

Macrocyclic P3HT Obtained by Intramolecular McMurry Coupling of Linear Bis-Aldehyde Polymer: A Direct Comparison with Linear Homologue

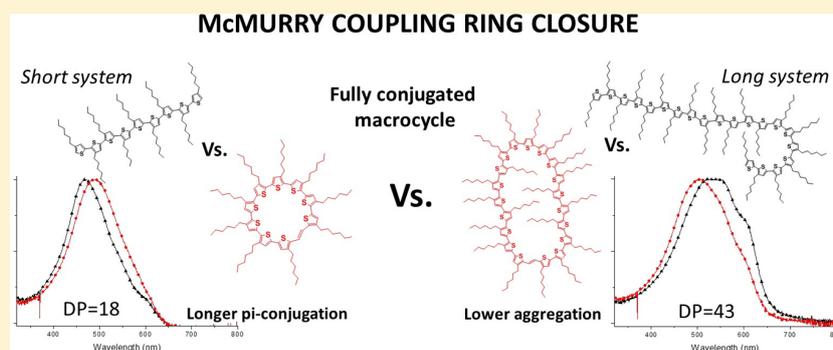
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Supporting Information



ABSTRACT: Different P3HT chain lengths have been synthesized, functionalized at both chain ends with aldehyde moieties and finally cyclized following the McMurry reaction in a pseudo high dilution process. The confirmation of the high yielded intramolecular coupling came from the decrease of the hydrodynamic radius observed by SEC, correlated to the conservation of the mass distribution by MALDI-ToF and by the very low content of residual linear precursor estimated by NMR. Different aggregation behaviors between linear and cyclic and between short and long systems have been pointed out by DSC and UV–vis absorption spectroscopy. We estimate that long cyclic structures present similar aggregation behavior than long linear ones mainly due to the folding of those chains.

INTRODUCTION

It is now well established that the polymer topology drives and impacts the macroscopic properties of macromolecular material. If complex architectures, i.e., star-shaped,¹ hyperbranched,² dendrimers,³ or cyclic polymers,⁴ have already been synthesized and widely investigated, it comes out that the most intriguing and synthetically challenging ones are the cyclic structures. The lack of chain ends and the ring conformation induce a complete different behavior in solution and solid state when compared to their linear homologues. For instance, it is commonly observed that cyclic polymers exhibit a lower hydrodynamic volume, a smaller gyration radius, and a decrease of the viscosity.^{5,6} Because of their confined nature and the absence of chain end, cyclic polymer also presents a higher glass transition⁷ and different melting and crystallization temperatures, lower⁸ or higher,⁹ according to the chemical nature of the backbone. Those characteristics have been investigated in terms of self-

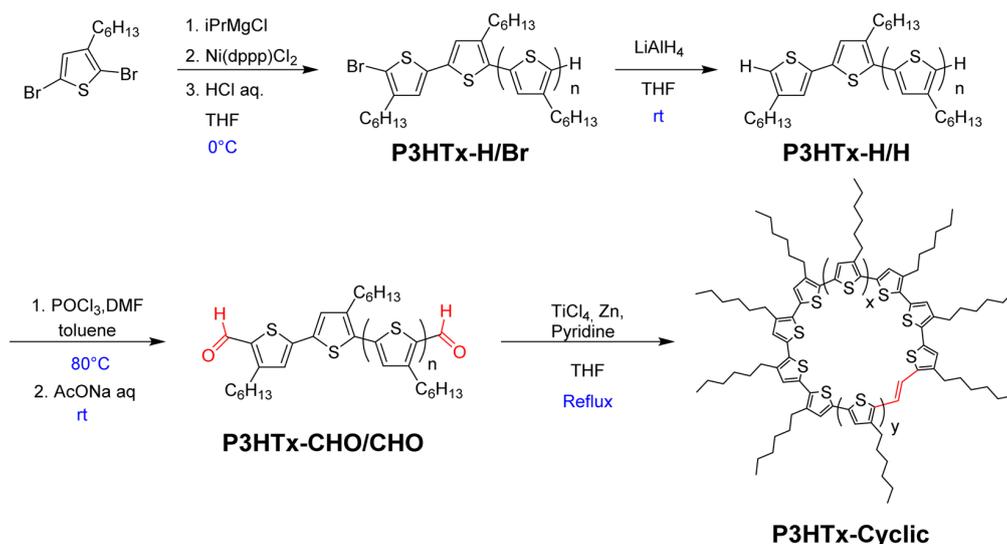
assembly¹⁰ and some potential bioapplications.^{11,12} Particularly, cyclic block copolymers, mainly due to their reduced hydrodynamic volume, have demonstrated a potential application in lithography by reducing the domain spacing between each block.¹³ Very recently, an organic macrocyclic n-type semiconductor has demonstrated a better photovoltaic efficiency compare to its linear homologue mainly due to its better intermolecular electronic charge transport, probably due to an optimal aggregation.¹⁴ Another interesting example is the use of two different π -conjugated cyclotrimers, obtained by McMurry coupling reaction, as monomers for ring-opening metathesis polymerization to the preparation of donor and acceptor block copolymer comprising poly(arylenevinylene)s.¹⁵

