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Structurally Dynamic Conjugated Polymers

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ABSTRACT: Conjugated polymers (CPs) have become essential to a diverse array of fields, ranging from biosensing to photovoltaics to optoelectronic materials. Given their widespread use, there is a growing need for variants whose functions may be modulated via exogenous stimuli. Alteration of CP structure could effect the desired changes and may be actuated in response to (1) chemical, (2) electrochemical, (3) photochemical, or (4) thermal impetuses. In this Perspective, we present a review of CPs reported to respond to chemical, electrochemical, and photochemical stimuli along with our own efforts using thermal stimuli. A particular emphasis has been directed toward structurally dynamic CPs that exhibit changes in their electronic properties, which could enable access to new classes of smart and other functional materials. During the course of our discussion, we consider the advantages and disadvantages inherent to each of the aforementioned methods, along with the potential applications of the polymers derived therefrom. We conclude this Perspective with a brief overview of the accomplishments in this nascent field, reflecting upon the unconquered challenges and contemplating the opportunities present for future discoveries involving structurally dynamic CPs.

Introduction

Conjugated polymers (CPs) are a unique subset of synthetic macromolecules that exhibit formal chemical unsaturation along their main chains,[1] wherein π-conjugation extends across multiple repeat units.[2] The highly delocalized nature of CPs endows them with useful characteristics, such as intense UV/vis absorptions (typically due to their $\pi \rightarrow \pi^*$ transitions), accessible band-gap potentials, and photo- and electroluminescence. Consequently, CPs have enabled significant advances in applications ranging from sensing[3,4] to photovoltaics[5,6] to optoelectronic materials.[7−11] Given the burgeoning scope of CP-based applications, there is significant interest in variants that undergo functional changes in response to exogenous stimuli. Considering that the physical and electronic properties displayed by CPs are intimately linked to their structures,[5,12−17] one avenue to effect such functional changes is through the development of structurally dynamic derivatives.

Structural dynamism in CPs is manifested by the reversible depolymerization/repolymerization of the polymer main chain, which ultimately involves the reversible disruption and restoration of σ- and π-bonds.[18] In general, these changes may occur in response to (1) chemical, (2) electrochemical, (3) photochemical, and (4) thermal impetuses (Figure 1). Each stimulus features unique advantages and disadvantages, and thus some may be better suited for one application vs another. Chemical impetuses, for example, can be administered in a well-controlled fashion, given that reagents can be conveniently added and, in many cases, removed. Electrochemically impelled structural dynamism, however, can display significantly improved atom economy and benefits from the ease by which electrons can be supplied to or removed from solutions or films. Contrary to the need for specialized functionalities to engage in chemical or electrochemical reactions, all molecules will interact with light, and photon absorption occurs on fast time scales, thus enabling the potential for generalized CP scaffolds that exhibit dynamic structures in response to photochemical impetuses. Imbuing any of the three aforementioned impetuses in a homogeneous manner, however, adds an additional level of complexity, particularly when applied to bulk materials. Moreover, each strategy generally necessitates impetus-specific functional groups (i.e., to chemically react with a specific molecule, to undergo redox change at a specific potential, to absorb light at a specific wavelength, etc.). In contrast, solutions and solid materials can both be evenly heated with less difficulty, and thus thermally impelled structural dynamism may be used in situations where the others may not.

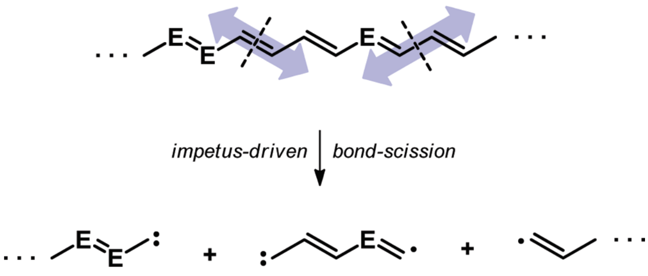

Figure 1. Conceptual dissection of polyacetylene or a derivative thereof containing heteroatoms, wherein reversible σ- and π-bond scission can occur in response to a chemical, electrochemical, photochemical, or thermal impetus. E = sp^2-hybridized atom such as C, N, P, etc.

In this Perspective, we précis[19] structurally dynamic CPs with a historical account of reversible covalent bonds in small molecules and nonconjugated polymers, review advances in the literature toward CPs that respond to chemical, electrochemical, and photochemical stimuli, and conclude with a discussion of recent efforts toward thermally responsive CPs. We discuss the advantages and disadvantages inherent to each impetus, along with their potential applications. Following detailed analyses and discussions of the different classes of structurally dynamic CPs, we summarize the overall progress in the field of structurally dynamic CPs. Finally, we conclude with a discussion of outstanding challenges and consider the opportunities therein for discoveries and advances in other areas.

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Andrew G. Tennyson is currently an Assistant Professor of Inorganic Chemistry at Clemson University. He received S.B.Hon. and S.M. degrees from the University of Chicago in 2003 under the guidance of Prof. Gregory L. Hillhouse and a Ph.D. in Inorganic Chemistry in 2008 at MIT under the mentorship of Prof. Stephen J. Lippard, and he spent the next two years as a postdoctoral fellow at the University of Texas at Austin working in the group of Prof. Christopher W. Bielawski. His research expertise includes conjugated polyelectrolyte design/synthesis, electroanalytical techniques, photoluminescence measurements, and molecular weight determination methods for rigid, charged polymers. Prof. Tennyson is especially interested in exciton localization and structure−property relationships in conjugated polymers.

Brent Norris received a B.S. degree in Chemistry from the Texas A&M University working under the tutelage of Raymond E. Schaak (now at the Pennsylvania State University) and Manuel P. Soriaga. Soon after receiving a B.S. degree in chemistry in May 2005, he spent the following summer in the laboratories of Paul F. Barbara. In the fall of 2005, he joined the research group of Christopher W. Bielawski at UT-Austin and focused on the development and applications of polymeric materials based on bis(NHC) scaffolds. Brent recently finished his Ph.D. thesis and will begin a new position at Royal Dutch Shell in Houston, TX, later this year.

Chemical Impetus

In many ways, the simplest strategy for impelling controllable structural dynamism in a CP is with the use of chemical reagents. If a polymer can only undergo structural change upon reaction with an exogenously supplied molecule, it will never exhibit this dynamism in its absence. Frequently, similar sets of compounds and reagents may be used to effect changes in these materials, thus precluding the need to incorporate multiple chemically reactive or other stimulus-responsive functionalities. As a result, chemically impelled structural dynamism can be generally initiated and controlled in a straightforward manner.

Two chemical reactions well-known to exist in equilibrium are amine−carbonyl condensation and its opposite process, imine hydrolysis. Because the forward and backward reactions occur with such high fidelity, these chemical functionalities have been widely used for reversible covalent bonding strategies.[20,21] For example, Meyer demonstrated that transition-metal complexes could catalyze imine metathesis reactions,[22,23] including the ring-opening metathesis polymerization of cyclic aliphatic imines to afford nonconjugated polymers.[24] Shortly thereafter, Moore harnessed imine metathesis reactivity to prepare a CP that exhibited structural dynamism.[25] Condensation of imine-terminated *m*-phenylene ethynylene tetramers **1a** and **1b** with catalytic oxalic acid in $CHCl_3$ afforded primarily unreacted starting materials, along with dimers ($n = 2$) and trimers ($n = 3$) of **P1** ($M_w = 1.8$ kDa) and byproduct **1c** after 6 days (Figure 2). However, when the same reaction was performed in CH_3CN, nearly a 200-fold increase in the molecular weight of **P1** was observed ($M_w = 350$ kDa). The authors attributed this variation to the dependence of *m*-phenylene ethynylene oligomer conformation on the chemical environment, where polar solvents induce the formation of helical structures,[26] thus stabilizing the polymeric structure and templating it for further reaction with monomer.

Christopher W. Bielawski was born in Chicago and lived in the city as well as the surrounding suburbs for most of his formative years. After receiving a B.S. degree in Chemistry from the University of Illinois at Urbana−Champaign (1996), he moved west and enrolled in the graduate studies program at the California Institute of Technology, where he was awarded a Ph.D. in 2003. After a postdoctoral stint (also at Caltech), he became an Assistant Professor at The University of Texas at Austin in 2004 and was promoted to Associate Professor in 2009. Prof. Bielawski's research program lies at the interface of organic, inorganic, and polymer chemistry and focuses on the synthesis and study of novel catalysts and materials.

