Impact of Pendant Substituents on Post-Polymerization Functionalization and Electronic Properties in Stereoregular Non-Conjugated Pendant Electroactive Polymers

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Abstract

Recent reports on non-conjugated pendant electroactive polymers (NCPEPs) have demonstrated the significance of altering structural variables specifically the stereoregularity, the nature of the pendant group and the length of the spacer connecting that group to the backbone for tuning of their optoelectronic properties. The only synthetic approach that allows for selectively studying the effects of tuning these variables without additional superimposed effects of varied molecular weights and tacticities is the post-polymerization functionalization methodology in which parent polymers are synthesized first and then functionalized with the respective pendant groups and spacers. However, specifically for tuning of the pendant group itself, the scope of such post-polymerization functionalization methods remains largely underexplored. Here, the compatibility of the established photochemical thiol-ene post-polymerization method with various pendant groups is investigated for functionalization of stereoregular and stereorandom poly(allyl methacrylates) made via anionic polymerization using an organolithium initiator. Carbazole and a family of four 3,6-disubstituted carbazoles with phenyl, methoxy, nitrile and *t*-butyl substituents were investigated as the respective pendant groups. With the phenyl, methoxy and nitrile substituted pendant groups limitations of the scope of the thiol-ene methodology due to limited solubility and vulnerability to photochemical side reactions could be demonstrated. In contrast, *t*-butyl substituents did not impede the post-polymerization functionalization. The corresponding functionalized NCPEPs

were characterized and effects of substitution of the carbazole pendant group with *t*-butyl groups on the optoelectronic properties of the polymers are discussed. Overall, this work demonstrates critical limitations of the thiol-ene functionalization method as well as their origin when applied to differently substituted pendant groups.

1. Introduction

Motivated by the unique advantages associated with organic electronic devices such as organic light emitting diodes (OLEDs), organic photovoltaics (OPVs) and organic field effect transistors (OFETs) compared to their inorganic counterparts including lighter weights, lower costs, flexibility and the prospect of convenient roll-to-roll processing, conjugated polymers (CPs) gained considerable attention over the last decades.[1-6] However, despite impressive progress in the field of CPs that has enabled record breaking device performances, there are still a number of critical limitations associated with CPs. Molecular weights are significantly lower compared to non-conjugated polymers, environmental and mechanical stability are very limited and there are only a few polymerization methodologies available which generally do not allow for the synthesis of advanced architectures such as block-copolymers.[4,7,8]

In response to these challenges, the novel class of non-conjugated pendant electroactive polymers (NCPEPs) is receiving increasing interest as an alternative to CPs with the potential to overcome these limitations without compromising the advantageous properties associated with CPs. NCPEPs are polymers based on fully non-conjugated backbones with electroactive pendant groups attached to their side chains. While CPs generally outperform most NCPEPs reported to date in terms of charge-carrier mobility by orders of magnitude, recent work in our group demonstrated that through careful optimization of structural variables such as stereoregularity of the backbone and length of the spacer between the backbone and the pendant group, hole mobilities can be significantly improved and even outperform the well-known CP poly(3-hexylthiophene) (P3HT).[9-11]

To allow for improved rational design of high performance NCPEPs with enhanced charge carrier mobilities, exploring the scope of available strategies for the synthesis of this emerging class of materials and developing a better understanding of their fundamental structure-property relationships is imperative. Amongst the available synthetic methods, those utilizing the post-polymerization approach in which the non-conjugated polymer backbone is synthesized first followed by functionalization of that parent polymer with the respective electroactive pendant groups are particularly suited for establishing these fundamental relationships. The post-polymerization functionalization approach does not only exhibit a higher tolerance towards various polymerization methods since compatibility of the electroactive group with the reaction conditions does not have to be considered, it is also the only approach that allows for investigating the effects of varying structural variables such as the pendant group or the spacer connecting the pendant group to the backbone on the properties of the respective polymers without having to consider superimposed effects of varied molecular weights and tacticities in between the differently functionalized NCPEPs that would be the results of individual polymerization of each of the already fully functionalized monomers.

