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Selective Chain-End Postpolymerization Reactions and Property Tuning of a Highly Conjugated and All-Thiophene Polyazomethine

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ABSTRACT: A highly conjugated polyazomethine (**3**) consisting uniquely of thiophenes was investigated for sustaining postpolymerization property tuning. This was courtesy of the ever-present and reactive amino and aldehyde chain ends. Subjecting the polymer to polymerization conditions in the absence of monomers resulted in a DP_n increase from 15 to 70. The aldehyde chain end was selectively reacted with an aliphatic amine by undergoing reductive amination with sodium triacetoxyborohydride ($NaBH(OAc)_3$) while the imines along the conjugated polymer framework remained intact. This illustrates the robustness of the azomethine bond. Reductive amination of **3** with a monofunctional amine resulted in selective chain-end capping and prevented repolymerization. **3** was resistant to dynamic component exchange and monomer shuffling as a result of its high degree of conjugation. Conversely, chain extension was possible both by reductive amination with an α−ω-diamine and by reheating the polymer. Covalent attachment of two separate segments of **3** was possible by reductive amination with a 2:1 polymer/α−ω-diamine stoichiometry. This resulted in molecular weight doubling and serves to illustrate the possibility of multiblock tethering via the ever-active chain ends. Meanwhile, a 1:1 polymer/α−ω-diamine stoichiometry gave rise to a polymer with an aliphatic and aromatic amine functionalized at either chain end. As a result of the noncomplementary of the two chain ends, the polymer could not be repolymerized. However, it exhibited consistent molecular weight under various repolymerization reaction conditions indicating the robustness of the heteroconjugated bonds and their tolerance toward dynamic component exchange. The color of **3** was also changed from its inherent blue color to green via the covalent attachment of a yellow dansyl derivative by reductive amination at the aldehyde chain end. The collective property modification including repolymerization, coblock tethering, color modification, and increased degree of polymerization presenting unequivocal evidence that polyazomethines are capable of undergoing postpolymerization property tailoring.

Conjugated polymers have gained a wide importance because of their spectroscopic and electrochemical properties that are suited for plastic electronics, such as light-emitting, photovoltaic, and electrochromic devices.[1−3] New materials with expanded properties are nonetheless required to meet the demands of new plastic devices.[4] Such desired spectroscopic and electronic properties are possible by incorporating vinylene linkages.[5] These vinylene connections not only require stringent reaction conditions, but they also produce significant amounts of undesired byproducts that affect the material's optoelectronic properties if they are not removed.[6,7]

Azomethines (−N=CH−) are interesting alternatives to vinylene linkages for polymer preparation in part owing to their isoelectronic character to their carbon counterparts.[8] The synthesis of azomethines is additionally advantageous because water is the only byproduct produced. As a result, little purification is required. Despite the synthetic advantages of azomethine polymers, these have not been pursued as alternate functional materials to their carbon counterparts. This is in part due to the understanding that these heteroatomic materials are hydrolytically, oxidatively, and reductively unstable.[9,10] This is compounded with the limited optoelectronic properties of homoaryl polyazomethines that are unsuited for electronic devices.[10−13]

We recently addressed the challenge of limited azomethine properties by preparing conjugated azomethines derived exclusively from heterocycles (Chart 1).[14−16] These compounds exhibited interesting optoelectronics that are compatible for use in electrochromic devices. Heterocyclic derivatives such as **1**−**3** are further interesting because they are hydrolytically, oxidatively, and reductively resistant.[14−21] The added advantage of polyazomethines is their ever-present terminal functional groups (amine and aldehyde) that should remain active postpolymerization. These potentially could sustain additional coupling reactions postpolymerization affording the means to tailor the polymer properties including mechanical, spectroscopic, solubility, and/or electronic properties. Multiblock tethering could also be possible and beneficial for controlling the morphology, for example, in bulk heterojunctions leading to organic photovoltaics with improved and consistent efficiencies. This is in contrast to their carbon analogues whose properties cannot be readily modified postpolymerization.[2,6,7]

Given that polyazomethines possess two different terminal groups, each can be selectively reacted. Each polymer terminus could therefore be modified separately, resulting in controlled property adjustment. Although polymer property tuning postpolymerization such as molecular weight, color, degree of conjugation, T_g, and repolymerization, to name but a few, are expected with polyazomethines, such property tailoring has not been previously demonstrated. Despite many polyazomethines investigations, terminal modification of conjugated polymers, such as **3**, involving postpolymerization reductive amination has also not been demonstrated.[22−26] This is in part owing to the instability and limited solubility of previously investigated systems.

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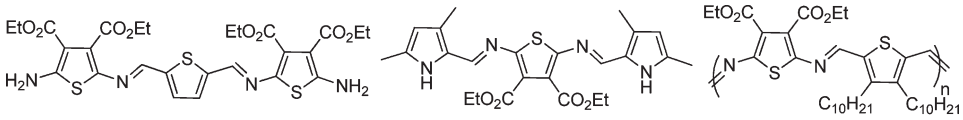
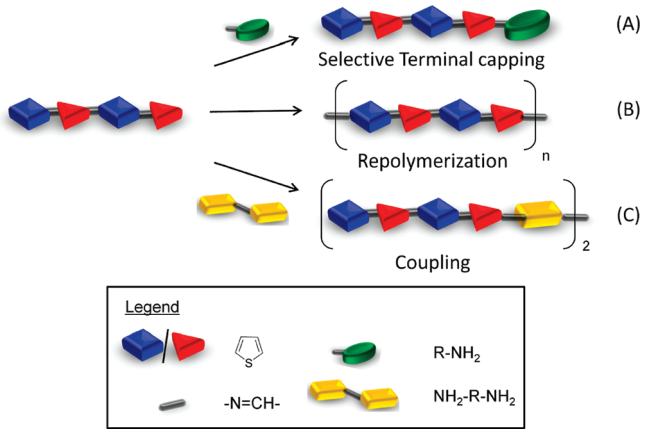
Chart 1