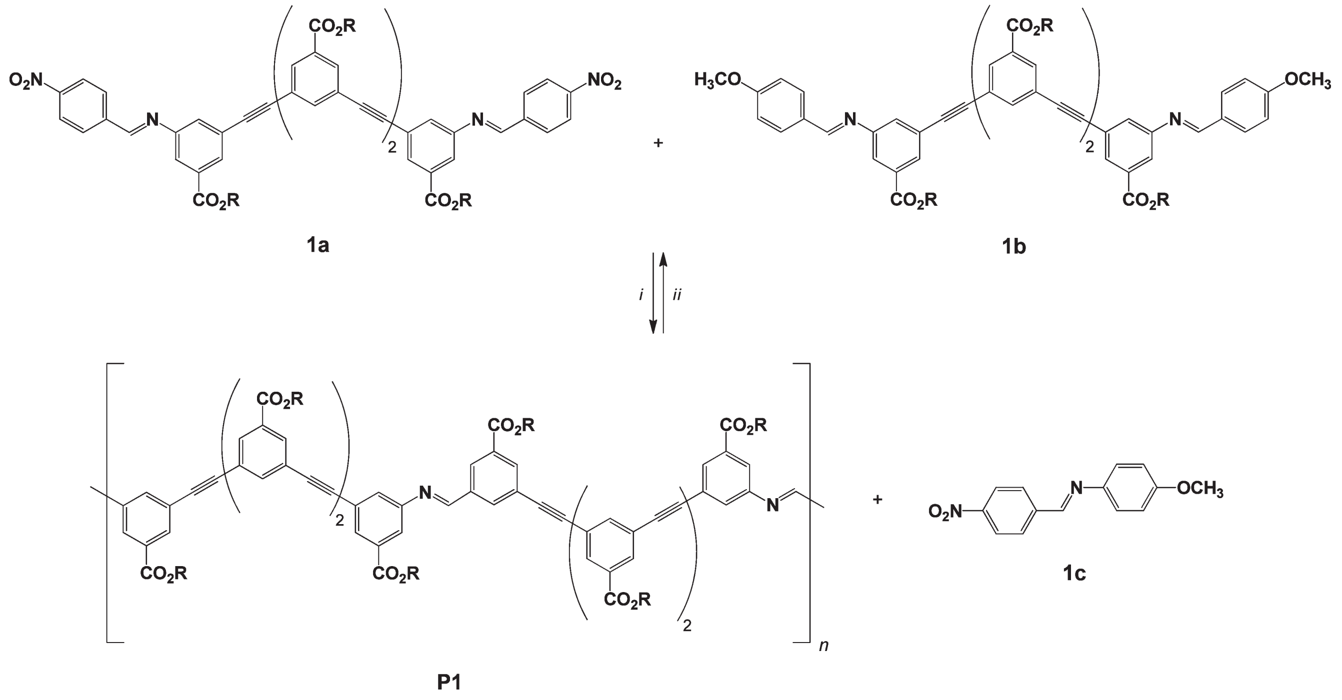

Figure 2. Reversible formation of poly(*m*-phenylene ethynylene)s via imine condensation. R = $(CH_2CH_2O)_3CH_3$. Conditions: 0.1 equiv of $C_2H_2O_4$, RT, 6 days; (i) CH_3CN; (ii) $CHCl_3$.

To confirm this hypothesis, the condensation polymerization of **1a** and **1b** was performed in mixed $CH_3CN/CHCl_3$ solvent systems ($CHCl_3$ ranging from 0 to 75 vol %), which resulted in a steep drop-off in the molecular weight of **P1**, even upon going from 0% to 5% $CHCl_3$ (M_w = 350 and 60 kDa, respectively), consistent with the disruption of the polymer's helical architecture. Further spectroscopic evidence for these structural changes was obtained by measuring the ratio of the absorbance at 313 vs 295 nm.[27] As the degree of polymerization increases, a greater percentage of *m*-phenylene ethynylene tetramers become coiled within the helix and thus are sandwiched between other *m*-phenylene ethynylene tetramers. Because of this helically enforced $\pi-\pi$ stacking, the *m*-phenylene ethynylene dipoles interact and become energetically perturbed, enabling UV/vis spectroscopic measurement of both the degree of polymerization and structure. Thus, the creation and reduction of higher-order structure in these *m*-phenylene ethynylene-derived macromolecules serves to dynamically modulate the electronic properties of this material.

Subsequent studies by Moore confirmed the generality of the solvent polarity dependence, where increasing solvent polarity ($CHCl_3 \approx$ THF < EtOAc < CH_3CN) correlated with increasing molecular weight of **P1** (M_w = 3.9, 3.9, 34.0, and 350.2 kDa, respectively).[28] Higher M_w values were accompanied by diminished absorbance at the wavelength characteristic to the repeat unit, reflecting the effects of the π-stacking enforced by the growing helix. As might be expected, the helical structure necessary for polymer growth was dependent on the identity of the monomers. For example, replacing tetramers **1a** and **1b** with trimers **1d** and **1e** in the condensation reaction produced macrocycle **1f** (Figure 3). Similar to that observed for **P1**, the extent of the exchange reaction could be controlled via solvent polarity: $CHCl_3$ afforded a significant amount of unreacted **1d** and **1e**, yet CH_3CN afforded nearly complete conversion to **1f**. The authors attributed this behavior to an underlying mechanism similar to the one operating for **P1**, namely that in polar solvents the macrocycles **1f** form a π-stacked aggregate that ultimately drives the condensation reaction to completion.

In a related approach, Lehn and co-workers described the condensation of diamines **2a** and **2c** with bis(aldehyde) **2b** to afford polymer **P2**, comprising a statistical distribution of alkyl and aryl diamines (i.e., $0 \leq x \leq 1$ and $y = 1 - x$; Figure 4).[29] Analysis by ^1H NMR, UV/vis, and fluorescence spectroscopies indicated a larger percent incorporation of **2a** (~80%), reflecting its greater nucleophilicity compared to **2c**. Adding 2 equiv of $Zn(BF_4)_2 \cdot 8H_2O$ caused a 3-fold increase in absorbance at 418 nm, a greater than 100 nm shift in λ_{em} (365 to 475 nm), and complete disappearance of the ^1H NMR signals attributable to the alkyl imines. Subsequent addition of hexamethylhexacyclen (stoichiometric with respect to added Zn^{2+}) restored the spectroscopic features of the original statistical polymeric mixture. Thus, **P2** exists in equilibrium with its component monomers **2a**–**c**, and the polymer distribution can be driven to the fully aromatic **P2** ($x = 0$, $y = 1$) by trapping **2a** with Zn^{2+} ions or returned to the statistical mixture by sequestering the metal ions with hexamethylhexacyclen. Collectively, these results showed that **P2** ($x = 0$, $y = 1$) may be reversibly generated and consumed, enabling dynamic chemical control over the effective conjugation length—and hence the electronic properties—of the respective polymer. Subsequent studies by Lehn have shown that this strategy can be applied to a wide variety of diamines and that the structural dynamism is retained.[30] One limitation to using reversible carbon–nitrogen double-bond linkages is that they, under certain conditions, can interrupt conjugation and long-range electronic communication.[31,32]

Carbon–carbon multiple bonds typically have both greater thermodynamic and kinetic stability than their heteroatomic analogues and can often be efficiently formed and broken via metathesis catalysts. However, a complication inherent to the preparation of CPs via ring-opening metathesis polymerization (ROMP) reactions, for example, is the competitive formation between linear polymers and cyclic oligomers; e.g., the ROMP 1,3,5,7-cyclooctatetraene affords benzene in addition to polyacetylene,[33−35] reflecting the competing entropic and enthalpic contributions to (reversible) metathesis reactions.[36−38] However, Moore demonstrated that this reversibility could be harnessed productively in alkyne-containing polymers, whereby treating poly(*m*-phenylene ethynylene) **P3a** with the molybdenum–alkyne