The importance of the pendant group as a key structural variable was recently demonstrated by reports on the effects of changing the position of substituents on the pendant group to afford structural isomers, extending the size of the pendant moiety and even introducing electron-donating and withdrawing substituents onto the pendant group, on the optoelectronic properties of atactic NCPEPs.[12-15] Systematic investigations of pendant group effects in stereoregular NCPEPs however remain largely underexplored despite the significance of stereocontrol for most notably the electronic properties of NCPEPs which was demonstrated by our group through significantly increased hole mobilities for isotactic poly((*N*-carbazolylethylthio)propyl methacrylate) (PCzETPMA) over its atactic analogue.[11] Therefore, there is considerable interest in selectively studying pendant group effects in stereoregular NCPEPs which

consequently requires investigating the compatibility of post-polymerization functionalization methodologies with such pendant groups.

In this study we investigate the scope of the post-polymerization functionalization method based on photochemical thiol-ene click chemistry that was successfully established by our group for the synthesis of stereoregular NCPEP homopolymers and block-copolymers.[11,16] Based on these previously reported NCPEPs which were exclusively functionalized with carbazole groups, we decided to synthesize four substituted carbazole derivatives, specifically 3,6-disubstituted carbazolyl-ethanethiols, with alkyl (*t*-butyl), aryl (phenyl), electron donating (methoxy) and electron withdrawing (nitrile) substituents for functionalization of poly(allyl methacrylate) (PAMA) parent polymers (Figure 1).[11,16] We selected these substituents so that the scope of the thiol-ene functionalization method across varied electron density of the pendant group, extension of this conjugated system and introduction of sterically demanding substituents could be studied.

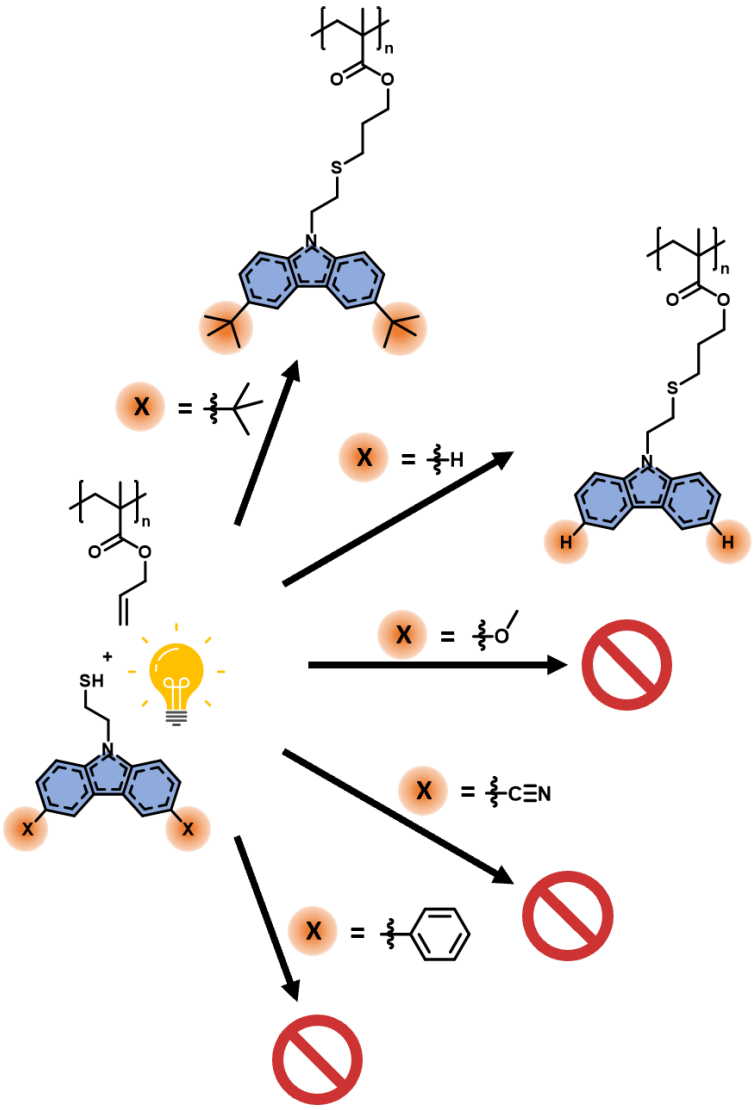


Figure 1. Compatibility of the photochemical thiol-ene post-polymerization functionalization method for functionalization of PAMA with various 3,6-disubstituted carbazole pendant groups.

