Dynamic covalent polymers based upon carbene dimerization†

Justin W. Kamplain and Christopher W. Bielawski*

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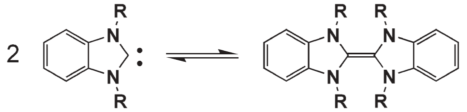
Thermally-reversible covalent polymers featuring dynamic carbon–carbon double bonds and tunable molecular weights were prepared from difunctional carbenes; addition of transition metal complexes to these materials afforded the respective main-chain organometallic polymers.

The synthesis of macromolecules linked together *via* weak covalent bonds has received considerable interest recently.[1] Bond breaking, and thus a reduction in molecular weight, occurs upon exposure to a stimulus such as heat, radiation, or exogenous catalyst, whereas removal of the stimulus re-establishes the formation of high molecular weight material. This unique feature provides responsive or dynamic polymeric materials which have already found applications in combinatorial chemistry,[2] artificial self-sorting[3] and self-replicating systems,[4] and in autonomous-healing materials.[5,6] Although a range of reversible covalent interactions have been incorporated into macromolecular building blocks (*e.g.*, amino/carbonyl condensations,[7] [2 + 2][8] and [4 + 2][6] cycloadditions, olefin[4,5] and imine[9] metathesis, radical combination,[10] thiol–disulfide exchange,[11] transesterification,[12] and transacetalation[13]), there exists considerable demand to expand this synthetic repertoire to address new challenges and demands. In particular, we have recently launched a program focused on the development of responsive materials with tunable electronic properties.[14] An ideal system suitable for this purpose would: (1) conserve chemical unsaturation and/or increase electronic delocalization from monomer to its respective polymer, (2) exhibit high atom economy (*i.e.*, no small molecule byproducts would evolve during polymerization or depolymerization), and (3) possess a modular molecular framework for rapidly optimizing and tuning physical and electronic properties.

In the early 1960s, Wanzlick and Buchler proposed that an equilibrium exists between certain imidazol-2-ylidenes (**1**) and their respective enetetraamine dimers (**1′**) (see eqn (1)).[15] Landmark contributions from Arduengo *et al.*[16] on the synthesis and isolation of stable free imidazolylidenes subsequently enabled experimental verification of this phenomenon;[17] although the dimerization mechanism remains in debate.[18] Regardless, it is well known that the equilibrium can be finely controlled by varying the heterocyclic ring (electronics) and the pendant N-substituent (sterics).[17] Collectively, this interaction appeared to possess each of the desired features noted above and prompted us to explore carbene dimerization—the reversible formation of carbon–carbon double bonds—as a new module for constructing dynamic covalent polymers.



1 **1′** (1)

We targeted rigid benzimidazole-based frameworks with bifacially opposing carbene moieties as the basic monomeric scaffold to reduce the formation of cyclic species and maximize the formation of the respective linear polymer.[19] As such, the requisite precursor benzobisimidazolium (**2**) and [5,5′]-bibenzimidazolium dibromides (**3**) with N-substituents of various sizes were obtained in moderate yields by four-fold alkylation of readily available benzobisimidazole or [5,5′]-bibenzimidazole in accord with our previously reported route.[14] Polymerizations were initiated by suspending the bisazolium salts in benzene, toluene, THF, or DMF followed by deprotonation with NaH (proton transfer in the heterogeneous suspension was facilitated by adding a catalytic amount of KOtBu).‡ After 12 h at room temperature, the resulting dark red mixtures were filtered to remove NaI or NaBr salts which precipitated during the polymerizations and analyzed directly or isolated after precipitation from excess pentane.§