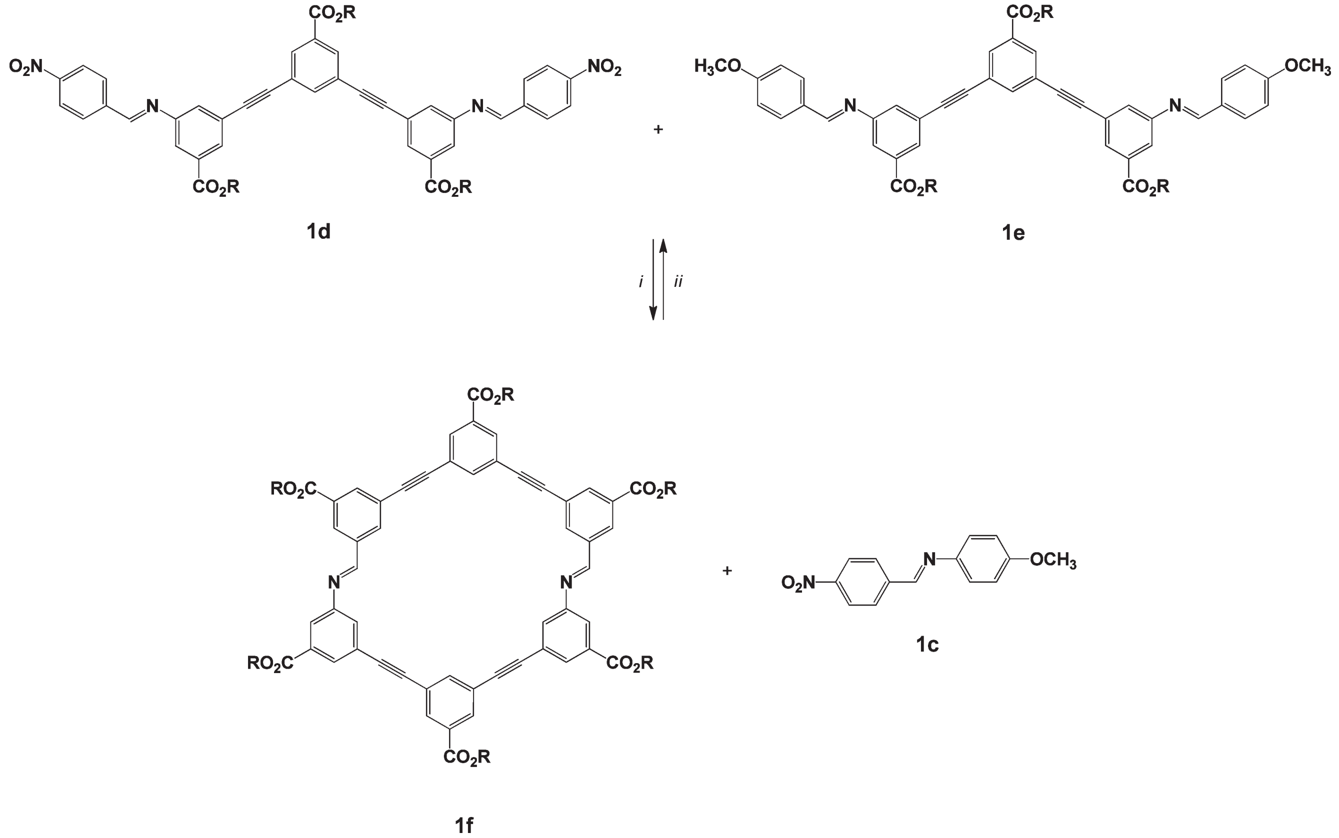

Figure 3. Reversible formation of cyclic *m*-phenylene ethynylene dimers via imine condensation. R = $(CH_2CH_2O)_3CH_3$. Conditions: 0.1 equiv of $C_2H_2O_4$, RT, 6 days; (i) CH_3CN; (ii) $CHCl_3$.

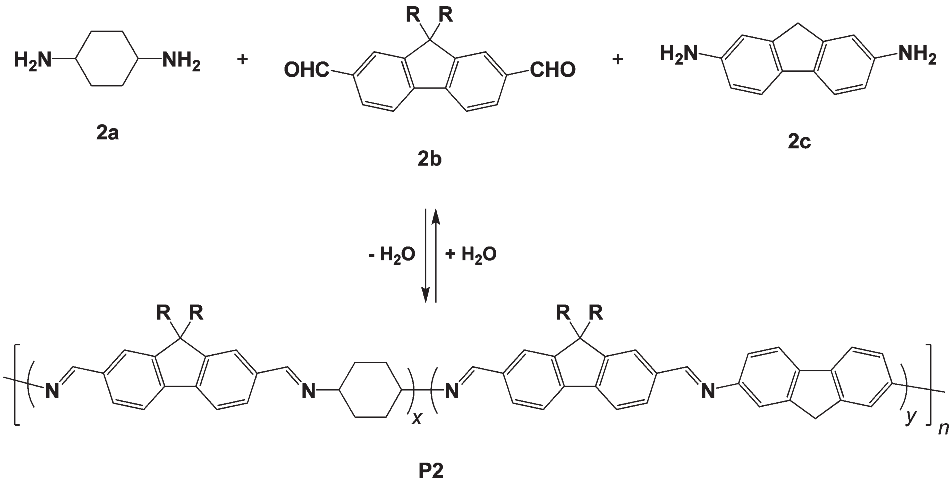

Figure 4. Reversible formation of poly(cyclohexyl-*co*-fluorene)s via imine condensation. R = *n*-hexyl. Conditions: RT, CH_3CN. Addition of $Zn(BF_4)_2\cdot 8H_2O$ to **P2** comprising a statistical mixture of monomers drives it to a fully aromatic state ($x = 0$, $y = 1$). Subsequent chelation of Zn(II) restores the original distribution.

complex [Mo(≡CEt){N(3,5-Me_2Ph)(*t*Bu)}$_3$] resulted in conversion of the open-chain polymer into macrocycle **3**, along with small amounts of short, open-chain oligomers (Figure 5).[39] Conversely, reaction of **3** with diphenylacetylene in the presence of the same Mo catalyst led to the regeneration of polymeric material (**P3b**, R^4 = Ph).

Overall, chemically impelled structural dynamism benefits from the excellent controllability inherent to this methodology. In practice, however, this approach is often impeded by the phases of the components, where the polymer is typically a solid and the exogenous reagents are either in the liquid or solid state. Moreover, embedding the required reagents into a polymer matrix to be released and reactive only in response to a specific stimulus necessitates complicated and time-consuming fabrication techniques. Given these characteristics, chemical impetuses are ideally suited for applications where significant changes in CP structure and properties, including such extremes as complete depolymerization or disruption of conjugation, must occur automatically. In stark contrast to the detailed molecular weight and macromolecular studies of CPs that exhibit chemically impelled structural dynamism, however, very little attention has been directed toward attendant variations in the electronic properties

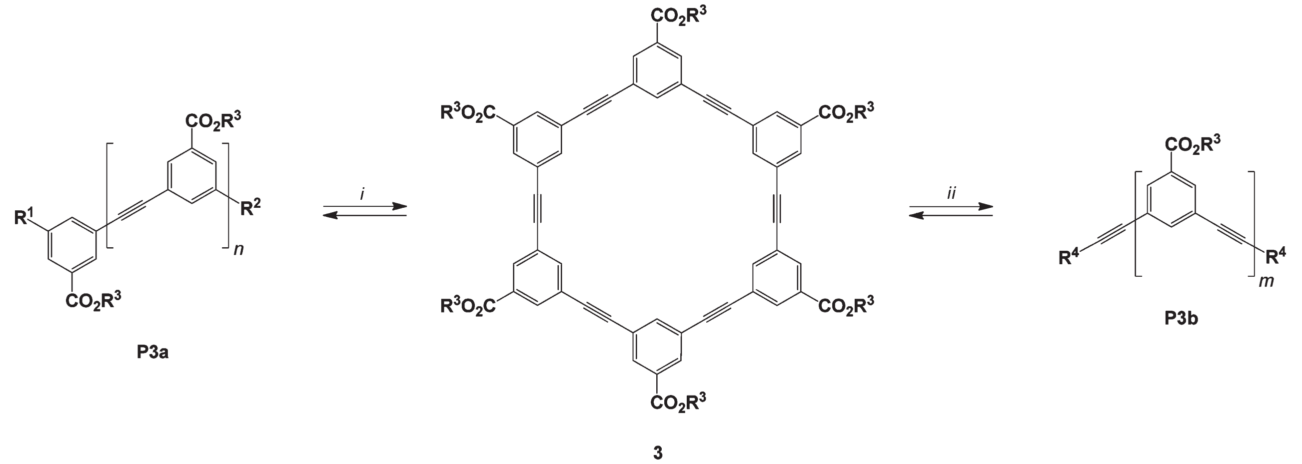

Figure 5. Reversible cyclodepolymerization and subsequent repolymerization of poly(*m*-phenylene ethynylene)s via alkyne metathesis. R^1, R^2 = I or C≡CH, R^3 = $(CH_2CH_2O)_3CH_3$, R^4 = Ph. Conditions: [Mo(≡CEt){N(3,5-Me_2Ph)(*t*Bu)}$_3$], 4-nitrophenol, 30 °C; (i) 1,2,4-trichlorobenzene; (ii) CCl_4.

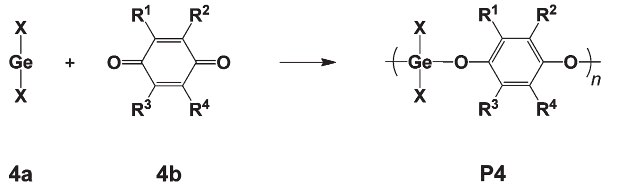

Figure 6. Copolymerization of Ge(II) imides with *p*-benzoquinones via intramolecular redox processes to afford Ge(IV)- and *p*-dioxybenzene-containing **P4**. X = $N(SiMe_3)_2$ or $N(SiMe_3)$(*t*Bu). R^1, R^2, R^3, R^4 = H, Me, *t*Bu, *t*Am, Ph, vinyl, OMe, Cl.

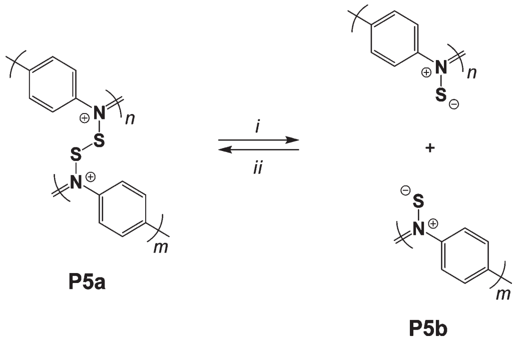

Figure 7. Reversible cleavage and re-formation of interchain cross-links via electrochemical reduction of disulfide (i) and oxidation of dithiolate (ii) moieties, respectively. Perchlorate (ClO_4^-) counterions for **P5a** are omitted for clarity. Conditions: 0.5 M $LiClO_4$, RT, CH_3CN; (i) E_{app} = −0.2 V; (ii) E_{app} = +1.0 V.

of these materials. As a result, much of the structure−property relationships remain unexplored and thus present opportunities for discovery as well as greater understanding of their fundamental electronic and physical characteristics.