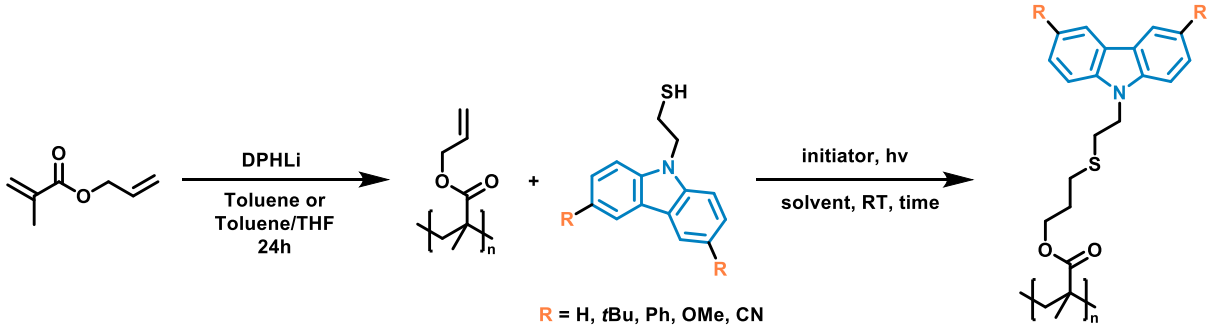
For the family of 3,6-disubtituted carbazoles as the pendant groups in this study, it was found that the thiol-ene methodology is only compatible with the carbazole bearing the alkyl-substituent (*t*-butyl). The attempted functionalizations with the remaining disubstituted carbazolyl-ethanethiols are presented and the observed limitations of the thiol-ene reactions in these cases are discussed. To study the effects of the successful introduction of *t*-butyl into the carbazole pendant group on the optoelectronic properties of the NCPEPs, both an isotactic and an atactic PCzETPMA were synthesized and compared to their analogues that were functionalized with unsubstituted carbazole.

2. Results and Discussion

As illustrated in Scheme 1, the PAMA parent polymers were synthesized via anionic polymerization using DPHLi as the initiator. For the synthesis of isotactic PAMA we followed our established procedure for anionic polymerizations in toluene at low temperatures which was demonstrated to afford highly stereoregular PAMAs and yielded 81% triad isotactic PAMA with a molecular weight of 49.74 kg/mol and a dispersity of 1.73.[11] For the synthesis of the atactic parent polymer we switched to a toluene/THF cosolvent system based on a report by Brownstein et al. showing that addition of as little as 2.5 vol.-% THF to the reaction mixture leads to stereorandom polymers.[17] Here atactic PAMA with a molecular weight of 28.42 kg/mol and a dispersity of 2.49 was prepared. As described in detail in the Supporting Information, triad tacticities were determined from 1H-NMR according to our previous published method for PAMAs.[11,17]

For functionalization of the PAMAs using thiol-ene click chemistry, a family of four 3,6-disubstituted carbazolyl-ethanethiols with chemically distinct substituents was synthesized in addition to an unsubstituted carbazolyl-ethanethiol. Substituents include an alkyl, -t-Bu, an aryl, -Ph, an electron donating substituent, -OMe and an electron withdrawing substituent, -CN. Synthetic routes for all respective compounds are described in the Supporting Information. The conditions for the post-polymerization functionalizations via photochemical thiol-ene reaction were based on our previous report detailing the successful functionalization of PCzETPMA of varied tacticity with carbazole as the pendant group.[11] The thiol-ene functionalization method was found to be incompatible with the carbazolyl-ethanethiols substituted with -Ph, -OMe and -CN for which partially functionalized polymers were obtained at best. The detailed observations for these attempted functionalizations are discussed in depth in the following paragraph. As depicted in Scheme 1, fully functionalized atactic and isotactic polymers were

obtained with 3,6-di(tBu)-carbazole and with unsubstituted carbazole as the pendant groups when the PAMAs were reacted with N-carbazolylethanthioate and di-t-butyl-N-carbazolylethylthioate respectively under UV irradiation (λ = 300 nm) in the presence of the photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA) yielding the functionalized PCzETPMAs in ≥96% conversion. Functionalization was monitored by 1H-NMR spectroscopy via disappearance of the characteristic alkene peaks in the PAMAs and the simultaneous appearance of the aliphatic spacer, substituent peaks, and the aromatic carbazole peaks. Functionalization with N-carbazolylethanthioate afforded PCzETPMAs with Mn = 20.31-24.55 kg/mol and Đ ≤ 1.82 while functionalization with di-t-butyl-N-carbazolylethylthioate afforded PCzETPMAs with Mn = 65.01-66.92 kg/mol and Đ ≤ 2.98 (Table 1).