The products of the polymerization reactions described above were characterized by a combination of NMR spectroscopy, viscosity measurements, and UV-Vis spectroscopy. Notably, two distinct sets of signals were observable in the ^{1}H and ^{13}C NMR spectra: one set was broad, as expected for a polydisperse macromolecule, and one set was narrow with relative ratios dependent on the size of the N-substituent. In particular, signals attributable to the N–CH_2– fragment on free carbene species (δ = 4.2 ppm) were clearly resolvable from its enetetraamine dimer (δ = 3.4 ppm) in the ^{1}H NMR spectra which permitted an accurate measurement of the total amount of free carbene species and polyenetetraamine (see Scheme 1 and Table 1). Monomers possessing relatively small N-methyl substituents (**4·Me** and **5·Me**), where dimerization would be favored, afforded insoluble high molecular weight polymeric materials. However, as the size of the N-substituent increased, the equilibrium between monomer and polymer shifted toward the former. Monomer **5·Et**, which contained N-ethyl groups, showed an optimal balance between solubility and polymerizability, and was used for subsequent experiments and measurements.

To further confirm the polymeric nature of these samples, viscosity measurements were performed on a solution of **5·Et** in THF at a variety of concentrations (10 μM–200 μM, 23.0 °C) using a Cannon-Ubbellohde viscometer. Shown in Fig. 1A is a logarithmic plot of relative viscosity *vs.* concentration for

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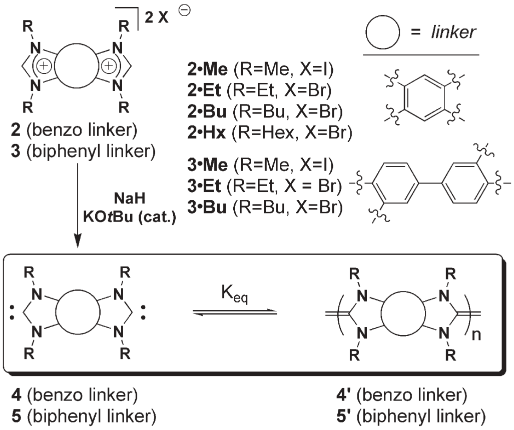
Department of Chemistry and Biochemistry, The University of Texas at Austin, 1 University Station A5300, Austin, TX 78712, USA.
E-mail: bielawski@cm.utexas.edu; Fax: +1 512 232 8696;
Tel: +1 512 232 3839

† Electronic supplementary information (ESI) available: additional experimental details and spectroscopic data (^{1}H NMR, ^{13}C NMR and HR-MS) on prepared compounds. See DOI: 10.1039/b518246h



Scheme 1 Generation and polymerization of difunctional carbenes.

Table 1 Polymerization results[a]

Precursor	Monomer	Polymer	K_{eq}[b]
2·Me	**4·Me**	**4·Me′**	[c]
2·Et	**4·Et**	**4·Et′**	5.3, 130[d]
2·Bu	**4·Bu**	**4·Bu′**	2.1
2·Hx	**4·Hx**	**5·Hx′**	1.0
3·Me	**5·Me**	**5·Me′**	[c]
3·Et	**5·Et**	**5·Et′**	1.7
3·Bu	**5·Bu**	**5·Bu′**	1.1

[a] Monomer was generated by adding three equivalents of NaH (and a catalytic amount of KO*t*Bu) to the respective precursor bisazolium salt suspended in benzene-*d* 6([monomer]$_0$ = 0.2 M). [b] K_{eq} refers to the total concentration of polyenetetraamine divided by the total concentration of free carbene as measured by ^{1}H NMR spectroscopy. Value was obtained after 12 h and 23 °C. [c] Insoluble high molecular weight polymer was obtained. [d] Observed after 48 h at 23 °C.