1 **2** **3**

Scheme 1. Selective Reductive Amination Chain-End Capping Preventing Repolymerization (A), Repolymerization (B), and Molecular Weight Doubling by Coupling Complementary Chain Ends with the Addition of an α−ω-Diamine (C) Possible with Conjugated Polyazomethines



While previous efforts examined component shuffling leading exclusively to new polymers,[27−29] no effort has focused on selective chain-end reactions for adjusting various properties while preserving the azomethines in the original polymer. It is also commonly accepted that polyazomethines do not undergo quantitative chain-end functionalizaiton.[30] Although polyazomethine are assumed to undergo these possible reactions, there remains a lack of conclusive evidence to support this. This is particularly the case for selective chain-end reactions. As a result, we were incited to demonstrate postpolymerization property tuning of a conjugated polyazomethine (**3**) without reducing or perturbing its conjugated imine bonds. Property tuning including (i) color modification, (ii) molecular weight tuning, (iii) repolymerization, (iv) selective terminal capping by reductive amination of the terminal aldehyde, and (v) covalent tethering of block copolymers, according to Scheme 1, are herein described. These properties were targeted as proofs-of-concept for demonstrating the persistent reactivity of the terminal functional groups postpolymerization. These properties were additionally targeted for illustrating the robustness of the heteroatomic bonds of **3** and for confirming quantitative chain-end functionalization.

Experimental Section

All materials were obtained from commercial sources and were used as received, unless otherwise stated. Deaerated and anhydrous solvents for reactions and GPC analyses were obtained by passing them over an activated aluminum column system. $CDCl_3$ was purified by passing it over a plug activated neutral aluminum five times immediately prior to use. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer with the appropriate deuterated solvents.

Molecular Weight Measurements. GPC analysis was performed on a commercial system equipped with an autosampler, a binary HPLC pump, and a refractive index detector. Three size exclusion columns (7.8 × 300 mm) were used in series for resolving the different molecular weight. The flow rate of the eluent (THF) was 1 mL/min. The temperature of the columns was 33 °C. A polystyrene kit consisting of 10 molecular weight samples was used for calibrating the molecular weights.

Synthesis Details. 3: Polythiophenoazomethine was synthesized using the TFA-catalyzed Knoevenagel polycondensation as reported earlier and well characterized.[16]

tert-Butyl (3-aminopropyl)carbamate. A solution of di-*tert*-butyldicarbonate (0.5 g, 2.29 mmol, 1 equiv) in THF (20 mL) was added dropwise to a solution of 1,3-diaminopropane (1.91 mL, 22.9 mmol, 10 equiv) in THF. The resulting reaction mixture was stirred at room temperature for 20 h. The product was then extracted in ethyl acetate (EtOAc) and washed with a saturated solution of Na_2CO_3 (2 × 20 mL), dried over $MgSO_4$, and concentrated *in vacuo* to furnish the desired product as a white foam (0.35 g, 89%). ^{1}H NMR ($CDCl_3$): 5.17 (bs, 1H, NH_2), 3.19−3.11 (m, 3H), 2.75 (t, 2H), 1.59 (p, 2H), 1.41 (s, 9H). ^{13}C NMR ($CDCl_3$): 156.6, 79.4, 39.5, 38.5, 32.0, 28.8. MS: $[M + H]^+$: 175.3.

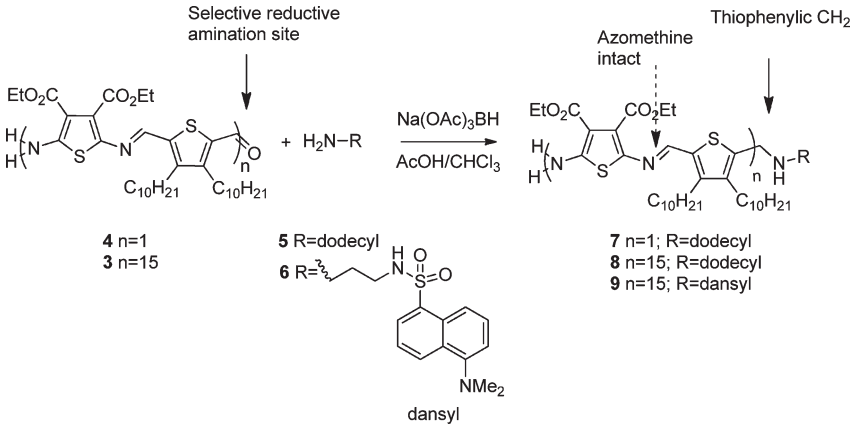
tert-Butyl (3-(5-(dimethylamino)naphthalene-1-sulfonamido)-propyl)carbamate. To a solution of dansyl chloride (200 mg, 0.741 mmol, 1 equiv) in anhydrous THF (15 mL) was added a solution of amine 3-*tert*-butoxycarbonyl 1-aminopropane (172 mg, 0.975 mmol, 1.3 equiv) and Et_3N (0.42 mL, 3.00 mmol, 2 equiv) in THF (10 mL) under a nitrogen atmosphere. After stirring at room temperature for 12 h the product was extracted in ethyl acetate (EtOAc), and the organic layer was washed with a saturated solution of $NaHCO_3$ (3 × 40 mL), dried over $MgSO_4$, and concentrated *in vacuo* to yield quantitatively the title compound as green foam. ^{1}H NMR ($CDCl_3$): 8.52 (d, 1H), 8.24 (d, 1H), 8.22 (d, 1H), 7.49 (m, 2H), 7.18 (d, 1H), 5.82 (bs, 1H, NH), 4.62 (bs, 1H, NH), 3.11 (t, 2H), 2.94 (m, 2H), 2.89 (s, 6H), 1.4 (p, 2H), 1.35 (s, 9H). ^{13}C NMR ($CDCl_3$): 157.1, 152.2, 135.7, 130.6, 130.2, 129.9, 129.6, 128.7, 123.5, 118.4, 115.6, 79.9, 53.8, 45.8, 40.3, 37.2, 30.8, 28.6. MS: $[M + H]^+$: 408.2.