Scheme 1. General synthesis of PAMA parent polymers and functionalization with (substituted) *N*-carbazolylethanethioate to give poly((*N*-carbazolylethylthio)propyl methacrylates) (PCzETPMAs). For R = H, *t*Bu the initiator in the thiol-ene reaction was DMPA, the solvent was toluene and the reaction time was 24 hours.

Table 1. Molar mass, *Đ*, yield/conversion and triad tacticity for PAMA and PCzETPMA poymers.

Entry	Polymer	M_n [kg/mol]	*Đ*	Yield [%][a),b)]	Triad Tacticity [mm/mr/rr]
1	PAMA-ata	28.42	2.49	54[a)]	57/18/25
2	PAMA-iso	49.74	1.73	29[a)]	86/11/3
3	Cz-iso	24.55	1.78	97[b)]	57/18/25
4	Cz-ata	20.31	1.82	96[b)]	86/11/3
5	tBuCz-ata	65.01	2.17	>99[b)]	57/18/25
6	tBuCz-iso	66.92	2.98	98[b)]	86/11/3

[a)]Isolated polymerization yields after purification.; [b)] Thiol-ene conversion as determined from ^{1}H-NMR.

For 3,6-di(Ph)-carbazolyl-ethanethiol the low solubility of the pendant group in common organic solvents required significantly higher dilution of the reaction mixture for the thiol-ene reaction. As determined from 1H-NMR analysis of the filtrate after filtration of the polymer products, this favored the photochemical dimerization of the thiols to 1,2-bis(2-(3,6-diphenyl-9H-carbazol-9-yl)ethyl)disulfane over the thiol-ene reaction and resulted in a virtually insoluble product. Such photodimerization in the presence of DMPA when irradiated with UV light has previously been observed for phenylmethanethiol by Kokotos et al.[18]

In the case of 3,6-di(CN)-carbazolyl-ethanethiol not even a partially functionalized polymer could be recovered suggesting that photochemical side reactions occurred instead of the intended thiol-ene click reaction. This could be explained by the aromatic nitrile-moieties acting as photochemically active groups themselves analogously to the established photochemical behavior of benzonitriles which have been shown in literature to undergo photochemical [2+2] cycloaddition in the presence of unsaturated carbohydrates under conditions very similar to those of the thiol-ene reaction in this study.[19-21]

In thiol-ene reactions with 3,6-di(OMe)-carbazolyl-ethanethiol only partially functionalized polymers could be obtained. Due to the absence of any obvious issues related to solubility or a photochemically active substituent, we conducted an extensive optimization study of the thiol-ene reaction condition for this pendant group. However, tuning of the catalyst loading, the equivalents of thiol used, the reaction time and the identity of the photoinitiator were unsuccessful in affording a fully functionalized polymer. Additionally, an altered reaction setup in which a solution of the polymer was slowly added over time to a mixture of the thiol and the photoinitiator stirring under UV-light irradiation also failed. Detailed reaction conditions for all attempted thiol-ene reactions are included in the Supporting Information.

These results demonstrate that while photochemical thiol-ene chemistry can be a mild and highly efficient method for post-polymerization functionalization of non-conjugated polymers, translating to more complex pendant groups requires considerations of compatibility of these groups with the methodology especially in terms of potential photoactive behavior of the pendant group and sufficient solubility to minimize photochemically induced side reactions.

The fully functionalized polymers were characterized by several techniques. Differential scanning calorimetry (DSC) of tBuCz-ata and tBuCz-iso showed small endothermic peaks around 105 °C likely stemming from the glass transitions of the polymers but no features could be observed for the polymer functionalized with unsubstituted carbazole. The absence of any peaks that could be associated with crystallization or melting indicates amorphous morphologies across the family of polymers.