Electrochemical Impetus

Despite the controllability of a chemical reaction (i.e., it will not proceed without all necessary reagents present), the reversible scission of covalent bonds via chemical reactions can suffer from poor atom economy and bulk heterogeneity. Electrons, however, can often be easily added and removed from both solutions and solids via bulk electrolysis. Moreover, the time scales for such electrochemical processes are typically short, facilitating rapid activation and shutdown of the structural dynamism response. Biological macromolecules, such as enzymes and other proteins, for example, undergo redox-mediated disulfide−dithiolate interconversions, which Nature uses to alter the structure and function of these biopolymers in a reversible and well-defined manner with perfect atom economy.[40−42]

Imitation and implementation of this strategy by chemists have endowed them with redox control over a wide variety of applications, ranging from molecular recognition[43] to template-directed synthesis[44] to targeted drug delivery.[45] For example, nearly 20 years ago, Kobayashi reported that Ge(II) imides (**4a**) react with a variety of *p*-benzoquinones (**4b**) to afford copolymers comprising Ge(IV) and *p*-dioxybenzene subunits (**P4**), representing the utility of redox processes in the synthesis of novel polymeric materials (albeit nonconjugated and structurally static; see Figure 6).[46,47] It was not until much later (2004) that Su and co-workers demonstrated that electrochemical processes could be used to impart structural dynamism on **P5a**, which was prepared via chemical and electrochemical polymerization of the corresponding disulfide−aniline precursor (Figure 7).[48] Cyclic voltammetric analysis of **P5a** revealed that the disulfide−dithiolate redox couple occurred at a lower energy and with greater electrochemical reversibility than the monomer. Whereas conversion of **P5a** to **P5b** afforded a material with greater conductivity when combined with Brønsted- or Lewis-acid doping, cleavage of these interchain cross-links under oxidative conditions resulted in the disappearance of the characteristic main-chain absorption for **P5a** and appearance of an intense band at lower energy in **P5b** (~400 nm vs 820 nm), reflecting the lower band-gap potential in the latter. Because **P5a** is positively charged, it exhibited much higher negative vs positive charge mobility. Although **P5b** is formally neutral, it is zwitterionic, wherein the thiolate moieties interact with cations (e.g., H^+ and Li^+) and enable it to transport both negative and positive charges.

Collectively, these results represent electrochemically impelled control over the electron/hole transport ability of a CP, as effected by the disruption and formation of interchain cross-links. Moreover, the band-gap potential may be adjusted by altering the overall charge on the CP. Thus, redox modulation of a CP by electrochemical methods can produce significant changes in polymer structure as well as its bulk electronic properties. Given these features, a material composed of a redox-active CP, such as **P5**, may be toggled between charge-transport and charge-storage functions, with potential for applications as smart materials for use in energy storage.

Electrochemically impelled structural dynamism akin to that exhibited by **P5** has the potential to actuate reversible covalent bonding with perfect atom economy and to enable near-instantaneous control over this process. However, the generality of this method is limited by the need for an electrically or ionically conductive medium and is only effective with solutions with high ionic strengths or materials that are intrinsically conducting or doped. Additionally, because the extended π-conjugation inherent to the CP scaffold renders its HOMO and LUMO energetically accessible, the addition of chemical redox agents could potentially cause oxidation or reduction of the polymer. As a result, this strategy is best suited to CPs designed for use in conductive materials whose function must be rapidly controlled, such as electronic self-protection, whereby a device is modulated between power-delivery and -storage behavior in response to abnormal operating conditions (e.g., short circuits, power surges, etc.).

Despite its potential, electrochemically impelled structural dynamism in CPs has so far been limited to the formation and disruption of interchain cross-links. To achieve significantly greater control over properties and function, a similarly responsive CP should incorporate redox active functional groups within the main chain. Because such a material has not yet been prepared, we believe there are great opportunities for electrochemically impelled structurally dynamic CPs.

Photochemical Impetus

Electrochemical methods significantly improve the atom economy of reversible covalent bonding interactions and can enable rapid modulation of various functions, but the need for a conductive medium limits their scope. Photons, in contrast, can be absorbed and emitted by any molecule, while still effecting structural changes therein with complete chemical fidelity and on fast time scales. Photochemically impelled structural dynamism serves as the mechanism of vision in humans: the retinyl chromophore in rhodopsin undergoes a *cis*-to-*trans* isomerization upon absorbing a photon, initiating the signal transmission cascade.[49−51] Pioneering efforts by Bowman have highlighted the appeal of similarly photoresponsive synthetic macromolecules,[52] which can yield polymers with novel functions and potential applications, ranging from materials with dynamic stress/strain properties[53,54] to biomedical devices and prosthetics.[55] Given the unique transformations that occur in nonconjugated polymers via irreversible photochemical changes, incorporating a subunit within a CP that can undergo reversible structural changes in response to light will greatly expand the scope of these materials.

Azobenzene has been known to undergo a reversible *trans*-to-*cis* isomerization in response to light for more than 70 years.[56] Since then, the experimental and theoretical understanding of this process has been thoroughly explored, and a variety of derivatives have been prepared.[57] Benefitting from a relatively simple structure, azobenzene has been used in a wide range of stimulus-responsive applications, from photoswitchable superconductors[58] to holographic data storage.[59] Seminal work by Masuda and coworkers in 2000 demonstrated the practical potential of incorporating azobenzene units into a CP scaffold to endow it with photochemically impelled structural dynamism.[60] Azobenzene-functionalized poly(phenylene)s **P6a** were prepared in near-quantitative yields via Suzuki coupling of the corresponding azobenzene boronic acids and diiodoarenes (Figure 8). Synthesis by this method afforded exclusively the *trans*-isomers with relatively sharp absorbances at ~370 nm (e.g., **P6a** with R^1 = *n*-hexyl, R^2 = H; λ_{max} = 368 nm), characteristic of the $\pi \rightarrow \pi^*$ transition in *trans*-azobenzenes. Irradiation in the 300−400 nm range caused a decrease in peak intensity at 368 nm and the appearance of a new peak at 450 nm attributed to *cis*-**P6a**. Loss of intensity at the wavelength attributed to the $\pi \rightarrow \pi^*$ transition was indicative of conjugation disruption, consistent with the structural change induced in the diazo linkage. Conversely, bathochromically shifting the irradiation wavelength to 450 nm to excite the *cis*-isomer selectively restored the optical profile to match the original UV/vis spectrum of 100% *trans*-**P6a**. Hence, the interconversion of the *trans*- and *cis*-isomers of **P6a** using photons of different wavelength illustrates tuning of the polymer's effective conjugation length via geometric dynamism in response to photochemical impetuses.

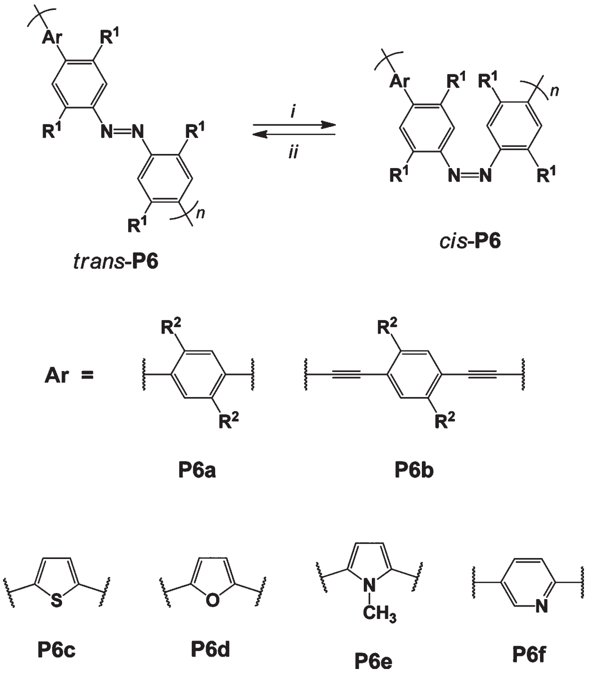

Figure 8. Reversible *cis*−*trans* isomerization in poly(*p*-phenylene)s via photoirradiation. R^1, R^2 = H, *n*-hexyl. Conditions: 20 °C, toluene; (i) 300 nm < λ_{ex} < 400 nm, 5 min; (ii) λ_{ex} > 450 nm, 12 min.