5-((3-Aminopropyl)sulfonyl)-N,N-dimethylnaphthalen-1-amine (**6**). Under a nitrogen atmosphere at room temperature were combined amide *N*-[3-*tert*-butoxycarbonylamino]-1-dimethylamino-5-naphthalene-sulfonamide propane (100 mg, 0.24 mmol, 1 equiv) and trifluoroacetic acid (8 mL). The reaction mixture was stirred for 2.5 h, concentrated *in vacuo*, triturated with Et_2O (20 mL), filtered, and dried to afford **6** quantitatively as its trifluoroacetate salt (30 mg). ^{1}H NMR (CD_3OD): 8.72 (d, 2H), 8.55 (d, 1H), 8.32 (dd, 1H), 7.77 (m, 3H), 5.19 (s, 1H), 2.99 (s, 6H), 2.05 (m, 4H), 1.70 (p, 2H). ^{13}C NMR (CD_3OD): 143.9, 136.8, 129.8, 129.6, 127.8, 127.2, 125.7, 124.6, 118.2, 114.8, 65.9 (O−**C**H_2 from Et_2O), 46.0, 39.8, 37.2, 28.0, 14.4 (O−CH_2−**C**H_3, Et_2O) MS: $[M + H]^+$: 308.18.

General Reductive Amination Procedure (*Scheme 2*). To a solution polythiophenoazomethine (**3** and **4**) (1.0 mmol), 1-aminododecane or **6** (2.0 mmol), and $CHCl_3$ (2 mL) was added glacial acetic acid (one drop). The reaction was heated to 40 °C for 1 h. The reaction was cooled to room temperature, and sodium triacetoxyborohydride (3.0 mmol) was added. The reaction mixture was allowed to stir at room temperature for 18 h. The stock solution was taken up and precipitated from a acetone/water mixture. The precipitates were filtered and washed with water (3 times), methanol (2 times), and acetone (2 times) and dried to give the coupled products **7**−**9**.

7: ^{1}H NMR ($CDCl_3$): 8.09 (s, 1*H*, −C=N), 6.12 (1H, −NH), 4.40 (q, 2H, −O−CH_2−), 4.25 (q, 2H, −O−CH_2−), 3.76 (s, 2H, −CH_2−NH−), 3.63 (t, 2H, −NH−CH_2−), 2.67 (p, 4H),

Scheme 2. Selective Reductive Amination of the Aldehyde Chain End of Conjugated Thiophenoazomethines



2.47 (t, 4H), 1.43 (m, 6H), 1.30 (t, 6H), 1.28 (m, 40H), 0.88 (t, 9H, $-CH_3$). ^{13}C NMR ($CDCl_3$): 165.5, 164.8, 159.3, 146.9, 144.8, 140.5, 135.0, 130.0, 103.8, 61.9, 60.7, 32.3, 32.1, 30.0, 29.7, 27.1, 23.1, 14.89, 14.80, 14.6. ESI-MS: 830.5 (M + H).

8: ^1H NMR ($CDCl_3$): 8.51 (m, 1*H*, −C═N), 4.42 (m, 6H), 3.51 (m, 2H, $-CH_2-NH-$), 2.77 (m, 6H), 2.0 (m, 6H), 1.28 (m, 40H), 0.88 (m, 9H).

9: ^1H NMR ($CDCl_3$): 8.37 (m, 1H), 8.0 (bs, 1H), 7.56 (bs, 1H), 7.45 (bs, 1H), 7.33 (bs, 1H), 7.0 (bs, 1H), 4.42 (bs, 4H), 4.26 (bs, 2H), 4.11 (bs, 4H), 3.58 (m, 2H, $-CH_2-NH-$), 2.82 (m, 8H), 1.93 (m, 8H), 1.27 (m, 40H), 0.88 (m, 9H).

*Coblock Tethering with **10** (Scheme 3)*. To a solution of **3** (3.5 mg, 0.42 mmol), 1,10-diaminodecane (3.6 mg, 0.21 mmol), and $CHCl_3$ (2 mL) was added glacial acetic acid (one drop). The reaction was heated to 40 °C for 1 h. The reaction was cooled to room temperature, and sodium triacetoxyborohydride (3.0 mmol) was added. The reaction mixture was allowed to stir at room temperature for 18 h. The reductive aminated product was precipitated form an acetone/water mixture. The precipitates were washed with water (2 times), methanol (2 times), and acetone (2 times) and then dried. ^1H NMR ($CDCl_3$): 8.37 (m, 1*H*, −C═N), 4.26 (m, 6H), 3.67 (m, 1H, $-CH_2-NH-$), 2.78 (m, 6H), 1.28 (m, 40H), 0.88 (m, 9H).