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Scheme 1. Synthetic Pathway of Macrocylic P3HT Structures



Cyclic polymers can be distinguished in two main classes regarding the chemical structure of the skeleton. The first one contains aliphatic macrocyclic polymers like polystyrene,^{16,17} polyester,¹⁸ polyether¹⁹ or their block copolymer analogues.^{13,20,21} Those macromolecular architectures are highly flexible and theoretically present a lower hydrodynamic radius and a lower intrinsic viscosity of a factor ca. 0.66.²² The second class gathers more rigid structures composed by π -conjugated segments, generally a combination of aromatic rings and ethynylene bonds.²³ Those macromolecular systems present a noncollapsible backbone, a shape persistency,^{24–27} and so a tunable cavity in the nanometer scale, which can serve as versatile host for specific supramolecular encapsulation,²⁸ modifying the properties of the macrocycle.²⁹ Those described by Moore,^{24,25} Höger,^{26,27} or Yoshida²⁹ are non-fully conjugated ones due to the meta disubstitution of some of the phenylene ring in the backbone.

Fully conjugated macrocycles can be considered as an infinite π -conjugated system with different properties compared to linear chains as demonstrated by Mayor.³⁰ The groups of Bäuerle^{31,32} and Iyoda^{33,34} described the synthesis respectively based on intramolecular Glaser coupling and McMurry coupling reactions of macrocycles containing thiophene repeating units. Some crystalline properties are pointed out, but the comparison with linear homologues cannot be done since the preparation of such macrocycle is related to a cyclization of very short linear systems. Among the few articles dealing with cyclic oligothiophenes, one exhibits the ring closure of an entire chain, with a synthetic strategy based on an aldol ring closure of a poly(3-hexylthiophene) functionalized with an acetyl moiety at one end and aldehyde at the other.³⁵ As attested by ^1H NMR spectroscopy, different unexpected side reactions led to different ring closure links, most of them being nonconjugated. A second recent study by the group of Seferos deals with the alkyne homocoupling ring closure of linear polythiophene and polyselenophene substituted at each chain end with pentynyl moieties. The elegant strategy to separate cyclics to unreacted linears allowed a direct comparison of the two architectures. The organization of those cyclic systems investigated by TEM and STM has been found less ordered than their linear homologues due to the bent of the

chains.³⁶ Both of those studies point out the different aggregation behavior between linear and cyclic chains and the nonpersistent character of π -conjugated rodlike cyclic structure.

In this study, different chain lengths of poly(3-hexylthiophene) were synthesized, functionalized at each extremity with a formyl function, and finally cyclized following a McMurry coupling reaction. This reaction has been chosen because of the resulting ethylene bond, which should keep the conjugation (π -electron delocalization) on the whole macrocycle. And, due to the rodlike nature of π -conjugated polymer, the high temperature required to perform this reaction will also favor the chain folding and so to make then possible the ring closure. In order to probe the different aggregation behaviors between linear and cyclic systems, spectroscopic and thermal studies will be carried out.

■ SYNTHESIS AND CHARACTERIZATION

It appears more synthetically interesting to identically functionalize both chain ends and to perform a homodifunctional ring closure strategy.³⁷ Therefore, the first step of the preparation of our macrocyclic structures is the synthesis of the linear precursors according to the method developed by McCullough³⁸ and Yokozawa.³⁹ The 2,5-dibromo-3-hexylthiophene is activated on the 5-position by isopropylmagnesium chloride according to a GRIM reaction, and then Ni(dppp)Cl_2 catalyst is added to initiate the Kumada catalyst transfer polymerization (KCTP) reaction. This leads to chain ends with regioisomers thiophene ring, i.e., with the alkyl side chain in a “head” configuration.

The quenching of the reaction with a 5 M HCl solution ensures the removal of the inserted Ni center (between thiophene and bromine), before purification and fractionation by Soxhlet extraction. A polymer with H and Br chain ends is obtained and called P3HT_x-H/Br. The bromine termination is reduced by treatment with LiAlH_4 to obtain hydrogen at both chain ends (Scheme 1) and sample called P3HT_x-H/H. The formylation of both chain ends is performed according to the Vilsmeier–Haack–Arnold reaction by reacting the polymer with POCl_3 and DMF in toluene before a basic treatment^{40,41} (P3HT_x-CHO/CHO).