Subsequent efforts to encompass a wider range of wavelengths with **P6**(**b**−**f**) were met with limited success.[61] Only **P6f** (R^1 = *n*-hexyl) exhibited photoisomerism, being driven to a 2:1 *trans*/*cis* ratio upon irradiation in the short wavelength regime and reverting back to 100% *trans* configuration with longer wavelengths. The authors attributed this variable efficacy to the different optical profiles of the CPs themselves: only in **P6f** is the *trans*-azobenzenes $\pi \rightarrow \pi^*$ transition well-separated from the absorption of the main chain of the CP. When these two peaks are overlapping, the optical transitions within the polymer will siphon energy away from the photoexcited diazo units before they have time to rearrange to the *cis*-geometry. Although these results represent control of CP conjugation length via photochemically induced structural changes, this is a ubiquitous phenomenon among CPs and also beyond the scope of this Perspective (i.e., does not constitute reversible depolymerization/repolymerization reactivity).[62−64]

Surprisingly few examples of CPs that undergo photochemically impelled reversible bonding have been reported. In 1984, Miller reported that films of polysilane **P7** (R^1, R^2 = *n*-hexyl) exhibited a shift in λ_{max} from 374 to 317 nm upon heating, whereupon subsequent cooling restored the original optical profile (Figure 9).[65] Although these polysilanes feature sp^3-hybridized atoms in the backbone and are thus not formally π-conjugated, the thermodynamically preferred planar zigzag geometry enables extended conjugation via overlap of energetically compatible, silicon-centered σ and σ^* orbitals. Heating these films disrupts the planar zigzag geometry and attendant σ-conjugation, consistent with the observed 67 nm hypsochromic shift in λ_{max}, which is reversed upon cooling. Photolysis of similar polysilanes afforded a reduction in molecular weight, whereby detailed product analysis suggested that the depolymerization was proceeding via the

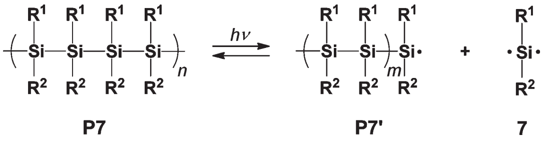

Figure 9. Photochemical depolymerization of polysilane **P7** via formation of silyl radicals (**P7'**) and silylenes (**7**). R^1, R^2 = methyl, *n*-hexyl, phenyl. Conditions: 35 °C, THF; 254 nm, 15 h.

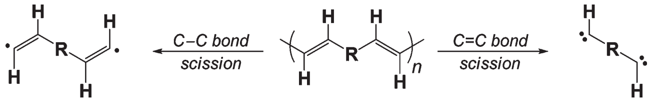

Figure 10. Deconstructions of a derivative of *trans*-polyacetylene into diradicals (left) or bis(carbene)s (right). R is an appropriate linker that maintains conjugation through the polymer's main chain.

formation of silyl radicals (**P7'**) and silylenes (**7**).[66] Unfortunately, the practical utility of these polysilanes is limited by the fact that the depolymerization process affords electronically unsaturated silicon centers, which can engage in irreversible uni- and bimolecular decomposition reactions.[67]

Excellent atom economy and fast time scales are advantages inherent to the use of photochemical methods for effecting structural changes in CPs. Additionally, this technique can allow precise energy delivery, whereby specific bonds or functionalities can be targeted upon irradiation at a given wavelength. However, many CPs are intrinsically photon absorbing or emitting, thus reducing efficiency due to filter effects or energy transfer processes, respectively. Moreover, both solution and solid phases cause significant heterogeneity in light intensity due to attenuation, reflection, and refraction. To circumvent these limitations, the photoresponsive unit must be designed such that it absorbs at energies well-separated from the $\pi \rightarrow \pi^*$ and other transitions that occur within the polymer. Photochemically impelled structural dynamism is thus ideally suited for CPs whose applications necessitate rapid modulation of their conjugation-length-dependent properties and functions (e.g., emission wavelength or bandgap potential), given that this impetus operates on fast time scales (e.g., photon absorption) and can isomerize unsaturated bonds without disrupting the σ-framework.

Thermal Impetus

One disadvantage common to chemical, electrochemical, and photochemical stimuli is the challenge associated with supplying them in a homogeneous or isotropic manner. Moreover, many of the systems that exhibit dynamic structures in response to these stimuli are highly specialized and cannot be readily adapted for general use. Compelled by these limitations, we reasoned that thermal energy would be a suitable alternative, especially given that applying heat to a solution or material is relatively straightforward.

To understand the challenges associated with thermally reversible CPs, we first conceptualized this behavior in polyacetylene, a CP with a relatively simple structure. Retrosynthetic analysis of this polymer highlights how cleavage of the different C–C bonds therein can afford electronically orthogonal precursors. For example, dissection of an appropriate derivative of *trans*-polyacetylene along its carbon–carbon single or double bonds will afford either diradicals or bis(carbene)s (left or right, respectively; Figure 10). Although the carbon–carbon single bonds would have a lower thermodynamic activation barrier, the resulting vinyl radicals would be relatively unstable. Conversely, cleavage of the carbon–carbon double bonds would require more energy but produce carbenoid fragments with potential for achieving greater stability.

Thermally reversible carbon–carbon single bonds have been studied for over a century, with one of the most prominent historic examples detailed by Gomberg in 1900 ($\mathbf{A_2} \leftrightarrow 2\mathbf{A}$; Figure 11A).[68] He found that dehalogenation of trityl chloride produced an extremely air-sensitive compound that decomposed to trityl peroxide under aerobic conditions, presumably via trityl radical (**A**). It was later determined that this radical is capable of dimerizing (to form $\mathbf{A_2}$) in a thermally reversible manner.[69] In contrast, reversible carbon–carbon double bonds were not reported until 1963 by Wanzlick, presumably due to the obvious difficulty associated with effecting a reversible 2 → 0 bond-order reduction (Figure 11B).[70] Regardless, deprotonation of the imidazolinium precursor to **B** afforded the enetetramine $\mathbf{B_2}$, formally a dimer of two imidazolinylidene units. Subsequent reactivity studies indicated that $\mathbf{B_2}$ exists in equilibrium with its respective N-heterocyclic carbenes (NHCs).[71] Despite this literature precedence and the fact that reversible carbon–carbon single and double bonds have been successfully incorporated into nonconjugated polymers for nearly two decades,[72–75] these functionalities have remained relatively unexplored as components for thermoresponsive structurally dynamic CPs.

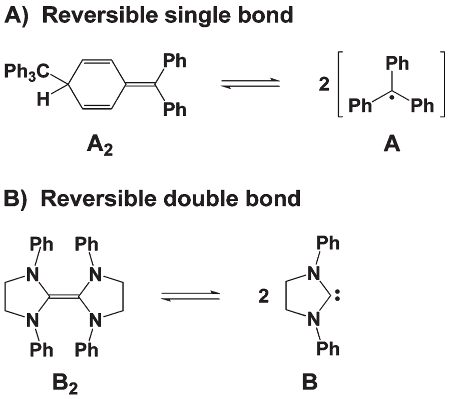

Figure 11. Examples of thermally reversible carbon–carbon (A) single and (B) double bonds.

Developing multitopic carbenes with a suitable combination of stability and reactivity is an ongoing challenge associated with accessing polymers with thermally reversible polymer structures via carbene chemistry. Whereas the simple (nonheteroatom stabilized) carbenes (e.g., CH_2:) have the appropriate electronic configuration and connectivity to re-form their parent CP, these and related species would likely exhibit high reactivities, leading to decomposition or other irreversible chemical behavior. Inclusion of electron-donating heteroatoms, such as sulfur or nitrogen, adjacent to the carbene nuclei could enhance their stability sufficiently to allow recombination. Indeed, NHCs feature a carbene nucleus stabilized by one or more adjacent nitrogen atoms embedded in a cyclic framework. Moreover, NHCs can exist as either their free carbenes (which generally requires bulky N-substituents for stabilization) or undergo dimerization to their respective enetetramines.[76] NHCs also have been shown to couple with a range of electrophiles (such as organic azides and isothiocyanates; Figure 12, left)[77–81] and to coordinate a variety of ML_n fragments (Figure 12, right),[82–85] whereby the resulting adducts and complexes, respectively, exhibit electronic properties and connectivity that are ideally suited for structurally dynamic CPs.

Capitalizing on the rich chemistry of NHCs,[86] we reasoned that appropriate bis(NHC)s[87,88] could be used to access three major classes of polymers, potentially even those that are conjugated or extensively delocalized: (1) homopolymers featuring enetetramine linkages (Figure 13, top right), (2) metallopolymers comprising alternating NHC and ML_n units (middle right),[89] and (3) alternating copolymers obtained via the condensation polymerization of bis(NHC)s with ditopic electrophiles (bottom right).[90] In addition, many of these reactions can be rendered thermally reversible by tuning the stereoelectronic properties of the NHC (e.g., incorporating bulkier N-substituents) or the electronics of the coupling partner. In addition, NHCs and bis(NHC)s are often stable and isolable molecules, which should significantly improve the stoichiometric control required of step-growth polymerizations (e.g., those shown in Figure 13) and thus facilitate access to high molecular weight CPs. Guided by this precedence, we have pursued the synthesis and study of structural dynamic bis(NHC)-derived polymers. Each of the polymer classes shown in Figure 13 will be discussed in more detail below.

