

Structurally Dynamic Materials Based on Bis(*N*-heterocyclic carbene)s and Bis(isothiocyanate)s: Toward Reversible, Conjugated Polymers

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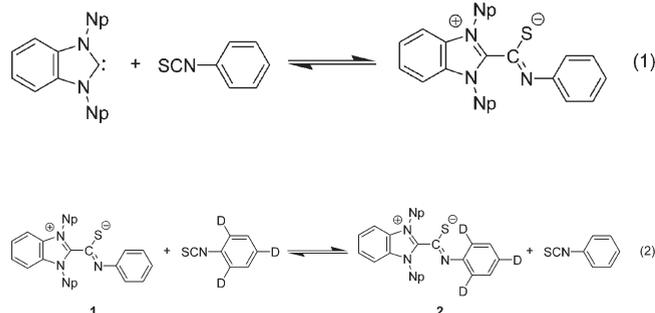
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Demand for reconfigurable and self-healing materials in electronic applications continues to grow at an escalating rate.¹ Although shape memory alloys offer promise for use in some of the aforementioned applications,² they function at relatively high temperatures and are challenging to process. As an alternative strategy, we envisioned polymers with conjugated π -systems capable of altering their molecular structures, specifically through depolymerization to fluidic monomers, in response to changes in externally applied stimuli. Accessing such reversible, conjugated polymers (RCPs) presents a fundamental challenge in finding sets of building blocks that are capable of assembling and disassembling while maintaining unsaturation. For practical reasons, this dynamic process should also exhibit perfect atom economy (i.e., no byproduct evolution) and function without the need for catalyst(s) or other exogenous species (i.e., solvents, etc.) Although an impressive range of dynamic covalent reactions and associated polymerizations are known,³ their underlying chemistries⁴ do not fulfill the aforementioned requirements.

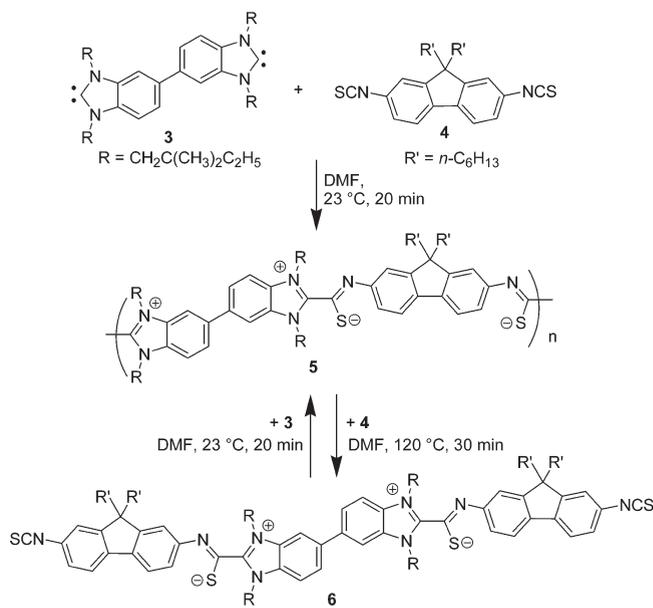
Herein we show that an answer to these challenges may lie in the chemistry of *N*-heterocyclic carbenes⁵ (NHCs), substrates which can form reversible adducts with a variety of reagents, including other NHCs, organic electrophiles, and transition metals.⁶ NHC coupling reactions with isothiocyanates⁷ were particularly appealing because they conserve unsaturation and create formally conjugated linkages between the two moieties (see eq 1), meeting two important design criteria for constructing RCPs. Analogous to NHC dimerization, we reasoned that the NHC–isothiocyanate coupling reaction may be rendered reversible^{6,8} through steric tuning of the *N*-substituents. Ultimately, we envisioned a new class of RCPs could be developed by combining aromatic bis(isothiocyanate)s with complementary bis(NHC)s.⁹



Initial efforts were directed toward investigating the reversible nature of the covalent bond formed between NHCs and isothiocyanates. As shown in eq 2, heating a toluene-*d*₈ solution of adduct 1, which was prepared from 1,3-dineopentylbenzimidazolylidene¹⁰

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Scheme 1. Synthetic Methodology Used To Form a Structurally Dynamic Polymer Derived from a Bis(NHC) and Various Bis(isothiocyanate)s



and phenylisothiocyanate, with stoichiometric 2,4,6-trideuterio-phenyl isothiocyanate at 120 °C resulted in the formation of an equimolar mixture of the starting materials and expected products after 20 h. The exchange reaction was found to be first order in adduct and zeroth order in isothiocyanate, and the NHC–isothiocyanate dissociation process exhibited a positive ΔS^\ddagger ($21 \pm 3 \text{ cal mol}^{-1} \text{ K}^{-1}$).¹¹ These results led us to believe that the aforementioned NHC–isothiocyanate exchange reaction proceeded via adduct dissociation followed by statistical recombination.