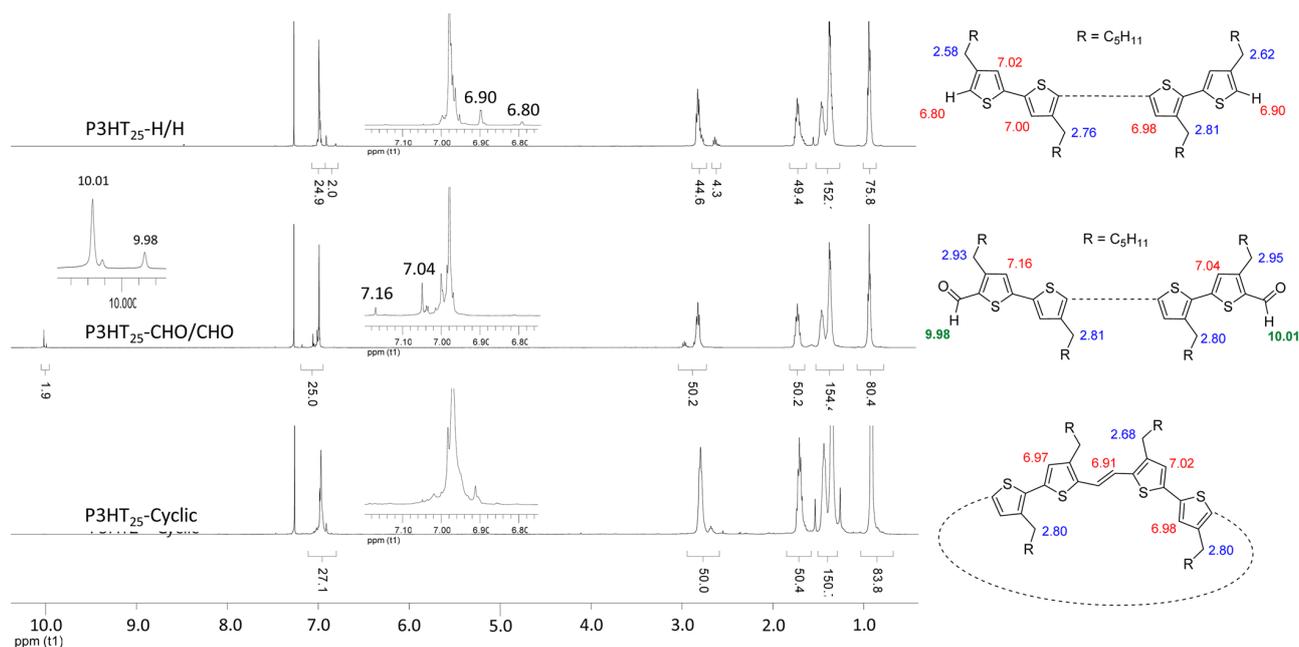


Figure 1. ^1H NMR spectra superposition of P3HT₂₅-H/H, P3HT₂₅-CHO/CHO, and P3HT₂₅-cyclic with a magnification of the aromatic region in the insets. Chemical structure of the polymers and chemical shifts of the different protons are presented next right to their associated NMR spectrum.

Table 1. Macromolecular Parameters of Linear P3HT_x-CHO/CHO and Cyclic P3HT_x Obtained after McMurry Coupling Reaction

polymer	M_n^a ($\times 10^3$ g mol ⁻¹)	M_w^a ($\times 10^3$ g mol ⁻¹)	D^a	M_p^a ($\times 10^3$ g mol ⁻¹)	DP_{NMR} (mass (g mol ⁻¹))	$r = M_{p,\text{cyclic}}/M_{p,\text{linear}}^b$
P3HT ₁₈ -CHO/CHO	3.8	4.4	1.18	4.3	18 (3051)	
P3HT ₁₈ -cyclic	2.9	3.4	1.20	3.1		0.71
P3HT ₂₅ -CHO/CHO	5.1	6.3	1.22	6.1	25 (4214)	
P3HT ₂₅ -cyclic	4.2	5.3	1.25	4.4		0.72
P3HT ₃₃ -CHO/CHO	7.2	9.1	1.26	8.3	33 (5544)	
P3HT ₃₃ -cyclic	5.9	7.6	1.27	6.2		0.75
P3HT ₄₂ -CHO/CHO	11.7	13.7	1.17	13.0	42 (7041)	
P3HT ₄₂ -cyclic	9.3	11.9	1.28	10.2		0.78

^aValue obtained by SEC analysis with polystyrene calibration. ^b r is the peak mass ratio of cyclic elugram on linear precursor elugram.

Since the length of polymeric chain is determined by the feed ratio of $[\text{M}]/[\text{cat.}]$, four samples with a DP_{theoric} of 20, 30, 50, and 70 have been prepared and subjected to the chemical pathway described earlier. The experimental macromolecular parameters have been estimated by size exclusion chromatography (SEC) for all the P3HT_x-H/Br (x is the value of the DP further determined by NMR). Molar masses values (M_n) of 3.8, 5.1, 7.2, and 11.8 kDa (polystyrene calibration) with a respective molar mass dispersity of 1.18, 1.22, 1.26, and 1.17 were found. Those mass values are overestimated due to the rodlike character of polythiophene, generally of a factor from 1.3 to 1.7 (for this range of molar masses) obtained by comparison with MALDI-ToF^{42,43} or ^1H NMR^{44,45} experiments. NMR spectroscopy was used to estimate the average degree of polymerization while MALDI-ToF mass spectrometry was mainly used in order to confirm the end-group modifications and then the ring closure efficiency.