1. Homopolymers. Building on the NHC−enetetramine equilibrium discovered by Wanzlick (**$B_2 \leftrightarrow 2B$**, Figure 11B),[70] we envisioned that a comparable bis(NHC) could afford homopolymer featuring enetetramine linkages between its respective repeating units (Figure 13, top right). Deprotonation of readily accessible bis(imidazolium) salts **8a** and **9a**, to generate bis(NHC)s **8b** and **9b** in situ, resulted in a gradual color change from near-colorless to dark red over the course of 12 h, consistent with the formation of a molecule with an extended π-system.[91] Interestingly, ^{1}H NMR spectroscopic analysis of these reactions revealed two unique sets of signals: one sharp and one broad, corresponding to free bis(NHC) (**8b** and **9b**) and polydisperse macromolecules (**P8** and **P9**), respectively (Figure 14). A dependence on the N-substituents was observed for the bis(NHC)/polymer ratio, whereby longer alkyl chains correlated with decreased macromolecular composition. Moreover, because the ^{1}H NMR signals for the *N*-methylene protons in the free bis(NHC)s and polymers could be resolved, the corresponding equilibrium constant could be measured and tuned (K_{eq} = 1.0−5.3 to >100, depending on the N-substituent).

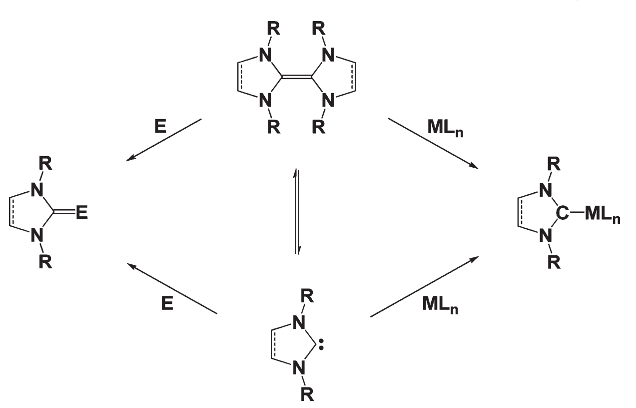

Figure 12. Wanzlick equilibrium between NHCs and enetetramines along with the organocoupling and metalation chemistries they undergo, where E = R−NCS, R−N_3, etc.

Replacing the primary alkyl groups in **8** and **9** with methyl groups afforded **P8** and **P9** as insoluble materials of high molecular weight due to the decreased steric influence of the N-substituents. Conversely, the equilibrium could be shifted toward greater relative monomer composition by increasing the N-substituent alkyl chain length. Heating a solution of **P9** (R = ethyl) to 90 °C decreased the relative amount of polymer and increased that of **9b**, as judged by variable-temperature ^{1}H NMR spectroscopy; subsequently, cooling of the solution to room temperature restored the equilibrium to its original distribution. Paralleling these experiments, analysis of the bis(NHC)−poly(enetetramine) mixture by UV/vis spectroscopy revealed characteristic absorbances at 300 and 450 nm, respectively, wherein the latter reflects the extended π-conjugation in **P8** and **P9**. As the relative amount of the bis(NHC) monomer increased, either by dilution or heating, the A_{300}/A_{450} ratio increased accordingly. Although these results represented an important fundamental achievement, i.e., thermally reversible C═C bond formation and breakage in a CP, **P8** and **P9** were unsuitable for practical applications as they decompose to their respective water adducts and bis(urea)s upon exposure to water and oxygen, respectively. Subsequent studies in our group showed that this propensity to oxidize could be harnessed to afford conjugated polyelectrolytes.[92]

2. Metallopolymers. Whereas enetetramine linkages rapidly decompose under ambient conditions, NHC−metal bonds exhibit significantly greater stability.[93,94] Guided by these observations, we concluded that inserting ML$_n$ spacers between the bis(NHC) monomers could afford an organometallic

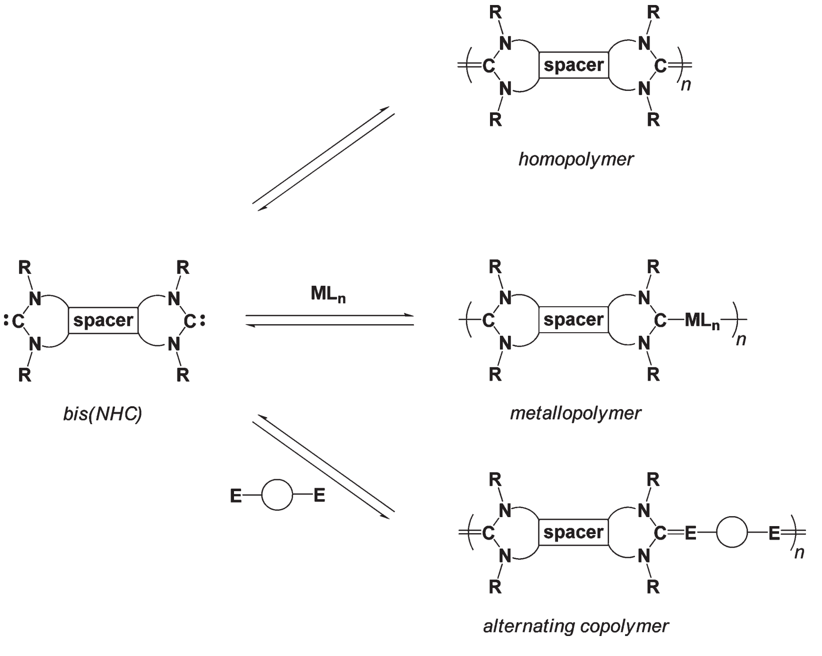

Figure 13. Conceptual homology depicting rationale for the bis(NHC) monomer scaffold (left) and the distinct classes of CPs they afford, ranging from homopolymers (top) to metallopolymers (middle) to alternating organic copolymers (bottom). The “spacer” shown refers to a scaffold that enables conjugation between each connected NHC moiety.

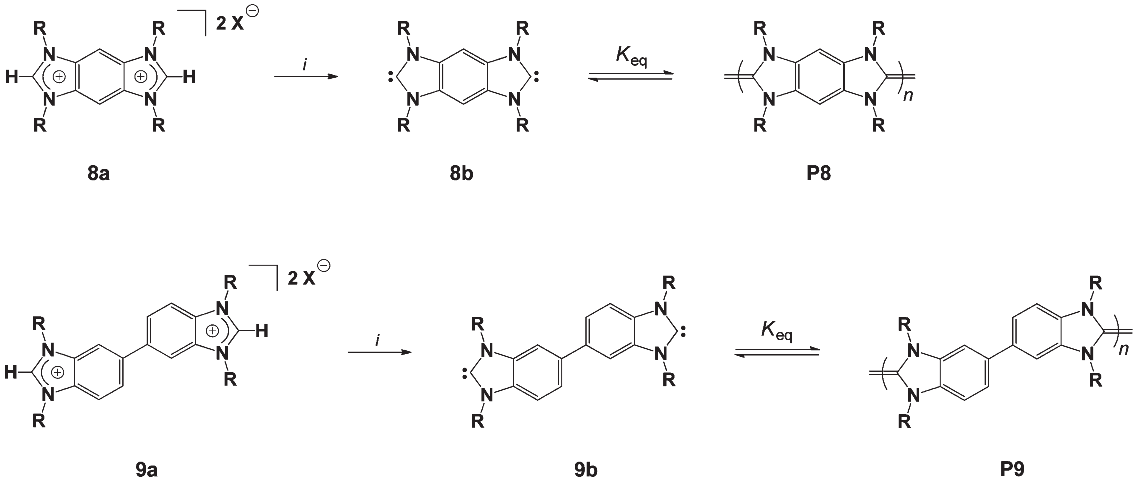

Figure 14. Synthesis and solution-phase structural dynamism of poly(enetetramines). Conditions: (i) 2 equiv of NaH, RT, THF. R = methyl, ethyl, *n*-butyl, or *n*-hexyl.

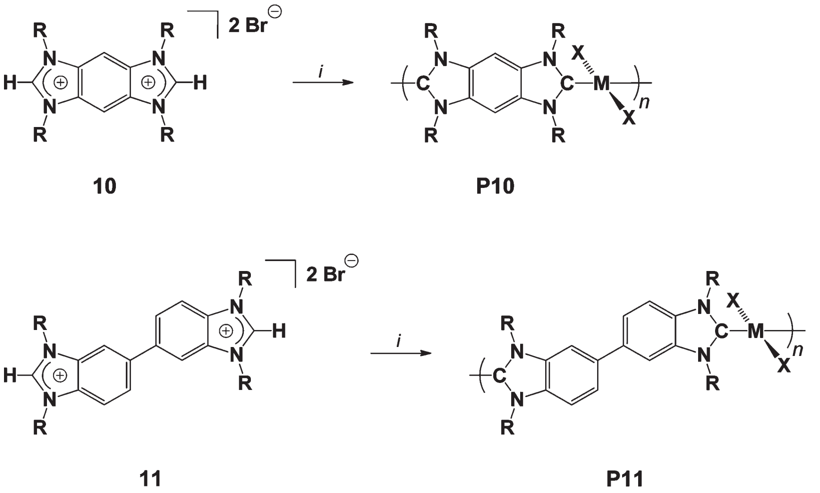

Figure 15. Synthesis of organometallic polymers comprising bis(NHC) linkers. R = *n*-butyl or benzyl, M = Pd or Pt, X = Cl or Br. Conditions: (i) $M(OAc)_2$ or NaOAc + MX_2.