*Repolymerization of **3***. To a solution of **3** (2.0 mg, 0.32 mmol) and $CHCl_3$ (2 mL) was added glacial acetic acid (diluted in $CHCl_3$). The reaction was heated to 40 °C for 1 h. The reaction was cooled to room temperature, and sodium triacetoxyborohydride (3.0 mmol) was added. The reaction mixture was allowed to stir at 50 °C for 66 h. The reductive aminated polymer was precipitated from a methanol/water mixture. The precipitate was filtered and washed with water (3 times), methanol (2 times), and acetone (2 times) and then dried. ^1H NMR ($CDCl_3$): 10.12 (m, 1H, CHO), 8.37 (m, 1*H*, −C═N), 4.44 (m, 6H), 3.76 (m, 1H, $-CH_2-NH$), 2.74 (m, 6H), 1.27 (m, 40H), 0.86 (m, 9H).

Results and Discussion

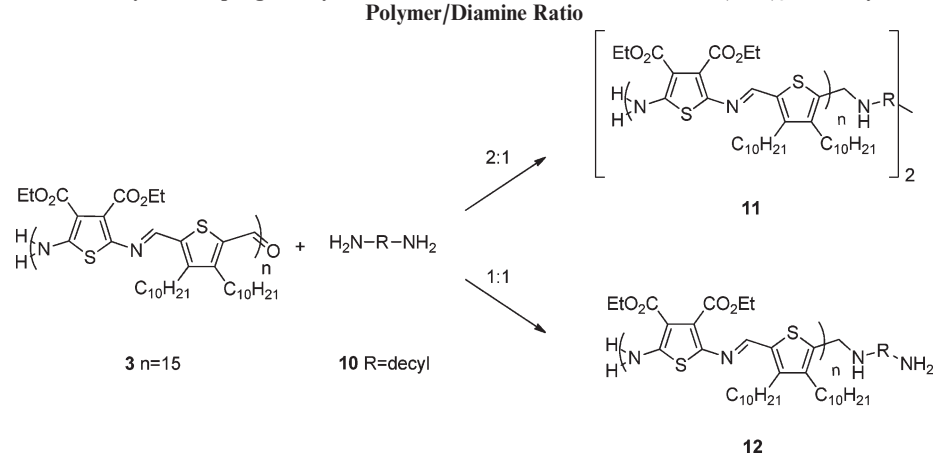
The postpolymerization property tuning was investigated with **3** because of its intense blue color as a result of its high degree of conjugation. The color therefore serves as an inherent indicator for visually detecting undesired destruction of the polymer's degree of conjugation that may occur by chemical reduction of the imine bonds, decomposition, hydrolysis, or component shuffling, known to occur with unconjugated imines and their acylhydrazone counterparts.[31,32] Although any of these undesired reactions is possible with the reaction conditions employed, the polyazomethine investigated was not expected to be either reduced or susceptible to hydrolysis owing to its high degree of conjugation (E_g^{spec} = 1.5 eV and E_{pa} = 0.75 V[16]). The added advantage of **3** is that the aromatic region of the ^1H NMR spectrum consists uniquely of imine and aldehyde protons. The clean aromatic region allows easy monitoring of these two groups for any imine decomposition, molecular weight changes, and successful reduction amination (vide infra).

Selective chain-end reaction of the terminal aldehyde was done to demonstrate that the terminal group remains active postpolymerization and that quantitative chain-end functionalization is possible. Demonstrating these properties is of importance given that polyazomethines are understood to be unstable and, as such, should not sustain these reactions. Furthermore, postpolymerization selective chain-end modification and selective reductive amination of polyazomethines have never been demonstrated. Reductive amination was done with sodium triacetoxyborohydride. This mild reducing reagent was chosen because it was expected to promote exclusive and selective reductive amination between the terminal aldehyde of **3** and an aliphatic amine such as **5**. This reducing agent was further anticipated not to reduce the conjugated imines along the polymer backbone, hence preserving the polymer's inherent high degree of conjugation. The reductive amination products would not only confirm that the aldehyde remains active postpolymerization and is capable of sustaining subsequent reactions, but they also would confirm that the polymer terminal aldehyde can be capped and undergoes chain-end postpolymerization, depicted in Schemes 1−3.

The reductive amination of the dyad **4** was first examined because complete and absolute characterization of the products by standard means (^1H NMR and MS) could be done, unlike its polymer counterpart. **4** was additionally chosen as a model for **3** owing to its similar polymer repeat unit. More importantly, it has a reduced degree of conjugation relative to **3** and would confirm whether $NaBH(OAc)_3$[33] undergoes exclusive chain-end reductive amination without reducing the imines along the conjugated framework. Meanwhile, the amine was selected because it could be accurately weighed and easily handled.

Sodium triacetoxyborohydride (3 equiv) was combined with **4** and dodecylamine in chloroform and reacted at room temperature for 18 h. The resulting ^1H NMR spectrum is found in Figure 1. One could argue that the disappearance of the aldehyde peak at ca. 10 ppm (Figure 1B) could be due to reduction to the corresponding alcohol with $NaBH(OAc)_3$ and not from reductive amination. We verified that this was not the case by reacting **4** with the reductant under the same reductive amination conditions, but in the absence of **5**. No noticeable change in the NMR spectra from that of Figure 1A was observed, confirming no reduction of the chain-end aldehydes with the reducing agent. Further evidence for selective amination without aldehyde reduction is had from Figure 1B. The singlet observed at 3.6 ppm is from the thiophene−$\mathbf{CH_2}$−NH− (thiophenylic, Scheme 2) and not a thiophene−$\mathbf{CH_2}$−OH proton. Meanwhile, the peak at 6.1 ppm is ascribed to the secondary amine proton, confirmed by its disappearance with the addition of D_2O (Figure 1C).