Both studies of the groups of McCullough³⁸ and Yokozawa³⁹ reveal the mechanism of KCTP where the first step is the reduction of the Ni(II) catalyst to Ni(0) through a tail-to-tail coupling (TT) of two 3-hexylthienylmagnesium chloride. Since the catalyst can randomly walk from one side to another of the

growing polymer after each reductive elimination,⁴⁶ this regiodefekt can be located anywhere in the main chain. Moreover, the quenching of the polymerization with acidic treatment leaves randomly one bromine and one hydrogen at the chain ends. This makes the ^1H NMR analysis of H/Br-terminated polythiophene more difficult to interpret. But, the ^1H NMR of the H/H appears easier, since both chain ends are hydrogen in position 2 of either a thiophene in a TT coupling or in a head-to-tail (HT) coupling. Only two signals represent the chain ends, and so the degree of polymerization can be estimated.

As already demonstrated by Sommer et al.,⁴⁷ the doublet signals at 6.80 and 6.90 ppm (with coupling constant of $^4J = 1.8$ Hz) correspond to the protons of the chain end respectively after the TT defect and HT dyad, which is coupled with the proton at position 4 of the same ring. Since the catalyst walks along the chain, the intensity of the TT defect signal is lower than the one of HT dyad signal. By setting the integration of these two signals at 2 (Figure 1), the DP can be estimated by the value of the integration of the signal around 6.98 ppm, which is attributed to the proton at the position 4 of all the