CP that exhibited a higher stability than a poly(enetetramine) and comparable conjugation (Figure 13).[95] Metallopolymers **P10** and **P11** were prepared via the Herrmann–Schwarz–Gardiner[96] method of simultaneous deprotonation and metalation of **10** and **11** with $M(OAc)_2$ or alternatively by cotreatment with MX_2 and NaOAc (M = Pd or Pt, X = Cl or Br; Figure 15).[97] Although this approach was successful for Pd and Pt, attempts to prepare the Ni congeners were unsuccessful, presumably due to the greater lability of Ni–NHC bonds.[98] Incorporating metal chelating groups into the N-substituents enabled access to organometallic CPs;[99] however, these systems lacked structural dynamism. Analysis of **P10** and **P11** by GPC revealed a wide range of molecular weights (M_n = 8–1800 kDa; relative to polystyrene standards) and narrow polydispersities (PDI = 1.7–2.0), values consistent with a step-growth polymerization process and dependent on the transition metals employed as well as the N-substituents of the respective bis(NHC) monomers.

To determine whether reversible metal–NHC dissociation/binding was operative in these polymers, monomer exchange studies were performed and monitored by ^1H NMR spectroscopy. Treatment of **P11a** with **11b** in the presence of base resulted in the incorporation of the corresponding bis(NHC), affording metallopolymer comprising both monomers (**P11c**, Figure 16). Comparable postpolymerization exchange and incorporation of monomers were also found to occur between two homopolymers of different molecular weights, whereby combining two independently prepared samples of **P11a** with different M_n values (10.4 and 13.0 kDa) afforded a homogeneous polymer with an intermediate molecular weight (M_n = 11.1 kDa). Recently, related bis(NHC)-based metallopolymers capable of this thermally impelled structural dynamism have received interest as recyclable catalysts[100] and self-assembled materials.[101] Given the similarities between the electron-donating abilities and steric parameters of NHCs and phosphines,[102,103] metal–phosphine linkages have also been shown to endow the analogous (albeit nonconjugated) polymers with comparable structurally dynamic character.[104,105]

To increase the mechanical properties of films comprised by **P10** and **P11**, a tritopic NHC capable of cross-linking various polymer chains was included in aforementioned polymeriziation reactions. More specifically, performing the polymerization of **P11a** in the presence of tris(imidazolium) **12a** (10–30 mol %) afforded cross-linked materials that were cast into films (Figure 17).[106] One important advantage to studying films comprised of **P11a** and related polymers is that they are intrinsically conducting (~10^{-3} S cm^{-1}),

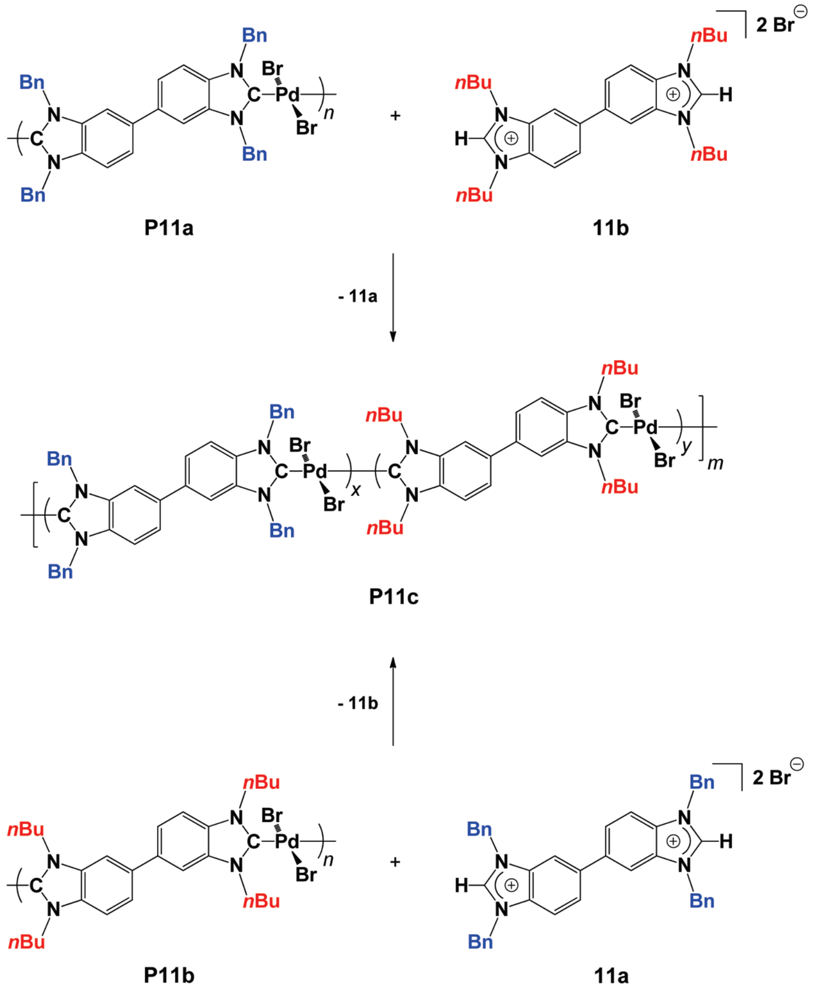

Figure 16. Monomer exchange experiments involving **P11**. Conditions: 110 °C, DMSO.

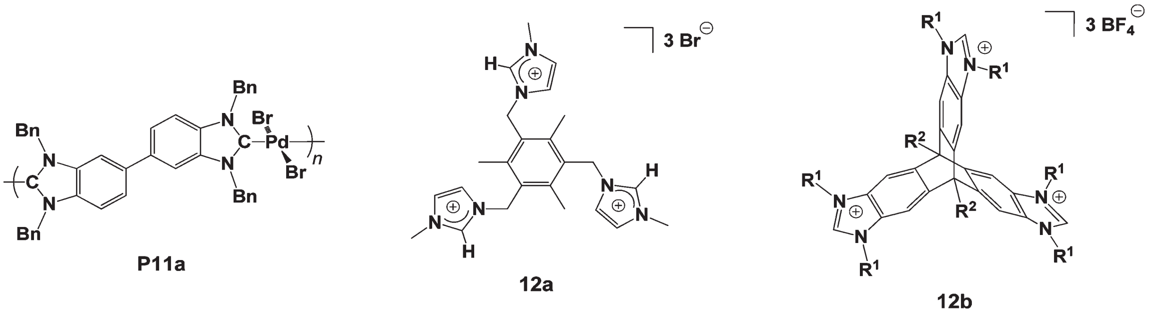

Figure 17. Components for the assembly of cross-linked organometallic polymer networks containing NHCs. R^1 = *t*-butyl; R^2 = *n*-butyl or *n*-hexyl.

allowing *undoped* films to be imaged via scanning electron microscopy (SEM). Additionally, the aforementioned cross-linked material exhibited thermoresponsive behavior, with a range of sol−gel transitions temperatures from 100 to 150 °C. To explore their potential in self-healing applications, scored films of these materials were visualized by SEM; subsequent heating to 150 °C for 15 min actuated a structural change which resulted in a noticeable smoothing and partial repair of the damaged areas. Current efforts are focused toward **12b** and related tris(NHC) building blocks for accessing other structurally dynamic organometallic polymers and metal−organic frameworks.[107]

3. Alternating Organic Copolymers. Despite the improved stability of the bis(NHC)-derived metallopolymers vs homopolymers, the electronic and geometric requirements for the ML_n linkages ultimately constrains the synthetic diversity which may be used to prepare these materials. In contrast, organic electrophiles span a much wider range of electronic properties; therefore, a combination of ditopic NHCs and ditopic electrophiles with complementary reactivities should enable access to a more diverse and tunable CP scaffold.[71,78,79] Isothiocyanates have been known to engage in reversible covalent bonding with transition metal complexes for over two decades;[108,109] thus, we proposed that bis(isothiocyanate)s could also react with a suitable ditopic coupling partner, potentially in a thermally reversible manner, to yield CPs. To test this hypothesis, **13a** was treated with stoichiometric **13b** (0.2 M each in DMF) at ambient temperature which afforded the corresponding CP in near-quantitative yield (**P13**, Figure 18).[110] Analysis of this material