For the fully functionalized polymers thin-film UV/Vis absorption was measured both for unannealed, as-cast films and for films after annealing at 150 °C for 30 min (Supporting Information). Consistent with our previous studies on carbazole functionalized NCPEPs, all samples displayed the absorption behaviour characteristic for pendant carbazole groups with a peak at 295 nm corresponding to π–π* transitions and peaks around 330 and 344 nm corresponding to n–π* transitions.[10.11] While the absorption features for tBuCz- and Cz-substituted polymers were virtually identical, tBuCz-ata and tBuCz-iso had lower absorption coefficients than their unsubstituted analogues. Upon annealing no significant changes in the absorption spectra could be observed.

Additionally, photoluminescence (PL) spectra were measured for both the unannealed (Figure 2a) and the annealed (Figure 2b) functionalized polymers. Cz-iso and Cz-ata exhibited the emission features typical for 0-0 transitions in pendant carbazoles with a peak at 350 nm and a vibronic band at 370 nm. Consistent with our previous reports on poly(methacrylates)

functionalized with carbazole pendant groups, peaks around 405-420 nm corresponding to excimer emission from fully overlapping carbazoles were absent, however a shoulder around 440 nm likely stemming from lower energy excimer emission as reported for adjacent carbazoles in 2,4-di-N-carbazolylpentane and norbornene-derived non-conjugated polymers with pendant carbazoles could be observed.[10,11,22.23] This suggests a limited degree of π-stacking for the unannealed samples. tBuCz-iso and tBuCz-ata displayed characteristic 0-0 transitions as well however a slight bathochromic shift of ~10 nm of the peaks was observed. The intensity of the shoulder at 440 nm relative to the intensity of the peaks corresponding to the 0-0 transition was decreased compared to the Cz-polymers which is indicative for a more limited degree of excimer formation in these di-substituted polymers relative to their unsubstituted analogues.

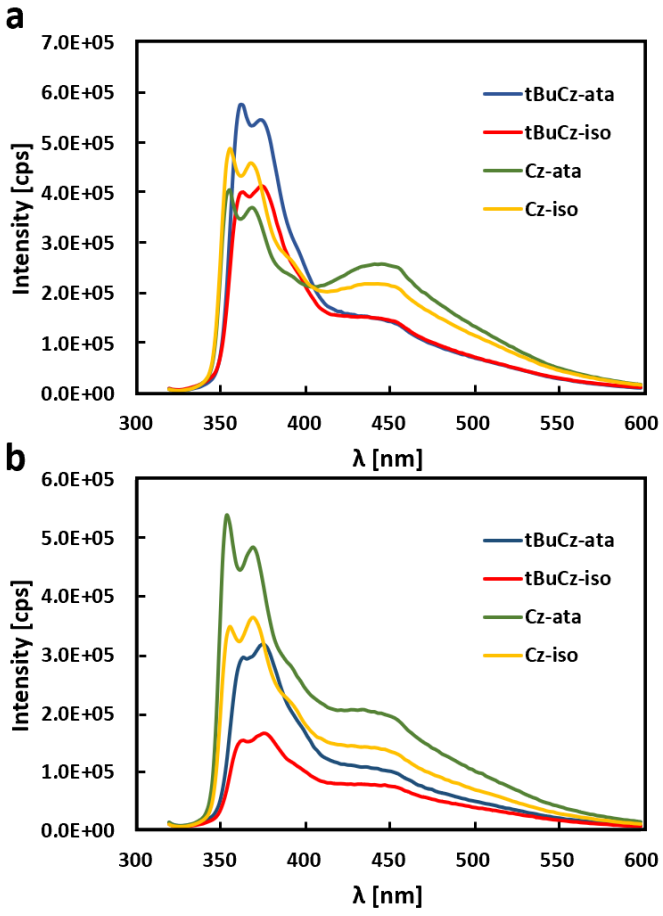


Figure 2. (a) PL spectra of PCzETPMAs for as-cast films. (b) PL spectra for PCzETPMAs after annealing at 150 °C for 30 min.

