Synthesis and energy transfer in original poly(3-alkylthiophene)-g-poly(fluorene) toothbrush copolymers

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Abstract

Conjugated toothbrush copolymers are prepared by connecting end-capped poly(9,9'-dioctylfluorene) (PF) side-chains (PF) to a poly(3-alkylthiophene) (P3AT) backbone via the CuAAC reaction. The ratio of grafted/nongrafted segment is varied. The influence of the covalent attachment of sidechains to the backbone on the self-assembly is studied by UV-vis spectroscopy. By excitation of the PF side-chains energy transfer to the P3HT backbone is studied.

1. Introduction

The domain of conjugated polymers with 2D topologies is slowly developing. The majority of the reported polymers are (hyper)branched conjugated polymers.¹⁻⁸ There are some reports of conjugated graft copolymers and only one about a conjugated star copolymer.⁹⁻¹³ Whereas conjugated graft copolymers already represent a very interesting architecture, the topology can be made even more advanced by adding a linear non-grafted segment to the backbone in order to form toothbrush (co)polymers. In the field of non-conjugated polymers, the properties of these toothbrush copolymers are already exploited.¹⁴⁻¹⁷ Block copolymers have been already demonstrated to be interesting drug carrier systems upon micelle formation. Nowadays, the versatility of the architecture of toothbrush-like polymers is exploited to optimize drug delivery systems. A whole range of macromolecular parameters can be optimized. For instance, parameters such as the linear vs brush segment ratio, the length of the grafted sidechain, the possibility to introduce multicomponent grafts, the grafting density... can be tuned. Conjugated polymers are mainly exploited for their optical properties, which depend on their molecular and supramolecular structures. By selecting the molecular structures of the backbone and the sidechains, broadband absorbance or energy funneling can be tuned. However, due to the presence of sidechains the self-assembly of the backbone by π - π -interactions will be compromised. Making use of the unique structure of toothbrush (co)polymers, this self-assembly can be tuned by changing the ratio of non-grafted vs grafted blocks. For the non-grafted parts, interaction will be much easier due to absence of polymer sidechains. In the present paper, we report the synthesis of original P3AT-*g*-PF toothbrush polymers with variation of the length of non-grafted vs grafted parts. Poly(3-alkylthiophene) (P3AT) homopolymer is known for its high self-assembly propensity, whereas the emission spectrum of the poly(fluorene) (PF) sidechains is known to overlap with the absorption spectrum of the P3AT backbone.

2. Results and discussion

2.1 Synthesis and characterization of the homo and block (co)polymers

For the preparation of the P3AT backbones, the controlled Kumada catalyst transfer polymerization (KCTCP) is employed. Using an *o*-tolyl external initiator (**1**)¹⁸, this method allows for the synthesis of AB block copolymers in a controlled way (Scheme 1). In a first step, the hexylthiophene monomer (**3**), after conversion of the premonomer (**2**) via Grignard metathesis (GRIM), is polymerized to form the X block. In a next step, the thiophene monomer with bromohexyl sidechain (**5**), after activation of the premonomer (**4**) via GRIM, is added, forming the Y block. We target polymers with DP = 40 and percentage of the Y block of 0, 25, 50, 75 and 100% (ratio of the number of monomer units).

Scheme 1. Synthesis of poly(thiophene) homo and block copolymers **P1-0/25/50/75/100** for the toothbrush polymer backbone.

$\bar{M}_n$ and $\bar{D}$, obtained via GPC, are listed in Table 1. The dispersities were measured around 1.1, whereas the $\bar{M}_n$ values lie within the same range, between 5000 and 7000 g/mol. DP estimation was also performed using ^1H -NMR (Figure 1). Signal a corresponds to the protons of the *o*-tolyl group on the initiator. Signal b corresponds to the $\alpha\text{-CH}_2$ of the internal thiophene units, while signal c corresponds to the $\alpha\text{-CH}_2$ of the terminal thiophene containing a hydrogen atom as the end-group. No signal of Br-terminated chains, resonating at 2.52 ppm,¹⁹ were observed.

Signal d corresponds to the CH₂ protons next to the bromine atom in the bromohexyl sidechains. The non 3/2 ratio for a to c protons may be attributed to protonated monomers acting as initiator leading to H/H terminated polymers.

Figure 1. ¹H-NMR analysis of **P1-50** for DP and % functionalization estimation.

The DP can then be calculated by dividing all units by half of the terminal units using the following formula: $DP = \frac{b+c}{\frac{c}{2} + \frac{a}{3}}$. The percentage of the Y block (Table 1) compared to the total length is calculated as follow: $\%(\text{blockY}) = \frac{d}{b+c} * 100$.