Building on these results, we next explored the feasibility of preparing structurally reversible polymers based on NHC–isothiocyanate coupling chemistry. Bis(NHC) 3 was selected as a suitable monomer because its reactive carbene moieties are connected via an extended π -system and features flexible branched alkyl *N*-substituents to enhance solubility in organic solvents.¹² To form high polymer with electronically delocalized structures, bis(isothiocyanate) fluorene derivative 4,¹³ which contains two *n*-hexyl chains at the 9-position to enhance solubility, was chosen as the complementary monomer.

Addition of 3 to an equimolar quantity of 4 in DMF ($[3]_0 + [4]_0 = 0.2 \text{ M}$) at ambient temperature resulted in the formation of a viscous solution within 20 min. Pouring the resulting mixture into excess diethyl ether caused polymer 5 to precipitate, which was subsequently collected in 98% isolated yield via filtration. The polymer was found to be highly soluble in nonpolar as well as polar organic solvents, which facilitated characterization by NMR spectroscopy. Compared to its monomers, the diagnostic signals of 5 were shifted downfield and were in accord with those expected from the structure shown in Scheme 1. Analysis of 5 using gel permeation chromatography (GPC) (eluent = 0.1 M LiBr in DMF) revealed that this material exhibited a number-average molecular weight (M_n) of 14.8 kDa and was polydisperse (PDI = 2.1),¹⁴ results typical for a step-growth polymerization (see Figure 1). Relatively high molecular weight (MW) polymers (M_n values up to 29.0 kDa) were prepared by performing the

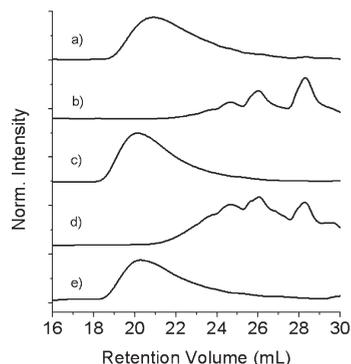


Figure 1. Gel permeation chromatograms (eluent: 0.1 M LiBr in DMF; rate: 1.0 mL/min): (a) polymer **5**; (b) polymer **5** with 1.0 equiv of **4** (per repeat unit); (c) solution obtained from (b) after the addition of 1.0 equiv of **3** (per repeat unit); (d) solution obtained from (c) after the addition of 1.0 equiv of **4** (per repeat unit); (e) solution obtained from (d) after the addition of 1.0 equiv of **3** (per repeat unit).

mentioned polymerization reactions at higher concentrations ($[\text{total monomer}]_0$ up to 0.8 M).

We next probed the structurally dynamic characteristics of **5**.¹⁵ Heating a DMF solution of this polymer ($M_n = 14.8$ kDa; PDI = 2.1) to 120 °C in the presence of 1.0 equiv of **4** (relative to the polymer's repeat unit) resulted in a significant decrease in the polymer's MW. Analysis of the crude reaction mixture by GPC resolved a series of low-MW peaks ranging from 1.5 to 6.1 kDa, of which the predominant peak was attributed to **6** (isolated from the reaction mixture and compared to an authentic sample; see below). Subsequent addition of **3** to the aforementioned reaction mixture resulted in the re-formation of polymer **5** with a $M_n = 18.0$ kDa (PDI = 2.9). Owing to the high fidelity of the NHC–isothiocyanate coupling reaction, these depolymerization/polymerization cycles were repeated twice on the same samples. Analogous results were obtained when **5** was depolymerized with **3** and then treated with **4** to re-establish the formation of polymer.

In parallel with molecular weight measurements, the aforementioned depolymerization/polymerization reactions were monitored via UV–vis spectroscopy (see Figure 2). Polymer **5** exhibited a $\lambda_{\text{max}} = 410$ nm (in DMF). However, upon depolymerization via treatment of **5** with excess **4**, as described above, this value shifted hypsochromically to 392 nm. Qualitatively, the longer λ_{max} of the polymer suggested that the effective conjugation length of these materials exceeded that of their lower MW analogues.

To gain additional insight into the electronic structure of this polymeric material, model compounds **6** and **7**, which approximate two possible repeating units of polymer **5**, were synthesized. The former was prepared by adding an excess (4.0 equiv) of **4** to a THF solution (14 mM) of **3**, followed by purification via column chromatography. As shown in Figure 3, compound **7** was synthesized by treating 1,3-di(2,2-dimethylbutyl)benzimidazolium tetrafluoroborate with sodium *tert*-butoxide (to generate the respective NHC in situ) in THF followed by the addition of 0.3 equiv of **4**. Analysis of **6** via UV–vis spectroscopy revealed a λ_{max} at 382 nm (DMF), a result which indicated that its effective chromophore is shorter than that of **5**. In contrast, the UV–vis spectrum of **7** ($\lambda_{\text{max}} = 409$ nm in DMF) was found to be similar to that exhibited by the polymer. Hence, although polymer **5** is formally conjugated, it appears to be comprised of repeating units that are related to **7** and that these repeating units exhibit minimal π -overlap with each other.¹⁶ The limited long-range electronic communication does not prohibit the polymer's ability to conduct electrical charge, however. For example, while thin (5 μm) films of **5** were found to be nonconductive ($\sigma < 10^{-10}$ S/cm), exposure to iodine vapor increased the material's electrical