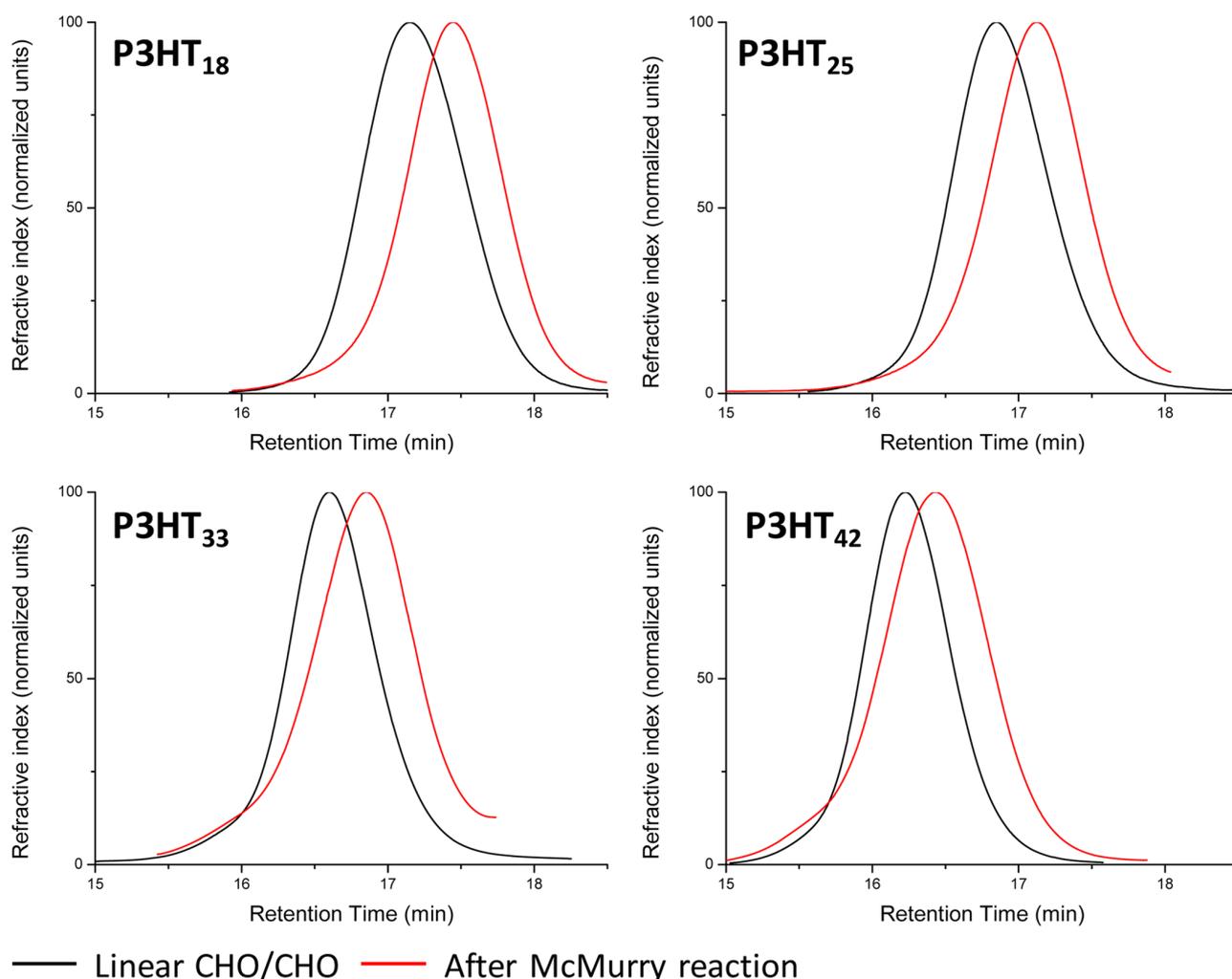


Figure 2. SEC elugrams of linear bis-CHO P3HT_x (black curves) of different molar masses and their derivatives after intramolecular coupling by McMurry (red curves).

thiophene rings. Figure 1 presents the ¹H NMR spectra of the P3HT with a DP_{theoric} of 30 after each postpolymerization reaction. Spectra of the other samples can be found in the Supporting Information. In this case, the DP is estimated at 25. The values of the DP of the other samples are reported in Table 1. Regarding the signals of the α-CH₂ of the hexyl side chain, the chemical shift of the methylene of thiophene chain end is 2.58 and 2.62 ppm respectively for thiophene after the TT defect and after HT dyad. The intensity of the first one is lower than the intensity of the second one.

The same observation can be done on the spectra of P3HT₂₅-CHO/CHO, where the signals of those characteristic protons are upfield shifted. We found at 7.16 and 7.04 ppm, the signal of the proton at position 4 of the thiophene chain end, and at 2.93 and 2.95 ppm the signal of α-CH₂ of the hexyl side chain respectively after the TT defect and the HT dyad. The signal of the aldehyde proton is also split at 10.01 and 9.98 ppm for the moiety after HT dyad and TT defect, respectively.

■ MCMURRY COUPLING REACTION

The McMurry reaction is performed in refluxing anhydrous THF with Zn powder and a low valent titanium, obtained *in situ* by reduction of TiCl₄ with Zn powder. To highlight the

efficiency of the coupling reaction with McMurry conditions, we realize an experiment at a concentration that favors the intermolecular coupling (2.5 mg mL⁻¹). For this, the sample P3HT₂₅-CHO/CHO has been selected (*M_n*(SEC) = 5.1 kDa). After 4 h of reaction, the sample is purified and characterized by SEC (Figure S1). We clearly observe, as attested by the refractive index signal, the presence of molar mass up to 100 kDa. Moreover, the signal of the maximum intensity has slightly shifted to higher elution time, which could indicate the presence of cyclic structure coming from the decrease of the starting polymer concentration. This sample is analyzed by MALDI-ToF, and the zoom over the spectra at lower molar mass reveals the presence of two major populations (Figure S2), a P3HT terminated with two CHO moieties and a P3HT terminated with C₂H₄, which is according to the McMurry mechanism the result of intramolecular coupling reaction, i.e., a cyclic structure. So, it is now just a matter of aldehyde bis-telechelic polymer concentration to avoid as much as possible intermolecular coupling but promoting intramolecular coupling to obtain macrocyclic polythiophenes.

The intramolecular reaction is favored in highly diluted solution, which is not easily reachable at laboratory scale. Therefore, pseudo high dilution conditions consisting in very