Table 1. GPC and ¹H-NMR analysis of **P1-0/25/50/75/100**.

Polymer	$\bar{M}_n$ (kg/mol)	$\bar{D}$	DP	Y block (%)	X block (units)	Y block (units)
P1-0	7.7	1.1	26	0	26	0
P1-25	6.2	1.2	22	8	20	2
P1-50	6.1	1.2	25	49	12	12
P1-75	6.2	1.1	25	71	7	18
P1-100	5.9	1.1	24	100	0	24

The percentages of the Y block are close to the targeted values, except for **P1-25**, only having a percentage of 8.

In a postpolymerization step, the bromo groups are substituted for azide groups (Scheme 2).²⁰ The reaction was monitored via ¹H-NMR (Figure 2) and IR-spectroscopy (see SI). The peaks

of the CH₂ protons next to the bromine atom shift from around 3.4 to 3.3 pm. In the IR spectrum, a significant peak around 2085 cm⁻¹ appears. A complete conversion was realized.

Scheme 2. Postpolymerization reaction for conversion of **P1-x** to **P2-x** by Br-N₃ exchange.

Figure 2. ¹H-NMR analysis for conversion of **P1-75** to **P2-75**

The polyfluorene polymers that will be grafted to the backbone were prepared using the Suzuki-Miyaura catalyst transfer condensative polymerization. To avoid problems with stability of the standard catalyst/initiator PhPd(*t*Bu)₃Br, we opted for a stable *t*Bu₃P-coordinated 2-phenylaniline-based palladacycle complex (**6**) as the precatalyst.^{21–24} This catalyst was activated in basic medium in presence of PhBr. After addition of monomer **7** and 3 hours of reaction, the polymerization is quenched with an endcapper bearing a terminal hydroxyl group (Scheme 3).

Scheme 3. Synthesis of **P3**.

The low dispersity of 1.2 is a first indication of the controlled nature of the polymerization (Table 2). The controlled nature of the polymerization was further confirmed using MALDI-ToF analysis. The MALDI-ToF spectrum shows only peaks which can be assigned to polymers that contain end-groups corresponding to the initiator and end-capper ($77+n.388.6+107$), confirming the controlled nature of the polymerization with the palladacycle precatalyst (Figure 3). Then, we determined the $DP = 15$ using 1H -NMR peaks of CH_2 protons of the end-capper (Scheme 3, SI), by calculating $\frac{b}{\frac{4}{a}}$. This value is close to the value of 14 calculated using the $\bar{M}_n$ value from GPC (Table 2), taking into account the correction factor determined by the group of Wang.²⁵

Figure 3. MALDI-ToF spectrum of **P3** (degree of polymerization is assigned on the top of each signal)

The terminal acetylene was introduced by end-capping with end-capper containing a terminal OH function followed by a postpolymerization esterification reaction with hexynoic acid (Scheme 4) in the presence of *N,N'*-4-dimethylaminopyridine (DMAP) and *N,N'*-dicyclohexyl carbodiimide (DCC). Using directly a conjugated terminal acetylene as end-capper was not an option as this leads to disproportionation.

Scheme 4. Postpolymerization esterification of **P3** to **P4**.

Complete conversion to **P4** was confirmed by MALDI-ToF (Figure 4) and ^1H -NMR (Figure 5).

Figure 4. MALDI-ToF spectrum of **P4** (degree of polymerization is assigned on the top of each signal)

Figure 5. Complete conversion of **P3** to **P4** via a postpolymerization reaction.

Table 2. GPC analysis of **P3** and **P4**

Polymer	$\bar{M}_n$ (kg/mol)	$\bar{D}$
P3	8.1	1.2
P4	8.0	1.2

2.2 Synthesis and characterization of graft copolymers

To graft **P4** to the **P2-x** backbone, the copper(I) catalyzed acetylene-azide cycloaddition (CuAAC) click reaction (Scheme 5) was selected.^{26–28} The high efficiency of this reaction already proved to be very efficient in the past. A complete grafting of the block with the hexylazide sidechains was aimed for. The reaction was monitored via GPC. Unreacted PF polymer was removed by preparative GPC.

Scheme 5. Grafting of **P4** to **P2-25/50/75/100** to form toothbrush polymers **P5-25/50/75/100**.

2.3 GPC and ^1H -NMR analysis

Via GPC, analysis of the molar mass of the toothbrush polymers **P5-x** was carried out. The chromatograms were recorded at two different wavelengths (440 and 380 nm) corresponding to the absorption maxima of the polythiophene backbone and the polyfluorene sidechains, respectively (Figure 6). As can be seen from Table 3 and Spectra in SI, $\bar{M}_n$ values for both

wavelengths were measured similar, ruling out the presence of significant amounts of residual homopolymers.

