbitals reside, respectively, on the triene and boron moieties in the main chains of **BDPA-CH** and **BDPA-Ph**, whereas the thienylphenyl side chains in **BDPA-PT** contribute significantly to the HOMO. As a result, the LUMO energies in all three polymers, as estimated by cyclic voltammetry, are comparable to one another, whereas the HOMO level increases with more-electron-rich side chains, leading to correspondingly reduced bandgaps. In comparison, conventional main-chain tripylborane CPs containing main-chain alkoxyphenyl[57b] or phenylenevinylene[60] groups, as reported by Chujo and co-workers, displayed λ_{max} values of 365 and 481 nm, respectively, and λ_{em} values of 400 and 437 nm, respectively, both of which are higher in energy when compared even with **BDPA-CH**. These observations confirmed our hypothesis that the BDPA structural designs can indeed promote main-chain electron delocalization and reduce polymer bandgaps.

Table 3 BDPA Properties

	BDPA-CH	BDAP-Ph	BDPA-PT
M_n (kDa)	5.7	12.2	12.6
Đ	1.3	1.5	1.4
λ_{max} (nm)	425 (442)	450 (452)	464 (492)
E_g (eV)	2.40 (2.39)	2.35 (2.50)	2.31 (2.30)
λ_{em} (nm)	505 (503)	522 (523)	561 (563)
Φ_f	24.6%	5.9%	4.5%

Although previous reports all claim that boron-main-chain CPs having tripyl groups on the boron atoms are air stable, we found that our newly prepared BDPAs were perfectly stable only in a water-free environment. When dissolved in wet THF, all three polymers showed a gradual blue shift in their absorption and emission spectra over the course of about one week, and ^{11}B NMR signal appeared at about 30 ppm, indicating the formation of tripylboronic acid. This hydrolytic sensitivity at the boron–vinyl carbon bonds is presumably caused by the smaller sizes of the main-chain double bonds in comparison with those of conventional polymers containing bigger rigid aromatic units. We are currently attempting to increase the steric protection around the the boron atoms in BDPAs by using bulkier substituents, including 2,4,6-tri-*tert*-butylphenyl (supermesityl) groups.

To conclude, we have developed synthetic methods that permit access to several series of unconventional nonaromatic main-chain conjugated polymers derived from a common set of *t*EDY monomers, originally designed for the preparation of substituted polyacetylenes.

As a natural extension from PDAs and PTAs, the gradual addition of triple bonds to each repeat unit is expected to lead to polytetraacetylene (PTeA), polypentaacetylene (PPA), and so on, namely, poly(X-acetylenes) (PXAs). Such PXAs can be considered as mimics of carbyne,[61] the hypothetical one-dimensional linear polymeric sp carbon allotrope analogous to three-dimensional diamond (sp^3 lattice) or two-dimensional graphite (sp^2 lattice), and the properties of PXAs might be extrapolated to provide an estimate of those of carbyne. Although carbyne remains synthetically elusive, its properties have been theoretically investigated[62] and estimated by extrapolating the properties of oligoynes[63] and [*n*]cumulenes[64] of increasing length. These oligoynes and [*n*]cumulenes are typically synthesized through iterative reactions and they the can reach respectable chain lengths, for example, up to 22 triple bonds in oligoynes and up to nine consecutive double bonds in [*n*]cumulenes; nevertheless, these have not reached the conjugation lengths of carbyne, estimated at ~48 consecutive triple bonds,[63e] nor can they be considered to possess the physical properties of macromolecules. In these oligoyne and [*n*]cumulene structures, only the two terminal positions are possible for substitution, which makes it difficult to fine tune the physical and electronic properties of these materials. Furthermore, extension of current oligoynes and [*n*]cumulenes to longer lengths is extremely difficult because of the increase in instability with increasing length. Although the main chains of the proposed series of PXAs are not constructed from all-sp carbon atoms, the polymers are fully conjugated and are expected to progressively possess carbyne-like properties and to display improved intrinsic stability through conjugation of short segments of oligoynes and through control of the characteristics of the side chains. Unique aspects of these all-carbon main-chain molecular wires includes their processability from polymeric structures and their side-chain substituents, which can be tailored to impart tunable electronic properties and controllable solid-state morphologies.

The field of conjugated polymers was initially intrigued by the discovery in the 1970s of metallic conductivity in poly(sulfur nitride) $(SN)_x$, which is still, four decades later, the only known example of a zero-bandgap CP in the ground state.[65] Although researches in the present field have been mainly focused on the semiconducting properties of CPs with applications primarily in OLEDs or OSCs, the pursuit of intrinsically conducting CPs remains a challenging but potentially rewarding topic. The incorporation of boron atoms into CP structures has been thought to be a viable means for generating partially filled valence-band structures, one requirement for metallic behavior.[66] For example, polyboracetylene, with alternating trisubstituted C and B atoms in the main chain has debatably[67] been predicted to be a metallic conductor in the ground state.[68] Despite some interesting perspectives, current research in boron-main-chain CPs has focused exclusively on their luminescence and sensory properties, with little attention being paid to conductivity studies. Our BDPA polymers contain no aromatic units in the main chains, thereby providing enhanced in-chain electronic delocalization, and they therefore constitute a suitable platform for studying the intrinsic effects of boron incorporation on the conductivity of materials. Although the current examples are all wide-bandgap materials, the BDPA design strategy provides flexibility in structural variation for detailed studies on the relationship between structures and intrinsic/doped conductivity in this unique set of heteroatom-containing polymers.

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