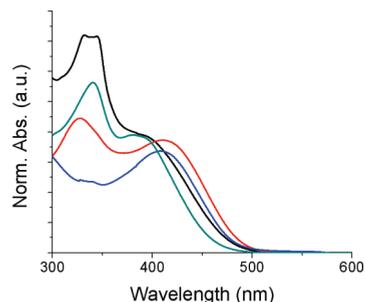


Figure 2. UV–vis spectra of polymer **5** before (red) and after (black) the addition of 1.0 equiv of **4** (per repeat unit) as well as model compounds **6** (green) and **7** (blue) in DMF.

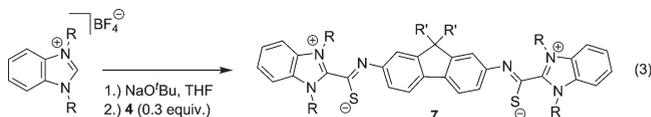


Figure 3. Synthesis of the model compound **7** used to evaluate the electronic structure of polymer **5**. R = $\text{CH}_2\text{C}(\text{CH}_3)_2\text{C}_2\text{H}_5$. R' = $n\text{-C}_6\text{H}_{13}$.

conductivity to $\sigma = 1.7$ mS/cm, as determined using a four-point probe technique.¹⁷ We are currently investigating other dopants which could provide additional insight into the charge transfer mechanisms exhibited by these doped materials.¹⁸

In conclusion, we have developed a new class of aromatic polymers using NHC–isothiocyanate coupling chemistry. Simple combination of bis(NHC)s with complementary bis(isothiocyanates) produced polymers that were found to be structurally dynamic. These results expand the utilities of free bis(NHC)s as polymer building blocks and create a new design strategy for accessing polyelectrolytes with charges as integral components of their main chains.¹⁹ The polymerization reaction reported herein is one of the few examples where chemical unsaturation is maintained as monomer is converted to polymer and remains poised for adaptation into a system that affords a structurally reversible, conjugated polymer. Efforts toward these goals will focus on increasing the effective conjugation length in the aforementioned materials, principally via desymmetrization of the NHC N-substituents as well as through varying the electronic properties of the bis(NHC) and bis(isothiocyanate) monomers.

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Supporting Information Available: Detailed experimental procedures and characterization of all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (11) See Supporting Information for additional details.
- (12) Bis(NHC)s featuring more common N-substituents (e.g., ethyl, *n*-butyl, *tert*-butyl, neopentyl, etc.) were found to be either prone to polymerization via NHC dimerization (see: Kamplain, J. W.; Bielawski, C. W. *Chem. Commun.* **2006**, 1727) or produced insoluble materials upon combination with **4**. As a result, such bis(NHC)s were not extensively examined.
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- (14) Molecular weights are reported as their polystyrene equivalents; see Supporting Information.
- (15) The thermal stability of **5** was evaluated using thermogravimetric analysis (10 °C min⁻¹, N₂) and found to lose ~10% of its mass at 300 °C under nitrogen.
- (16) The restricted electronic communication observed in **5** may stem from nonplanarity of its NHC–isothiocyanate or biphenyl components, or both. For example, the N–C–C–S dihedral angles found in the solid state structures of known NHC–isothiocyanate adducts range from 67.2° to 78.9°. See: (a) Akkurt, M.; Karaca, S.; Küçükbay, H.; Sireci, N.; Büyükgüngör, O. *Acta Crystallogr.* **2008**, *E64*, o809. (b) Akkurt, M.; Karaca, S.; Küçükbay, H.; Yilmaz, U.; Büyükgüngör, O. *Acta Crystallogr.* **2005**, *E61*, o2875. Likewise, a variety of 5,5'-bibenzimidazolylidenes were found to exhibit significant twisting about its biphenyl linkages in solution as well as in the solid state (dihedral angles up to 51.2° were observed). See: Er, J. A. V.; Tennyson, A. G.; Kamplain, J. W.; Lynch, V. M.; Bielawski, C. W. *Eur. J. Inorg. Chem.* **2009**, 1729.
- (17) Films of **5** exhibited a Young's modulus (*E*) of 65 GPa and a yield strength of 60 MPa. Upon doping with iodine, the resulting material exhibited a larger yield strength (140 MPa) and as well increased compliance (*E* = 3.3 GPa).
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