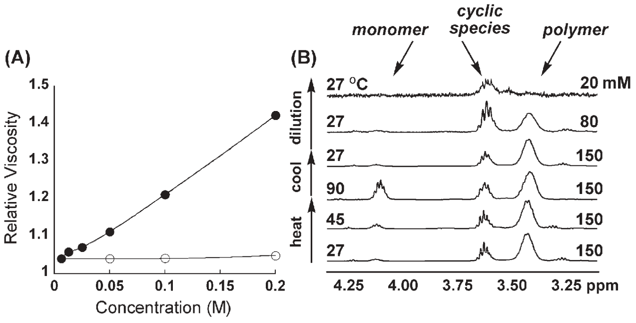
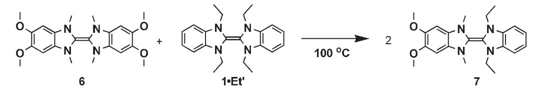


Fig. 1 (a) Plot of relative viscosity of **5·Et** (solid circles) and **1′** (R = Et, open circles) *vs.* THF as a function of concentration; Conditions: *T* = 23.0 °C, solvent = THF. (b) ^{1}H NMR analysis (solvent = toluene-d_8) of **5·Et** at a variety of temperatures (left) and concentrations (right). The bottom spectrum shows the initial conditions (27 °C, 150 mM) and progressive changes to the sample are indicated in the respective stacked spectra.

5·Et/**5·Et′**. For comparison, model substrate **1·Et′** (R = Et), designed to function as a small molecule to mimic the repeat unit of the polymer chain, was also synthesized and studied.¶ The relative viscosity of the small molecule model did not vary with concentration whereas the relative viscosity of the polymer solution increased (exponentially) over the same concentration range. This differential behavior was attributed to the formation of high molecular weight material that was strongly dependent on concentration.[20] UV-Vis spectroscopy was also used to confirm the concentration dependence. An absorption attributed to monomer (λ = 300 nm) was clearly resolved from the polymer (λ = 450 nm) with a relative ratio dependent on concentration in accord with NMR and viscosity measurements. Notably, the longer wavelength of radiation absorbed by the polymer suggests that electron delocalization character of the system was conserved or gained upon polymerization.

We subsequently focused our attention on investigating the reversible nature of these materials by studying how the temperature and concentration influence polymer formation. Using variable temperature ^{1}H NMR spectroscopy, a 150 mM toluene-d_8 solution of **5·Et** was heated from 27 to 90 °C.|| As shown in Fig. 1B, signals attributable to the polymer attenuated with a concomitant increase in signals corresponding to free carbene.[18] Subsequent cooling reversed the signal intensities to their original populations. Interestingly, at concentrations at or below 150 mM, a new signal at 3.6 ppm was observed. We attributed this signal to the formation of cyclic oligomers which are commonly observed at low concentrations during typical step-growth polymerizations.[21] To confirm, a solution of **5·Et** was successively diluted (200 mM–20 mM) and analyzed by ^{1}H NMR spectroscopy. As shown in Fig. 1B, the signal corresponding to polymer successively decreased in intensity while the signal corresponding to the cyclic oligomer increased. Collectively, these results demonstrated that formation of polymer was a step-growth, equilibrium controlled process.

The dynamic nature of the carbene-based polymerizations suggested that chain transfer agents (CTAs) could be used to control polymer formation and install functional groups at the termini of the polymer chains.[22] Supportive evidence was obtained from preliminary cross-over experiments (see eqn (2)) between **1·Et′** and the dimer of 1,3-dimethyl-5,6-dimethoxybenzimidazol-2-ylidene (**6**) (–OCH_3, δ = 2.75 ppm).** Heating stoichiometric amounts of these two compounds to 100 °C for 12 h in toluene afforded a statistical (1 : 2 : 1) mixture of **6** : **1·Et′** : **7**, where **7** was the heterodimeric product (δ = 2.70 ppm). These results poised us to explore the use of **6** as a CTA in the carbene polymerizations described above (see eqn (3)). In these experiments, benzene solutions of **6** and homopolymer **5·Et′** were heated to 100 °C for 12 h and analyzed by ^{1}H NMR spectroscopy. New sets of signals corresponding to **8** (δ = 2.70 ppm) were observed in accord with the model cross-over reaction which suggested **5·Et′** effectively depolymerized and reacted with 1,3-dimethyl-5,6-dimethoxybenzimidazolylidene to afford shorter chains with functionalized end-groups.