Scheme 3. Reaction Schemes of Polymer Coupling of 3 by Selective Reductive Amination with $NaBH(OAc)_3$ and Decyldiamine (10) as a Function of Polymer/Diamine Ratio



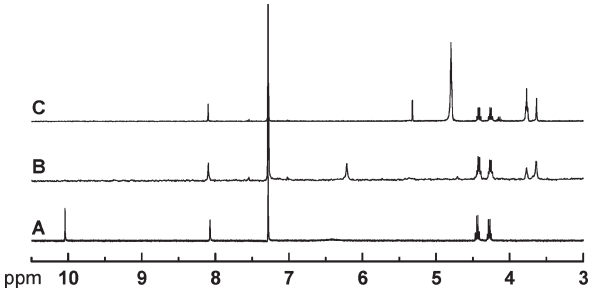


Figure 1. ^{1}H NMR of **4**: (A) crude **7** after selective reductive amination (B) and with the addition of D_2O (C). Peak at 7.28 ppm = solvent $CDCl_3$ and 5.3 ppm = residual CH_2Cl_2.

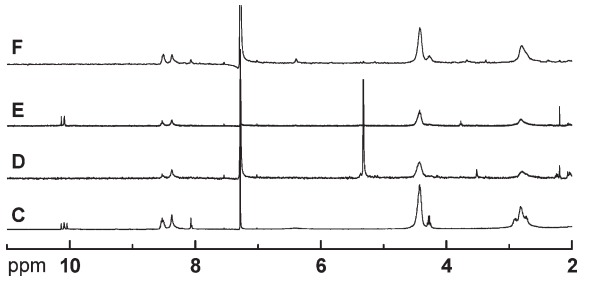


Figure 2. ^{1}H NMR spectra of **3** (C), **8** (D), **3** repolymerized (M_n = 21 900 g/mol) (E), and **11** (F). Peak at 7.28 ppm = solvent $CDCl_3$ and 5.3 ppm = residual CH_2Cl_2.

Further evidence for the desired reductive amination is had with the $-NH-\mathbf{CH_2}$ aliphatic triplet at 3.8 ppm. It should be noted that the imine peak at ca. 8 ppm persists after reductive amination (Figure 1B,C). The crude NMR spectrum therefore confirms that the reductive amination proceeds smoothly without secondary reactions. It is noteworthy that the imine resisted standard reductive amination protocols with $NaBH_4$. Moreover, no decomposition or exchange[34] products were observed by NMR while the absence of the aldehyde peak in Figure 1B confirms quantitative reductive amination of the terminal aldehyde. Additional confirmation for the desired reductive amination is had from both the ^{13}C NMR and mass spectrometry data (Supporting Information) and with a decyl derivative of **7** (see Supporting Information). The collective ^{1}H NMR, ^{13}C NMR, and MS data confirm the exclusive reductive amination product **7** is formed without reduction of the imine bond. The successful reductive amination of the model dyad **4** provides evidence that the selective chain-end reactions with the conjugated polymer **3** are expected without destroying the polymer's degree of conjugation, while the persistent imine peaks demonstrate the reductive robustness of the conjugated polymer.

The absence of aldehyde reduction to the corresponding alcohol with the polymer model compound **4** with sodium triacetoxyborohydride confirms that ^{1}H NMR is a viable method for verifying selective and quantitative chain-end reductive amination of the polymer **3**. Dodecylamine was subsequently used to selectively cap the aldehyde chain end of **3** for affording **8**. Similar to **4**, reductive amination of **3** and dodecylamine with $NaBH(OAc)_3$ occurred. This is evidenced by the disappearance of the aldehyde peaks in the 10 ppm region as seen in Figure 2D. The multiple aldehydes in Figure 2C imply that **3** is polydisperse, expected with step-growth polymerization. Reductive amination is additionally confirmed by the thiophenylic protons (Scheme 2) at ca. 3.8 ppm, whose chemical shifts are consistent with a neighboring amine. Most importantly, the imine peaks remain, confirming selective reduction exclusively at the chain end without reduction of the conjugated imines. This is further supported by the persistent blue color of the polymer, while no polymer decomposition was observed by NMR and GPC. The collective data of **3** and **4** provide sound evidence that the terminal aldehyde remains active postpolymerization and undergoes quantitative and selective chain-end reductive amination. Moreover, they confirm that reduction to the thiophenylic alcohol does not occur under these conditions, and they further demonstrate the robustness of the conjugated imine toward reduction with sodium triacetoxyborohydride.

The dodecyl-terminated polymer **8** was subjected to polymerization conditions (increased concentration, reaction time, and heating) used for preparing **3**. This was done for investigating whether the azomethine linkages could tolerate these repolymerization conditions. The average number molecular weight (M_n) measured both by NMR and GPC for **8** with the various repolymerization conditions (Figure 3) did not differ from the pristine **3**. The invariable M_n confirms that the dodecylamine caps the aldehyde chain end and prevents its repolymerization according to Scheme 1A. It provides further evidence that constitutional component exchange does not occur, unlike previously reported azomethines.[27,35] This is in contrast to polyhydrazines and unconjugated azomethines that undergo component exchange or polymer decomposition with similar reaction conditions resulting in variable molecular weight and decrease in degree of conjugation.[35−37]

Knowing that the azomethine bonds of **8** are robust and can tolerate the polymerization conditions, any molecular weight changes observed when repolymerizing **3** are therefore from chain extension and not from component shuffling or any other