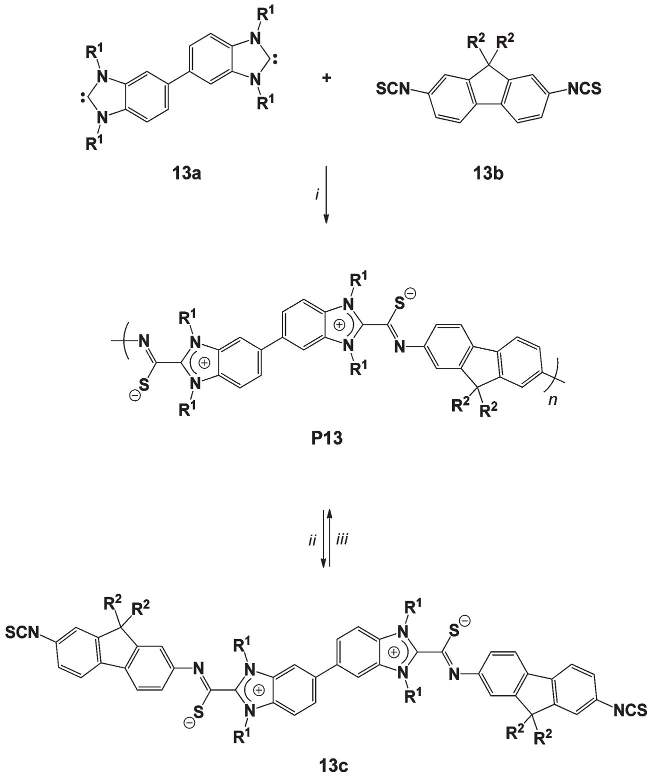

Figure 18. Synthesis of alternating bis(NHC)−bis(isothiocyanate) copolymers and their structural dynamism in solution. R^1 = 2,2-dimethylbutyl, R^2 = *n*-hexyl. Conditions: DMF; (i) RT; (ii) **13b**, 120 °C; (iii) **13a**, RT.

by GPC enabled determination of its molecular weight (M_n = 14.8 kDa) and polydispersity (PDI = 2.1), values consistent with a step-growth polymerization process. Higher molecular weight materials ($M_n \leq 29.0$ kDa) were obtained by increasing the initial monomer concentration from 0.2 to 0.8 M.

To explore the structural dynamic characteristics of **P13** (M_n = 14.8 kDa), a solution of the material containing 1.0 equiv of **13b** (relative to the aforementioned polymer's repeat unit) was heated to 120 °C, which caused the disappearance of the signal assigned to high polymer in the respective GPC trace, along with concomitant formation of multiple signals attributed to low molecular weight materials (M_n = 1.5−6.1 kDa). Analysis of this transformation by UV/vis spectroscopy revealed a decrease in the absorbance at 410 nm, accompanied by the formation of a new peak at 392 nm, consistent with the shorter effective conjugation length in **13c** vs **P13**. Following isolation and purification, the major component was unambiguously identified as **13c** via comparison to independently prepared material. Conversely, this mixture of low molecular weight oligomers was successfully used to reform **P13** (M_n = 18.0 kDa) upon addition of **13a**. Moreover, these depolymerization/repolymerization reactions could be cycled multiple times, indicating that the NHC−isothiocyanate bonds were fully reversible.

Heat can be generated and supplied to solutions and materials with greater ease and efficiency than chemical reagents, electricity, or light, reducing overall complexity and cost. Moreover, thermal applications do not require chemically reactive functional groups, conductive media, or optical transparency and thus are more general and compatible with a broader scope of materials. However, one disadvantage of using thermal energy to effect reversible structural changes in CPs is that the covalent bonds relevant to this process must be significantly weaker than the other bonds in the polymer. Given that molecules occupy a Boltzmann distribution, the energy required for a thermoresponse must be sufficiently lower than the corresponding activation barriers for other chemical reactions to avoid undesired structural or functional changes (typically in the range of 0−150 °C). Considering this limitation, thermally impelled structural dynamism could be employed in situations where chemical, electrochemical, or photochemical impetuses are infeasible or impractical. For example, device components or materials that cannot be accessed without causing damage, disrupting function, or requiring shutdown would benefit from CPs whose functions could be modulated via thermally impelled structural dynamism.

Summary

Despite the knowledge of reversible covalent bonds for over a century and their successful incorporation into nonconjugated macromolecular scaffolds, comparable structurally dynamic CPs comprising reversible covalent bonds have been a surprisingly recent development. This structural dynamism can be actuated by chemical, electrochemical, photochemical, and thermal impetuses. Structurally dynamic CPs that respond to chemical stimuli have been achieved via the reversibility intrinsic to imine and carbon metathetical reactions. However, this strategy has thus far been limited to the wholesale creation and disruption of extended π-conjugation. Electrochemical impetuses have been used to alter the charge-transport and -storage capacity of CPs, but only within the scope of the formation and cleavage of interchain disulfide cross-links. Photochemically impelled structural dynamism has been shown to induce significant changes in the HOMO−LUMO gap due to changes in the polymer main chain structure; however, this technique has only been successful with photoresponsive units that have absorptions well-separated from those of the CP. Because chemical, electrochemical, and photochemical impetuses suffer from inhomogeneous delivery methods and specialized conditions (e.g., chemically reactive functional groups, conductive media, optical transparency, etc.), our group has focused attention on the pursuit of structurally dynamic CPs that operate via thermally controlled processes. In particular, we have shown that bis(NHC)s can afford multiple classes of CPs whose structural and spectral features can be reversibly tuned using thermal energy. Although substantial progress has been made toward CPs that exhibit structural dynamism in response to various impetuses, most studies thus far have focused primarily on their macromolecular properties (e.g., molecular weight), and much less attention has been paid to their electronic properties (e.g., λ_{max}). Therefore, opportunities abound for investigating the structure−property relationships of structurally dynamic CPs.

Challenges and Outlook

The primary challenge in rendering a CP structurally dynamic is that the underlying processes formally involve the disruption and restoration of σ- and π-bonds, both of which must occur in a controlled mannter. Although chemical reactions can effect the necessary transformations, their efficacy significantly diminishes upon going from solution to the solid state. Moreover, these reactions often generate byproducts which could negatively interfere with both the electronic and material properties of the CP. In light of these considerations, an important goal for research in this area would be to develop multicatalyst or multicycle systems, wherein the byproduct from one reaction could be used in the reverse or a subsequent reaction.

Electrochemical methods have been shown to be viable for altering these features via modulation of interchain interactions but have not yet been used to alter CP main chain connectivity.

However, a limitation inherent to this technique is that a medium with sufficient conductivity must be present, by either intrinsic charge or electrolyte. To investigate how redox changes within a CP main chain could be used to tune its structure and electronics, the design and synthesis of a monomer that features extended conjugation and redox activity (e.g., quinone) must first be achieved.

Both CP structural and spectroscopic changes can be effected by photochemical impetuses, yet this strategy is only viable when the absorption of the photoresponsive subunit is not blocked by those of the CP itself. Adjusting the optical properties of the CP via the use of different monomers (e.g., replacing phenylene with thiophene spacers) could overcome this limitation; however, such modifications would fundamentally change the identity of the polymer. Moreover, the design and preparation of an alternate photoresponsive subunit could be time-consuming and synthetically daunting. Because most examples of structurally dynamic CPs that respond to photochemical stimuli exhibit modest structural changes (i.e., geometric isomerization), one opportunity would be to develop an architecture that undergoes main chain dissociation (e.g., with a metal−metal bond). Similarly, another possible research area is the adaptation of FRET to CPs, wherein light can be delivered to a molecular "antenna" at a wavelength well separated from the absorptions of the polymer, and energy would subsequently be transferred to a structurally dynamic functionality within the main chain.

Our efforts have demonstrated the ability of thermal impetuses to modulate CP degree of polymerization and, as a result, vary the attendant electronic properties. One appealing (but challenging) goal would be to achieve binary control of polymerization, whereby a polymer would be quantitatively depolymerized to monomer without proceeding through any oligomeric intermediates. From a practical perspective, such approaches will likely require a thermally reversible multiple bond whose dissociation energy is sufficiently low that adventitious reactivity pathways are not also accessed. Although the bis(NHC) building blocks enable CPs with structural dynamism that can be controlled by the introduction or removal thermal energy, these components are often sensitive to ambient conditions. To achieve greater scope and utility, a thermoresponsive unit that is stable to oxygen, water, and other environmental contaminants (e.g., acid) must be developed.

Taken together, significant progress has recently been made toward CPs that exhibit dynamic macromolecular properties in response to various stimuli. However, much less attention has been paid to the associated spectroscopic features, such as those dependent on the extended π-conjugation (e.g., optical transitions, band-gap potential, etc.) As a result, there are significant opportunities for fundamental studies of the relationship between CP structure and properties, particularly as they change in response to exogenous stimuli. Moreover, each impetus presented offers unique deficiencies and potential, with many fundamental discoveries and optimizations that have not yet been explored. Nonetheless, as the need for multifunctional materials continues to grow, so will the need for systematic studies of CPs that exhibit dynamic structures and electronic properties. Given the tremendous promise they show in a variety of fields, ranging from smart materials to energy storage to self-healing electronics, we believe that the synthesis, study, and application of structurally and electronically dynamic CPs has only just begun, and there is much to be done.

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References and Notes

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(18) To preserve clarity and brevity, we define "structural dynamism" as the reversible depolymerization effected via the disruption of σ- and π-bonds, where these concepts are discussed interchangeably. This term is distinct from "geometric dynamism", which is merely the variation in polymer geometric features (i.e., *trans*−*cis* isomerization) that is nearly ubiquitous among CPs in solutions under ambient temperatures.
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