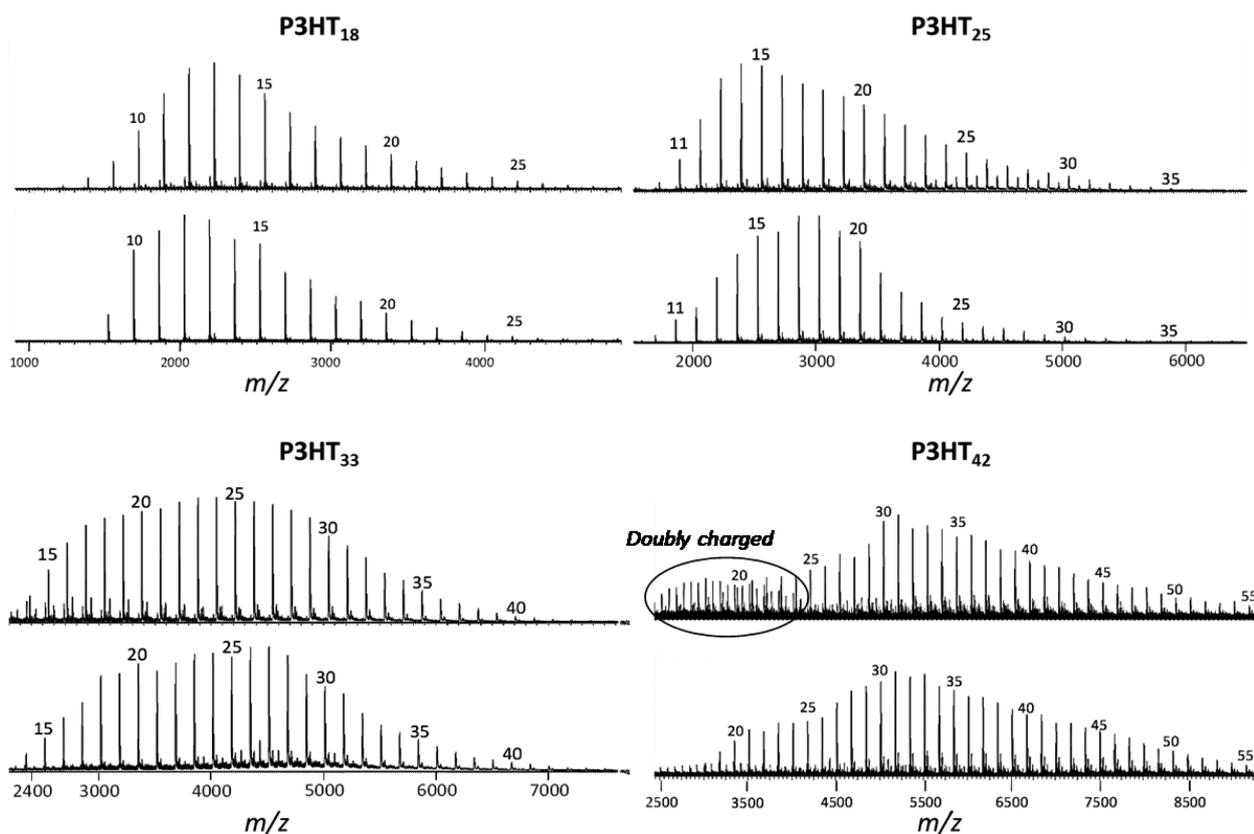


Figure 3. MALDI-ToF mass spectra of bis-CHO linear precursor (top of each figure) and after McMurry reaction (bottom of each figure).

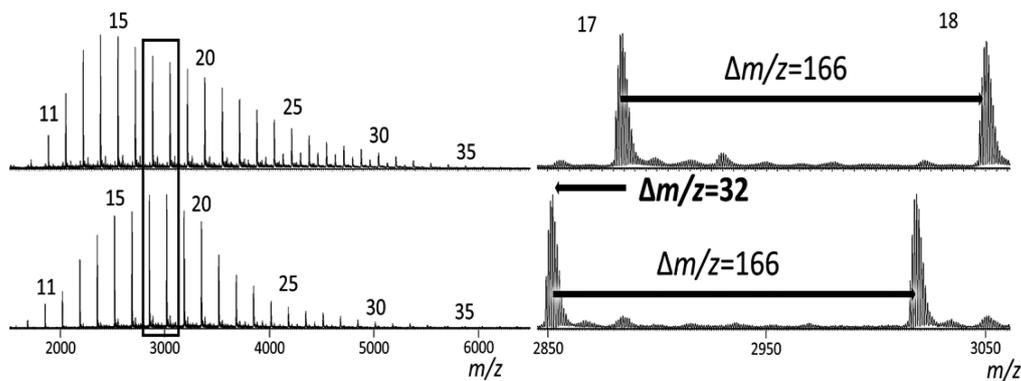


Figure 4. MALDI-ToF mass spectra of bis-CHO linear P3HT₂₅ precursor (top) and after McMurry reaction (bottom). An expanded region from m/z 2850 to m/z 3050 is illustrated on the right side.

slow addition of a feed solution of polymer into a solution containing the catalyst have been investigated. So, each sample of different molar mass has been diluted to a concentration of 0.2–0.12 mg mL⁻¹ and added to a large volume of solution containing 200 equiv of catalyst.

For each of the different molar mass systems, the SEC elugram of the reaction product recovered after the McMurry coupling reaction is shifted to higher retention time compared to the starting linear polymer (Figure 2). This agrees with the decrease of hydrodynamic radius, which likely indicates the efficiency of the intramolecular coupling reaction leading to the expected cyclic structure. Table 1 summarizes the macromolecular parameters of polymer samples before (-CHO/CHO) and after (-cyclic) the McMurry reaction. All the

parameters are of lower value after the reaction with a comparable molar mass dispersity below 1.3. The ratio of M_p (molecular weight of the highest peak) is more suitable than the ratio of M_n (number-average molar mass) to estimate the effectiveness of the cyclization reaction and has been used to compare batches of same molar masses. The increase of this ratio from 0.71 to 0.78 with the molar mass, from 4.28 to 12.96 kDa (equivalent PS), can be due to the columns used in SEC more or less efficient to separate short and long chains. Careful attention to the shape of the elugram at low retention time indicates the formation of few intermolecular couplings or the possible cyclic dimer formation. This effect is more pronounced for higher M_n and is consistent with the Jacobson–Stockmayer theory,⁴⁸ which supposes that long chains are more difficult to