In the PL spectra after annealing shown in Figure 2b the same features but at different relative intensity were observed. The intensity of the shoulder at 440 nm was decreased relative to the intensity of 0-0 transition and the vibronic band at 370 nm especially for Cz-iso and Cz-ata indicating a relative decrease of the contribution of emission stemming from excimers. While the overall PL intensity of Cz-ata is slightly increased upon annealing, the intensities for all other samples decrease.

Decreased intensities suggest increased aggregation-based PL quenching indicative of more pronounced π–π stacking of the carbazole groups in the annealed polymers. This is consistent with both our previous observations for annealed PCzETPMAs and the established phenomenon of "aggregation-causes quenching" (ACQ) for luminophores and fluorophores which has been observed in carbazole containing small molecules amongst numerous other comounds.[24-28] For Cz-ata however the increased PL intensity would suggest a decrease in the degree of π–π stacking despite an increase in hole mobility after annealing as discussed below. Overall, for PCzETPMAs with a six atom spacer, annealing appears to induce higher levels of aggregation of the *t*BuCz pendant group than for the Cz group.

To further elucidate the impact of structure and annealing on electronic properties, hole mobilities (μ_h) were measured for the functionalized polymers via the space charge limited current (SCLC) technique. Based on previous findings for PCzETPMA homopolymers that showed significantly improved mobilities after thermal annealing, we measured all samples as-cast and after annealing at 150 °C, however no attempts were made to optimize the annealing conditions. For each sample, measurements were repeated three times and the reported data shown in Figure 3 are the average over at least 20 pixels. The polymers were spin-coated from chloroform and gave film thicknesses of 56-70 nm (Supporting Information). Hole mobilities

were found to follow three major trends: μ_h was higher for the stereoregular polymers compared to their stereorandom analogues, for any given polymer backbone μ_h was higher when the attached pendant group was Cz rather than *t*BuCz, and μ_h increased for all samples after annealing. Prior to annealing, Cz-iso exhibited the highest hole mobility of 5.04×10^{-5} cm^2/V·s, which was about five times higher than measured for for *t*BuCz-iso. The mobility of Cz-ata, 3.94×10^{-5} cm^2/V·s, was lower than for its stereoregular analogue however the decrease was less significant than for *t*BuCz-ata which gave a μ_h that was an order of magnitude lower than all other samples. The superior mobility for the isotactic samples is consistent with our previous findings comparing stereoregular and stereorandom PCzETPMAs and can be attributed to a more favourable positioning of the pendant groups for intramolecular charge carrier transport.[10,11] The lower hole mobilities for the *t*BuCz-polymers compared to the Cz-polymers is likely the result of the additional steric bulk of the *t*-butyl substituents that hinder more optimal overlap of the π-conjugated system of the carbazole moieties needed for efficient hole transport. Such adverse π–π interactions as the result of terminal, bulky *t*-butyl groups have previously been described by Wang *et al*. for more extended 3,6-disubstituted-carbazole based pendant groups in atactic polymers which resulted in decreased performances for perovskite solar cell devices.[29]

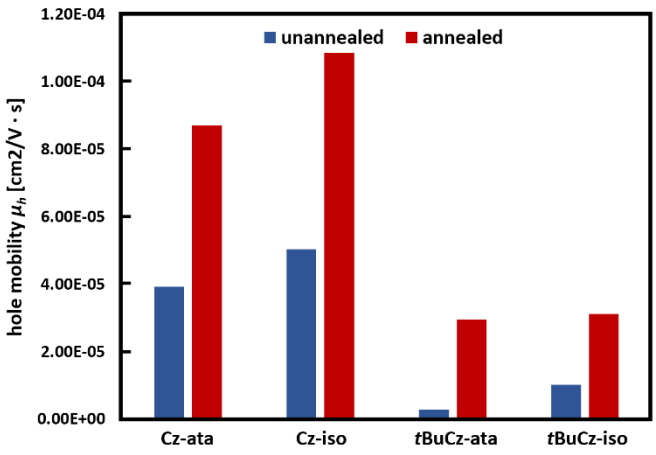


Figure 3. Hole mobilities of PCzETPMA polymer with Cz and *t*BuCz pendant groups as cast and after annealing at 150 °C for 30 min.