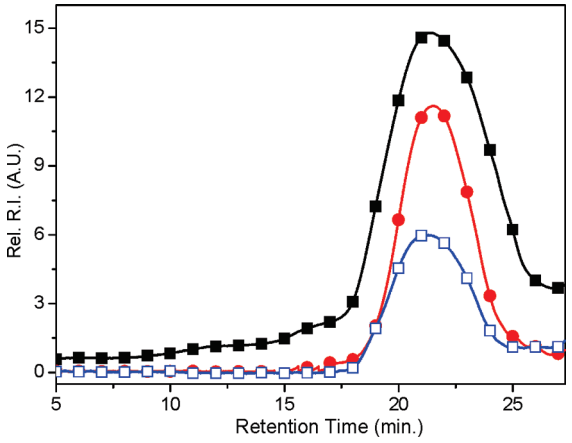


Figure 3. GPC analyses of pristine **8** (■) and after 18 (●) and 66 h (□) of reaction at temperature of 50 °C and concentration of 1 mg/mL in $CHCl_3$. The GPC signals are separated only for esthetic purposes.

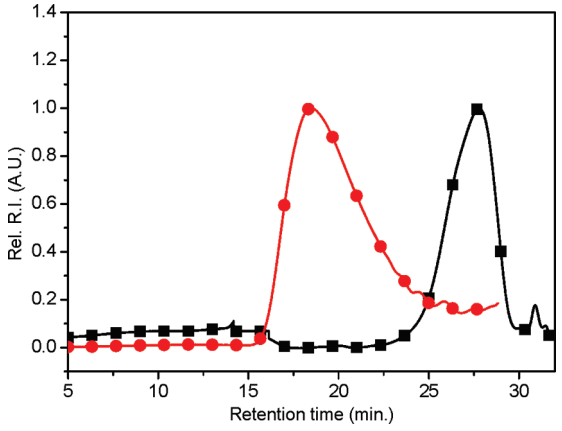


Figure 4. GPC of **3** (■) and after 66 h of repolymerization at 50 °C (●).

process. The free chain end **3** was therefore subjected to the same postpolymerization conditions as **8** above. Under similar conditions and in the absence of added monomers, the M_n of **3** increased from 9900 to 46 500 g/mol after 66 h (Figure 4). Such chain extension is possible only by autocondensation of the complementary terminal groups. The increased M_n also provides conclusive evidence that the terminal amine also remains reactive, similar to its complementary chain-end aldehyde. It additionally confirms that chain extension is possible postpolymerization, resulting in increased degree of polymerization (DP_n). For this preliminary repolymerization, the observed DP_n increase from 15 to 70 with repolymerization. The DP_n and extent of conjugation of polyazomethines can easily be adjusted postpolymerization, in contrast to its vinylene counterparts. Intuitively, repolymerization and selective chain-end reactions are expected with polyazomethines. However, this has not unequivocally been demonstrated because of the limited solubility and hydrolytic instability of previously investigated polyazomethines. The postpolymerization property tuning possible with **3** confirms that the termini remain active. It should be noted that the amino chain end is less reactive than its complementary aldehyde owing to the adjacent deactivating ester. As a result, it requires different reductive amination protocols. Reductive amination optimization of the terminal amine is currently being pursued and is outside the scope of this work. Nonetheless, this represents the first example of selective reductive amination of azomethines without destruction of the conjugated imine moiety.

Molecular weight modification postpolymerization was further examined using the diamine **10** (Scheme 3). Unlike dodecylamine

Table 1. Molecular Weight Increase with Covalent Coupling of 3 and 10 in a 2:1 Ratio at 25 °C by Reductive Amination at Different Time Intervals

reaction time (h)	M_n (g/mol)[a]	M_w (g/mol)[a]	PDI
0	8 300	13 100	1.6
6	9 700	13 700	1.4
18	11 700	22 400	1.9
66[b]	21 300	36 400	1.7

[a] Determined by GPC. [b] No molecular weight increase was observed for reaction times longer than 66 h.

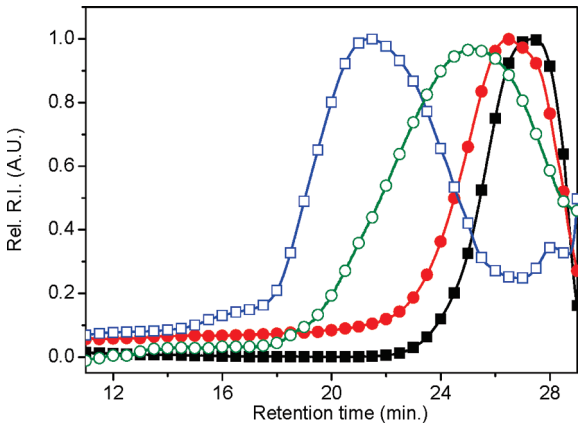


Figure 5. GPC chromatogram of room temperature reductive amination of a 2:1 ratio of **3** with **10** at different coupling times: 0 (■), 6 (●), 18 (○), and 66 h (□).