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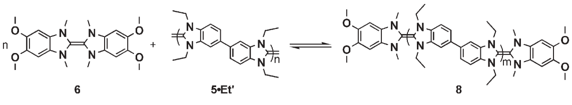
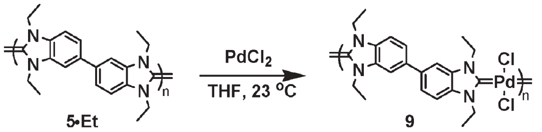


(3)

The dynamicity displayed by the carbene-based polymeric materials described above prompted us to explore their utility in the synthesis of organometallic polymers.[23] It is well known that carbenes such as imidazol-2-ylidenes and benzimidazol-2-ylidenes possess high affinities toward a broad range of transition metals.[17] Recently we exploited this propensity by combining various

N-alkylated bisazolium salts with group 8 metals to afford high yields of the respective main-chain organometallic copolymers. Polymer formation was dependent on the addition of base or the use of metal complexes with anionic ligands to effect carbene generation. In contrast, we envisioned that adding a transition metal complex directly to the dynamic covalent polymers described above would provide an atom-economical synthesis of the respective main-chain organometallic copolymers. Gratifyingly, addition of $PdCl_2$ to a solution of homopolymer **5·Et′** resulted in a rapid loss of the dark red color followed by precipitation of polymer **9** (see eqn (4)). Analysis of the precipitant by gel permeation chromatography indicated the material had a molecular weight of 5.5×10^4 Da (as a polystyrene equivalent) and a polydispersity index of 1.3. The structure of the polymer was confirmed by NMR spectroscopy to be identical to an authentic sample prepared from the corresponding bisazolium chloride and $Pd(OAc)_2$.[14]



(4)

In summary, we report a new reversible covalent polymerization based upon carbene dimerization. Requisite biscarbene monomers were prepared from readily available starting materials and generated under basic conditions. Polymer formation was found to be dependent on temperature and concentration and was conveniently tuned through simple structural modification of common precursors or through the inclusion of chain-transfer agents. These dynamic materials were also found to provide organometallic polymers efficiently upon the inclusion of a transition metal complex. Importantly, the system meets a number of ideal criteria for preparing dynamic materials that may ultimately be suitable for use in electronic, sensing, and catalytic applications. Advances toward these goals are under way and will be reported in due course.

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Notes and references

‡ *Representative polymerization procedure*: 1,1′,3,3′-Tetraethyl-5,5′-bibenzimidazolium dibromide **3·Et** (150 mg, 0.20 mmol), NaH (95 wt%, 15 mg, 0.60 mmol), *t*BuOK (1 mg, 0.01 mmol), and a magnetic stir bar were added to a vial in a N_2-filled drybox. The reactants were then suspended in benzene-d_6 (1 mL) and the vial was capped with a Teflon-lined septum. Under vigorous stirring, the resulting slurry was heated at 80 °C for 5 h and then stirred at room temperature for 12 h. The mixture was then filtered through a 0.2 μm Whatman PTFE filter which afforded a dark red solution. This solution was either analyzed directly or poured into a large volume (>10 mL) of dry, degassed pentane (under an atmosphere of N_2) which precipitated polymeric materials that were collected by filtration. Note: these materials oxyluminesce upon exposure to oxygen and ultimately decompose to the respective cyclic urea(s).

§ In general, polymerizations were performed for 12 h. However, longer reaction periods (>48 h) afforded higher conversions to polymer (most notable was **5·Et/5·Et′**: $K_{eq} = 130$, see Table 1). The addition of various electrophiles (K^+, Na^+, H^+, *etc.*) did not appear to increase polymerization rates.[17,18] Efforts toward understanding the reaction kinetics are in progress.

¶ **1·Et′** does not dissociate to **1·Et** at low concentrations.[17]

|| Complete depolymerization was not observed when **5·Hx/5·Hx′** was heated to 120 °C in DMF-d_4.

** See ESI† for the synthesis and characterization of **6**.

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