Consistent with our studies on carbazole functionalized NCPEPs, μ_h improved across all samples after annealing.[10,11] The trends observed for the annealed samples were the same as described for the as-cast samples with annealed Cz-iso giving the highest hole mobility of 1.09 × 10^{-4} $cm^2/V{\cdot}s$, an increase by about a factor of two. This is in good agreement with our previous report on isotactic PCzETPMA functionalized with a carbazole pendant group which gave a μ_h of 2.19 × 10^{-4} $cm^2/V{\cdot}s$ under the same annealing conditions. Annealing was found to have the most significant effect on *t*BuCz-ata for which μ_h increased by an order of magnitude resulting in a hole mobility of 2.96 × 10^{-5} $cm^2/V{\cdot}s$. μ_h of *t*BuCz-iso was only marginally higher suggesting that for a fixed spacer length of six atoms in PCzETPMAs with such bulky substituents the polymer conformations assumed after thermally induced rearrangement are more heavily influenced by the steric demand of the substituent than by the tacticity of the backbone which results in similar positioning of the pendant groups and thus similar charge transport properties in polymers of both tacticities. However, whether this effect upon introduction of bulky substituents can be more universally observed for PCzETPMAs with varied spacer lengths was not investigated in this study.

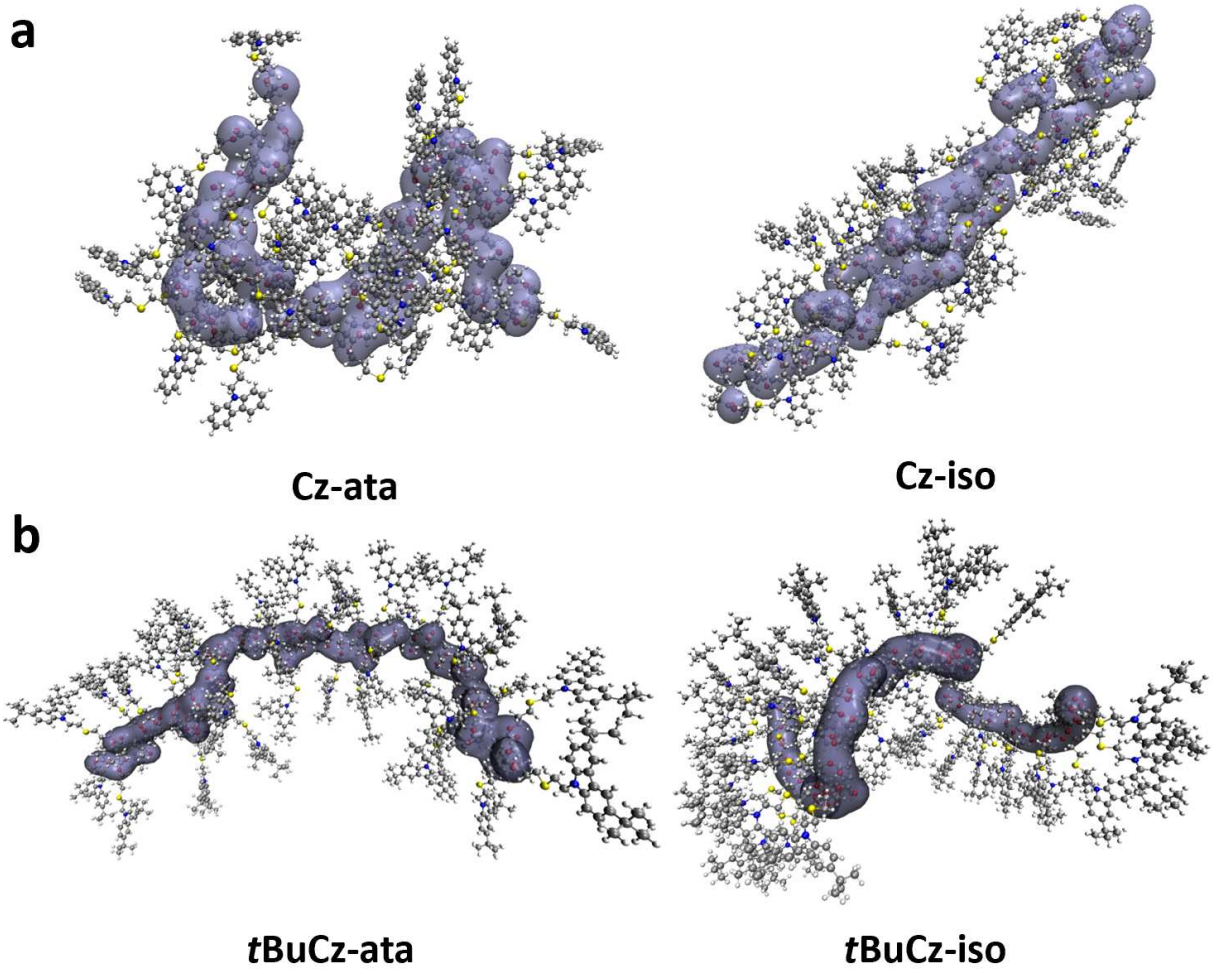


Figure 4. (a) DFT-optimized structures of Cz polymers with 40 repeating units with a highlighted polymer backbone. Reprinted with permission from Samal et al.[11] Copyright 2021 American Chemical Society. (b) DFT-optimized structures of *t*BuCz polymers with 40 repeating units with a highlighted polymer backbone.

Considering the amorphous nature of the polymers as determined from DSC, we decided to turn to simulations of the polymer chains by DFT to gain further insight into their packing behaviour (Figure 4). We followed the approach from our previous studies and optimized atactic and fully isotactic PCzETPMA chains with *t*BuCz pendant groups with 40 monomers using B3LYP/6-31+G in Q-Chem 5.2 (Figure 4b).[10,11,30] The obtained structures were compared to the optimized geometries for atactic and isotactic PCzETPMAs with Cz pendant groups from our previous report (Figure 4a).[11] Cz-ata showed a distinctly more clumped and randomized structure with very limited π–π stacking between the pendant groups compared to Cz-iso which had a significantly more ordered, elongated, helical backbone with only slight