Figure 6: Chromatograms of homopolymers **P1-0/P4** and toothbrush copolymers **P5-25/50/75/100**.

Table 3. $\bar{M}_n$ and $\bar{D}$ values of the brush copolymers determined via absorption at 2 different wavelengths: 380 and 440 nm.

Polymer	$\bar{M}_n$ (kg/mol) $\lambda=380$ nm	$\bar{M}_n$ (kg/mol) $\lambda=440$ nm	$\bar{D}$
P5-25	16.4	16.7	1.1
P5-50	49.4	51.6	1.3
P5-75	63.9	64.7	1.2
P5-100	70.0	70.2	1.1

Also $^1\text{H-NMR}$ spectra were recorded to elucidate the structure of the polymers. $^1\text{H-NMR}$ spectra of **P1-0**, **P4** and **P5-25** are shown in Figure 7. For this toothbrush copolymers, the poly(fluorene) and poly(thiophene) content are both clearly visible.

Figure 7. Overlaid ^1H -NMR spectra of brush copolymers **P5-25** and homopolymers **P4** and **P1-0**

The ^1H -NMR data were then used to determine the grafting percentage. This was done using the protons a of the polythiophene backbone and protons b of the polyfluorene sidechains. As the polyfluorene sidechain contains 15 units, the grafting percentage equals:

$$\text{grafting}\% = \frac{\frac{b}{4 \cdot 15}}{\frac{a}{2}}$$

Values of 8% and 25% were obtained for **P5-25** and **P5-50** (Table 4). For **P5-25**, this nearly equals the percentage of the length of the Y block and therefore this block is completely grafted. However, for **P5-50**, the percentage is only half of the percentage of the length of the Y block. For **P5-75/100**, the signals due to the P3AT segment are barely visible because of its low content and the spectra resemble the spectrum of pure PF. Therefore, the grafting percentage could not be calculated relying on ^1H -NMR spectra. In order to determine the grafting percentage, UV-vis spectra were exploited.

2.3 UV-vis spectroscopy

The optical properties and self-assembly of the homo and graft copolymers were studied by recording UV-vis spectra in mixtures of good solvent - chloroform - and poor solvent - methanol. Starting from pure chloroform solutions (Figure 9), the methanol content was gradually increased in steps of 10% (see SI). Only for **P1-25** and **P1-50**, absorption due to the P3AT content is still somewhat visible, while for **P1-75** and **P1-100** the UV-vis spectrum

strongly resembles the spectrum of the polyfluorene sidechain (**P4**). Both homopolymers start to aggregate from a 70/30 chloroform/methanol mixture (see SI). For the polyfluorene homopolymer, this is visible by appearance of an extra peak around 440 nm, while for polythiophene it is visible by the redshift of the signal.²⁹ The brush copolymers **P5-50/75/100**, however, only start to aggregate from a 60% chloroform solution and **P5-25** only from a 50% mixture (see SI). This means that the reduced freedom of motion due to covalent attachment to the P3AT backbone complicates the aggregation of the polyfluorene sidechains. Note that the vibronic fine-structure of the P3AT is not present, indicating that the P3ATs, also the X-block, does self-assemble.

Figure 9. UV-vis spectra of the homopolymers **P1-0** and **P4** and brush copolymer **P5-25/50/75/100**.

As the backbone and sidechains are completely dissolved in pure chloroform and behave independent of each other, it is possible to determine the mass% of P3AT and polyfluorene for each brush copolymer injecting the extinction coefficients for the homo and graft copolymers in pure chloroform in the next formula:

$$\text{mass\% (P3AT)} = \frac{\varepsilon(\text{P5-x}) - \varepsilon(\text{P4})}{\varepsilon(\text{P1-0}) - \varepsilon(\text{P4})}$$

Because the DP of the backbone and the sidechains are known, the average number of PF sidechains for each P3AT backbone can be calculated and, as a consequence, also the grafting percentage (Table 4) can be estimated.

Table 4. Mass and graft percentages of the brush (co)polymers.

Polymer	PF wt% (UV-vis)	P3AT wt% (UV-vis)	graft% (UV-vis)	graft% (NMR)
P5-25	74	26	7	8
P5-50	91	9	24	25
P5-75	94	6	34	/
P5-100	96	4	56	/

when the graft% determined via UV-vis and ^1H -NMR data are compared, a good agreement between the values for **P5-25** and **P5-50** is observed. While theoretically 8% and 49% (Table 1) could be grafted, **P5-25** is completely grafted while for **P5-50** only half of the Y block is grafted. This trend continues for **P5-75** and **P5-100**, where the grafting percentage is approximately half the value of what is theoretically possible. This observation can be explained by steric hindrance.