that prevents repolymerization by capping the aldehyde chain end, reductive amination of **3** with **10** yields two primary terminal amines. These can be selectively reacted leading to product tailoring as a function of stoichiometry. A 2:1 polymer/diamine ratio would result in molecular weight doubling. Conversely, no molecular weight change is expected with a 1:1 ratio given that the resulting polymer **12** would possess two terminal amines. These would have different reactivities (aryl vs aliphatic) that can be exploited for selective chain-end reaction for the covalent tethering of different block copolymers covalently together. A 2:1 ratio of **3**/**10** gave a polymer whose M_n evolved from 8300 g/mol to a maximum of 21 000 g/mol (Table 1 and Figure 5). The molecular weight increase is consistent with tethering two chains of **3** together.[38] Conversely, no M_n increase was observed for a 1:1 ratio regardless of concentration and reaction time. This is a result of two noncomplementary terminal amines being produced from the coupling of **3** with **10**. The invariable molecular weight observed with the different reaction conditions confirms that both the complementary terminal amine and aldehyde groups are required for molecular weight increase and, once again, that dynamic component exchange does not occur. Meanwhile, the increased M_n for the 2:1 ratio corroborates not only that the molecular weight can be tuned postpolymerization but also that the polyazomethine terminal groups remain active and are capable of sustaining additional coupling reactions as illustrated in Scheme 1. Given that **11** is a diblock copolymer prepared by reductively coupling two blocks of **3** bridged together by **10**, its successful formation serves as a proof-of-concept that multiblock copolymers can easily be prepared from polyazomethines.

The ever-present and reactive chain-end aldehyde was further investigated for property tailoring by changing the polymer's color via selective covalent attachment of **6** to **3**. Dansyl was chosen because it is a colored dye that can be easily modified to yield an aliphatic amine (**6**), for reductive amination with **3**. The added advantage of dansyl is that it has a comparable molar extinction coefficient to **3** while possessing a complementary

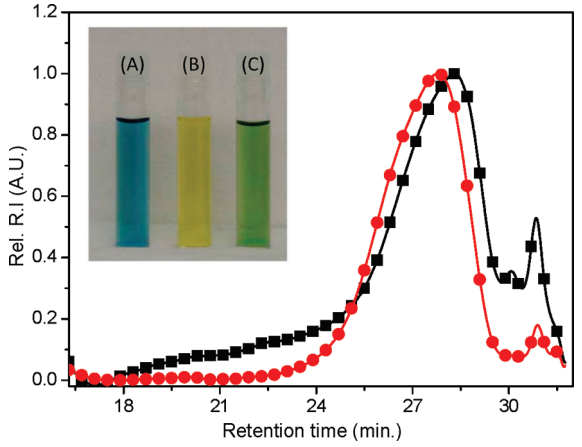


Figure 6. GPC chromatogram of **3** (●) and **9** (■). Inset: polymer color of postpolymerization covalent attachment of **6** to **3**: **3** (A), **6** (B), and **9** (C).

color to the polyazomethine. Combining both **3** and **6** not only would result in covalent attachment of the dye to the polymer similar to that described above, but the resulting polymer **9** would be colored significantly different than **3**, owing to their color complementarity. Successful color change would confirm that postpolymerization property tailoring is possible while providing additional evidence for the robustness of the azomethine bonds for sustaining reductive amination and the persistent reactivity of the chain ends.

Reductive amination was done with stoichiometric amounts of **3** and **6** with $NaBH(OAc)_3$, similar to above The resulting polymer was washed repeatedly to ensure that no **6** was adsorbed to the polymer and that any color change was uniquely from the covalent attachment of **6** to **3**. According to the NMR (see Supporting Information) and GPC data (Figure 6), **6** was quantitatively bound to **3** via clean reductive amination. Meanwhile, the M_n of the resulting polymer **9** did not differ from **3**. As seen in the inset of Figure 6 and Figure S1, **3** and **6** are inherently blue and yellow, respectively, while the reductively coupled **9** is green. The stark visible color change between **3** and **9** confirms that polyazomethine chain ends remain reactive and that their properties can be tailored postpolymerization. Although it was demonstrated that the polymer's spectroscopic properties can be modulated postpolymerization, property tuning is not limited to color. The variable color nonetheless demonstrates the unprecedented property modification that is possible with chain-end reactions.

Conclusion

In summary, we successfully demonstrated the first examples of postpolymerization property modification of a conjugated polyazomethine via both selective reductive amination and condensation leading to chain extension. Both the molecular weight and color of a highly conjugated polymer could be modified postpolymerization by exclusive reductive amination of the terminal aldehyde without reducing the conjugated imines along the polymer framework. Meanwhile, the consistently reactive chain ends can be further reacted by simple condensation leading to chain extension and, hence, increased degree of polymerization. Color modification and M_n tuning in addition to end-capping, chain extension, and covalent copolymer block tethering were demonstrated and serve as proofs-of-concept that virtually any polyazomethine property can be modified postpolymerization. These postpolymerization modifications imply the possibility of tailoring any property by chain-end reactions while preserving the conjugated imines along the polymer backbone. In particular, otherwise nonfluorescent polyazomethines could be made fluorescent with chain-end appended fluorescent enhancers. Nonetheless, postpolymerization chain-end reactions open the possibility of multiblock polymerization and polymer block tethering for controlled molecular weight in addition to other property tuning including mechanical, optoelectronic properties, and morphology postpolymerization, unlike their conjugated vinylene counterparts. Such property tuning provides the means of obtaining functional materials with targeted properties for desired applications, potentially leading to improved properties over their static counterparts.