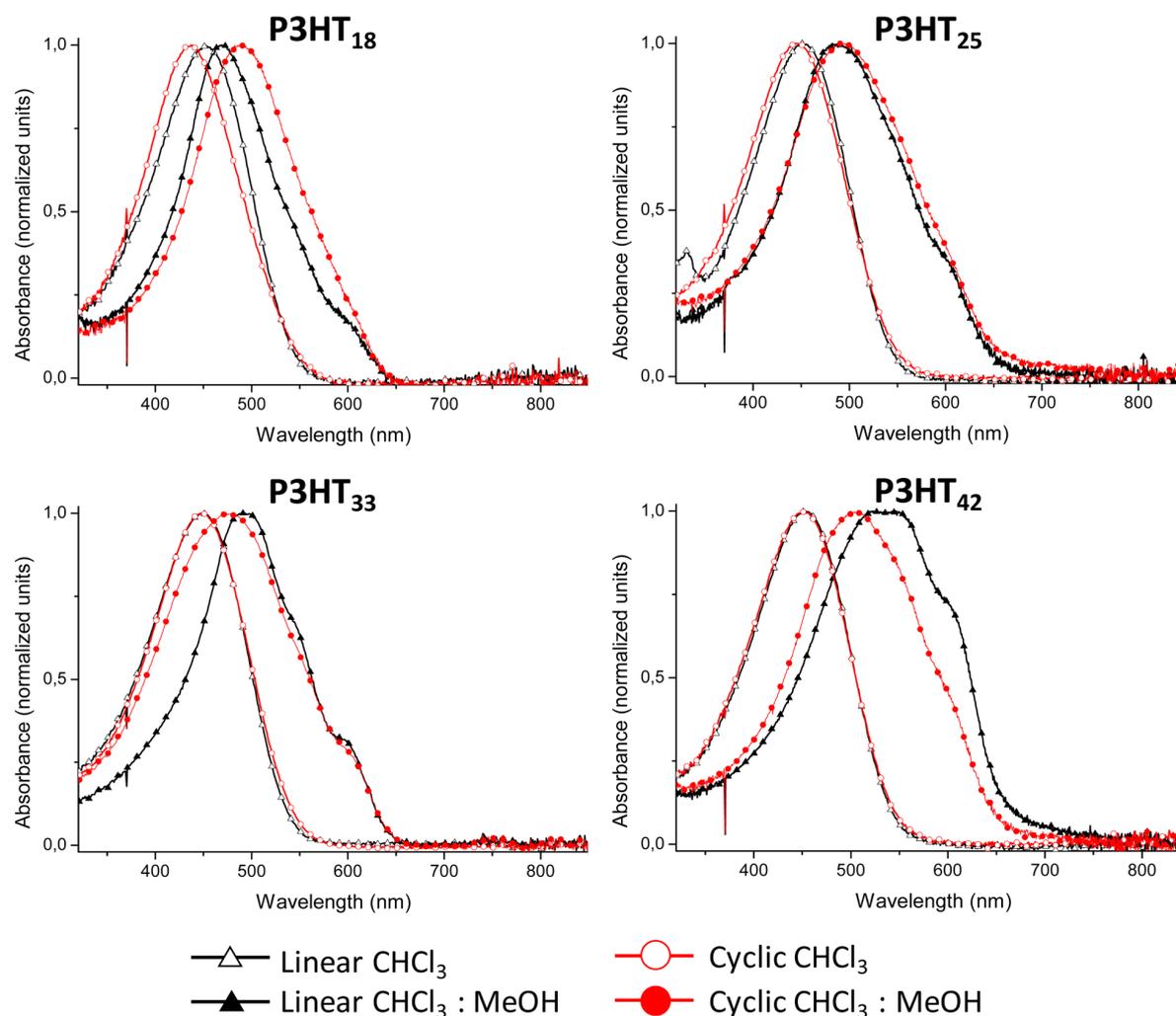


Figure 5. UV-vis spectra in solution of linear (black triangle) and cyclic (red circle) in CHCl_3 (empty symbol) and CHCl_3 :MeOH (20:80) (full symbol) for the four P3HT samples.

cyclize since the distance between both chain ends is higher. Therefore, the solution of longer linear polymer has to be more diluted than for shorter ones.

The SEC characterizations have been confronted to MALDI-ToF analyses on starting bis-CHO polythiophene and products formed after the McMurry coupling in diluted solution. The first observation of Figure 3 is the effective conservation of the molar mass distribution while the simple observation of SEC analyses would suggest a decrease of P3HT molecular weight. Actually, this observation can already be considered as a clear-cut evidence for the presence of cyclic structures.⁴⁹ Moreover, fine comparison between those mass spectra exhibits a shift of the mass to charge (m/z) signal of oligomer ions, i.e., a decrease of 32 mass units (Figure 4). This molar mass reduction is consistent with the McMurry mechanism involving the elimination of two oxygen atoms. It is worth pointing out that the smallest macrocycle obtained (in the P3HT₁₈ sample) contains nine thiophene rings and one ethylene bridge. This triggers a very high strain in the cycle with regards to the semicrystalline linear P3HT that contains seven thiophenic aromatic rings in an all-cis conformation to completely fold a linear chain.⁵⁰ On the other hand, the much larger macrocycle present in the P3HT₄₂ sample contains 55 thiophene rings.