distortion and displayed π–π stacked dimers and trimers. Upon introduction of the *t*-butyl substituents, the atactic polymer *t*BuCz-ata displayed a less clumped, more linearly stretched structure compared to Cz-ata with only very limited π–π stacking between the pendant groups. The backbone of *t*BuCz-iso displayed a helix like structure, however as a result of the increased steric demand of the substituted pendant groups, with significantly more distortion and significantly less elongated compared to the backbone of Cz-iso. Due to this pronounced distortion, π–π stacking between pendant groups was distinctly reduced in tBuCz-iso relative to Cz-iso with no trimers and only very limited stacked dimers. Overall, the optimized structures for both *t*BuCz polymers indicate significantly reduced π–π stacking relative to their Cz analogues which is in good agreement with the reported hole mobility data and support the hypothesis of significantly reduced ordering of the pendant groups in the *t*BuCz-polymers regardless of the tacticity of the backbone due to the introduction of such a bulky substituent which then leads to lower hole mobilities than in the Cz-polymers.

3. Conclusion

In summary, this work is the first study on the compatibility of differently substituted pendant groups with the established photochemical thiol-ene methodology for post-polymerization functionalization for the synthesis of stereoregular NCPEPs. A family of five carbazolyl-ethanethiols was synthesized and tested in photochemical thiol-ene post-polymerization reactions. Limitations for this functionalization method based on insufficient photochemical stability and limited solubility that prevented a complete functionalization of the PAMA parent polymer could be demonstrated for carbazole pendant groups substituted with phenyl, nitrile and methoxy groups. For the successfully functionalized PCzETPMAs with unsubstituted carbazolyl-ethanethiol and 3,6-di-t-butyl-N-carbazolylethylthioate a distinct effect of substitution on the electronic properties of the resulting polymers could be observed. Similar to

our previous findings for PCzETPMAs, annealing lead to significantly increased hole mobilities (μh) in both the atactic and isotactic polymers regardless of the nature of the pendant group. Overall, this work shows that despite the thiol-ene functionalization methodology being a mild and effective method for certain pendant groups, there are distinct limitations to its scope particularly in regards to solubility and photochemical activity of the pendant group. Consequently, this study can serve as a guideline for the choice of post-polymerization functionalization method for the synthesis of NCPEPs with substituted pendant groups to circumvent the observed limitations.

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