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Supporting Information Available: ^1H and ^{13}C NMR spectra and MS of compounds, GPC of polymers, and absorbance spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Saxena, V.; Malhotra, B. D. *Curr. Appl. Phys.* **2003**, *3*, 293–305.
(2) Grimsdale, A. C.; Leok Chan, K.; Martin, R. E.; Jokisz, P. G.; Holmes, A. B. *Chem. Rev.* **2009**, *109*, 897–1091.
(3) Lee, K.; Nair, P. R.; Scott, A.; Alam, M. A.; Janes, D. B. *J. Appl. Phys.* **2009**, *105*, 102046–13.
(4) Deng, X.; Wong, K. Y. *Macromol. Rapid Commun.* **2009**, *30*, 1570–1576.
(5) Mei, J.; Heston, N. C.; Vasilyeva, S. V.; Reynolds, J. R. *Macromolecules* **2009**, *42*, 1482–1487.
(6) Yu, N.; Zhu, R.; Peng, B.; Huang, W.; Wei, W. *J. Appl. Polym. Sci.* **2008**, *108*, 2438–2445.
(7) Morin, J.-F.; Drolet, N.; Tao, Y.; Leclerc, M. *Chem. Mater.* **2004**, *16*, 4619–4626.
(8) Yang, C.-J.; Jenekhe, S. A. *Chem. Mater.* **1991**, *3*, 878–887.
(9) Sek, D.; Iwan, A.; Kaczmarczyk, B.; Jarzabek, B.; Kasperczyk, J.; Bednarski, H. *High Perform. Polym.* **2007**, *19*, 401–426.
(10) Amari, C.; Pelizzi, C.; Predieri, G.; Destri, S.; Porzio, W. *Synth. Met.* **1995**, *72*, 7–12.
(11) El-Shekeil, A. G.; Al-Yusufy, F. A.; Saknidy, S. *Polym. Int.* **1997**, *42*, 39–44.
(12) El-Shekeil, A. G.; Al-Yusufy, F. A.; Saknidy, S. *Polym. Int.* **1997**, *53*, 777–788.
(13) Weaver, M. S.; Bradley, D. D. C. *Synth. Met.* **1996**, *83*, 61–66.
(14) Dufresne, S.; Bolduc, A.; Skene, W. G. *J. Mater. Chem.* **2010**, *20*, 4861–4866.
(15) Bolduc, A.; Dufresne, S.; Skene, W. G. *J. Mater. Chem.* **2010**, *20*, 4820–4826.
(16) Bourgeaux, M.; Skene, W. G. *Macromolecules* **2007**, *40*, 1792–1795.
(17) Dufresne, S.; Skene, W. G. *J. Org. Chem.* **2008**, *73*, 3859–3866.
(18) Pérez Guarìn, S. A.; Dufresne, S.; Tsang, D.; Sylla, A.; Skene, W. G. *J. Mater. Chem.* **2007**, *17*, 2801–2811.
(19) Pérez Guarìn, S. A.; Bourgeaux, M.; Dufresne, S.; Skene, W. G. *J. Org. Chem.* **2007**, *72*, 2631–2643.
(20) Bourgeaux, M.; Skene, W. G. *J. Org. Chem.* **2007**, *72*, 8882–8892.
(21) Bourgeaux, M.; Perez Guarin, S. A.; Skene, W. G. *J. Mater. Chem.* **2007**, *17*, 972–979.
(22) Sek, D.; Iwan, A.; Kaczmarczyk, B.; Jarzabek, B. *Mol. Cryst. Liq. Cryst.* **2007**, *468*, 119–129.
(23) Tsai, F.-C.; Chang, C.-C.; Liu, C.-L.; Chen, W.-C.; Jenekhe, S. A. *Macromolecules* **2005**, *38*, 1958–1966.
(24) Chang, C.-P.; Wang, C.-C.; Chao, C.-Y.; Lin, M.-S. *J. Polym. Res.* **2005**, *12*, 1–7.
(25) Destri, S.; Pasini, M.; Pelizzi, C.; Porzio, W.; Predieri, G.; Vignali, C. *Macromolecules* **1998**, *32*, 353–360.
(26) Yang, C.-J.; Jenekhe, S. A. *Macromolecules* **1995**, *28*, 1180–1196.

(27) Jackson, A. W.; Fulton, D. A. *Macromolecules* **2010**, *43*, 1069–1075.
(28) Ono, T.; Nobori, S. F. T.; Lehn, J.-M. *Chem. Commun.* **2007**, 46–48.
(29) Ono, T.; Fujii, S.; Nobori, T.; Lehn, J.-M. *Chem. Commun.* **2007**, 4360–4362.
(30) Miyake, J.; Tsuji, Y.; Nagai, A.; Chujo, Y. *Macromolecules* **2009**, *42*, 3463–3468.
(31) Deng, G.; Tang, C.; Li, F.; Jiang, H.; Chen, Y. *Macromolecules* **2010**, *43*, 1191–1194.
(32) Ruff, Y.; Buhler, E.; Candau, S.-J.; Kesselman, E.; Talmon, Y.; Lehn, J.-M. *J. Am. Chem. Soc.* **2010**, *132*, 2573−2584.
(33) Abdel-Magid, A. F.; Carson, K. G.; Harris, B. D.; Maryanoff, C. A.; Shah, R. D. *J. Org. Chem.* **1996**, *61*, 3849–3862.
(34) Skene, W. G.; Lehn, J.-M. P. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 8270–8275.
(35) Folmer-Andersen, J. F.; Lehn, J.-M. *Angew. Chem., Int. Ed.* **2009**, *48*, 7664–7667.
(36) Ruff, Y.; Lehn, J.-M. *Angew. Chem., Int. Ed.* **2008**, *47*, 3556–3559.
(37) Nasr, G.; Barboiu, M.; Ono, T.; Fujii, S.; Lehn, J.-M. *J. Membr. Sci.* **2008**, *321*, 8–14.
(38) Exact molecular weight doubling is not expected owing to experimental errors and molecular weight variances typical of relative GPC measurements.