2.4 Fluorescence spectroscopy

Chloroform solutions of the homo and brush polymers were excited at 380 nm, the $\lambda_{\text{max,abs}}$ of poly(fluorene), and emission spectra were recorded (Figure 10). As the $\lambda_{\text{max,em}}$ of PF (420 nm) is close and somewhat higher in energy than the $\lambda_{\text{max,abs}}$ of P3AT (440 nm), energy transfer is expected to occur.^{30–34} The spectra are corrected by dividing the values by the absorbance at the excitation wavelength.

Figure 10. Absorption corrected fluorescence spectra of homopolymers **P1-0** and **P4** and brush copolymers **P5-25/50/75/100**.

Taking into account the different weight percentage of P3AT and PF for the toothbrush copolymers and the fact that both absorb at the excitation wavelength with a different extinction coefficient, it is possible to calculate the fluorescence in absence of energy transfer. Taking the difference between experimental and calculated values and subsequent division by the calculated values without considering transfer, it is possible to get an indication of the extent of percentage of energy transfer. The obtained values (Table 5) show that transfer is indeed occurring. While the loss in fluorescence for the polyfluorene sidechains remains quite constant, except for **P5-25**, there is an increase in fluorescence of the poly(thiophene) backbone compared to what is expected on basis of the diminishing weight percentage of polythiophene without considering energy transfer. For example, **P5-50** with one third of the weight percentage of PT compared to **P5-25** (Table 4) has around 3 times higher percentage of transfer to the P3AT backbone (Table 5).

Table 5. Percentual difference in fluorescence between the experimental obtained values and the theoretical calculated fluorescence without considering energy transfer.

	Δ fluorescence (%)			
	P5-25	P5-50	P5-75	P5-100
PF-sidechains	-0.13	-0.82	-0.69	-0.73
P3AT backbone	1.8	6.2	10.8	12.7

If we compare this values to the energy transfer in the previous reported polymer systems where the polyfluorene polymers were randomly distributed over the polymer backbone, in case of graft copolymers, the transfer is more than one order of magnitude lower.¹² The previous reported polymers **P5** and **P6** can be correlated to **P5-25** and **P5-50** respectively, in terms of their grafting percentage of 10% and 17%.

3. Conclusions

The synthesis of conjugated toothbrush copolymers is reported for the first time. It is also the first report of conjugated graft copolymers with backbone and sidechains of different chemical nature for which both are prepared in a controlled way. The backbone consisted of a poly(thiophene) block copolymer prepared via KCTCP. The polyfluorene sidechains, prepared in a controlled way via Suzuki-Miyaura coupling using a protocol with a stable precatalyst, were connected to the backbone using the CuAAC click reaction. By removing non-reacted polyfluorene, clean monomodal GPC spectra were recorded. The Y blocks that can be grafted forming the brush part amount to percentages of 0, 8, 49, 73 and 100% of the total units. The corresponding total grafting percentages obtained are 0, 8, 25, 34 and 56%. This means that only **P5-25** is completely grafted, while all others are only grafted for a percentage that is half of what is theoretical possible due to steric constraints. UV-vis solvatochromism experiments indicated that aggregation of the polyfluorene is compromised due to their covalent attachment to the poly(thiophene) backbone. As the emission spectrum of the sidechains overlaps with the absorption of the backbone, the system is very suitable for the study of energy transfer. The occurrence of energy transfer was demonstrated with increasing efficiency for higher grafting percentages. However, the transfer seems much less efficient as for analog systems with the same grafting percentage but with the sidechains randomly distributed over the backbone instead of being packed on one small segment.

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Abbreviations

CuAAC (copper(I) catalyzed acetylene-azide cycloaddition); DCC (*N,N'*-dicyclohexyl carbodiimide); DP (degree of polymerization); DMAP (*N,N'*-4-dimethylaminopyridine); GRIM (Grignard metathesis); KCTP (Kumada condensative catalyst transfer polymerization); P3AT (poly(3-alkylthiophene)); PF (polyfluorene)

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Synthesis and energy transfer in original poly(3-alkylthiophene)-*g*-poly(fluorene) toothbrush copolymers

A series of P3AT-*g*-PF brush copolymers are prepared by grafting PF sidechains to different P3AT blockcopolymers. UV-vis spectra are recorded to probe the effect of the covalent attachment of the PF sidechains on their aggregation. Fluorescence spectra in pure chloroform are measured and subsequent calculations are performed to study the energy funneling from the sidechains to the backbone.