Concerning the ^1H NMR spectra of the compounds after the intramolecular coupling reaction, by setting the integration of the $\alpha\text{-CH}_2$ of the hexyl side chain at 50 for the P3HT₂₅-cyclic (Figure 1), the signal in the aromatic region has a value of 27, which perfectly corresponds to the 25 thiophene rings and the two protons of the ethylene bridge (estimated at 6.91). The spectra did not present, in the limit of detection, any signals of remaining aldehyde protons indicating the very high yield of the cyclization reaction.

OPTICAL PROPERTIES

The comparison of absorption spectra of P3HT samples in diluted solutions and after addition of a nonsolvent is very reliable to estimate the polymer aggregation ability.^{51–56} Indeed, when the P3HT tends to self-organize, it adopts a fibrillar structure, and a bathochromic shift of the absorption maximum (up to 520 nm) is observed. More importantly, the presence of vibronic absorption bands in the UV-vis spectra at 550 and 630 nm is directly related to the importance of the aggregation.⁵¹ To solubilize P3HT of relative high molar mass, chloroform (or THF)⁵² or any high boiling point solvent such as xylene,^{53,54} anisole, or 1,2-dimethoxybenzene³⁶ can be used.

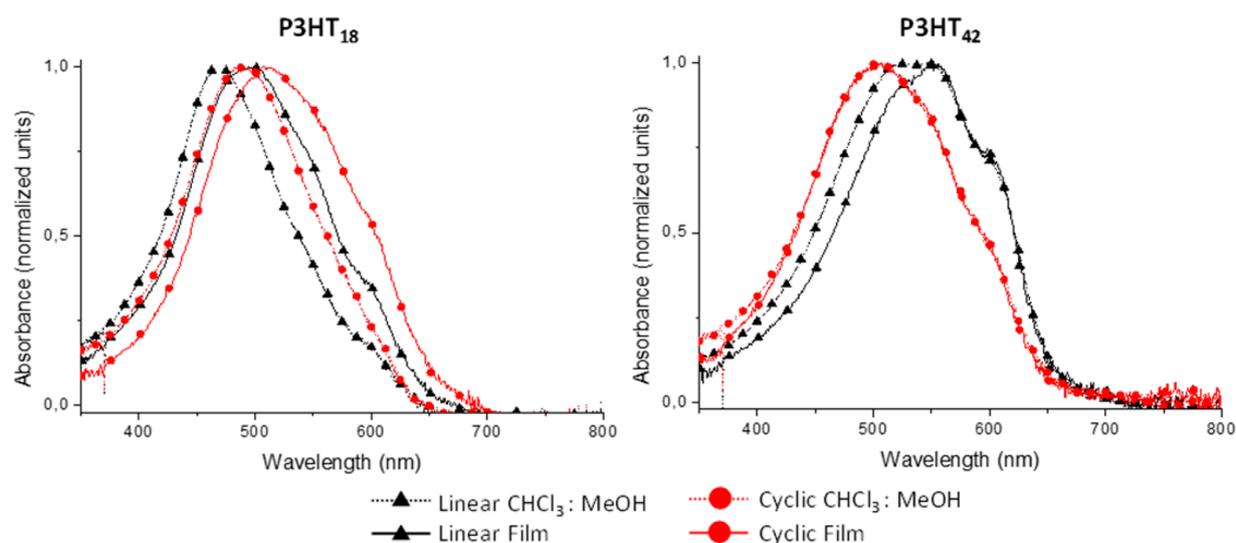


Figure 6. UV-vis spectra of linear (black triangle) and cyclic (red circle) P3HT₁₈ and P3HT₄₂ recorded in a CHCl₃:MeOH (20:80) solution (dashed line) and in their solid states (solid line).

The aggregation of this polymer can be observed in UV-vis spectroscopy by cooling down the solution⁵³ or by addition of a nonsolvent, like methanol⁵⁵ or hexane,⁵⁶ to the chloroform solution.

The absorption spectra in CHCl₃ for both long linear and cyclic systems (P3HT₃₃ and P3HT₄₂) are identical ($\lambda_{\max} = 450$ nm) since the effective conjugation length is reached and the bent of the chain has no influence on the spectroscopic properties. For short systems (P3HT₁₈ ($\lambda_{\max} = 437$ nm) and P3HT₂₅ ($\lambda_{\max} = 444$ nm)), the spectra of cyclic compounds are blue-shifted compared to linear ones with a more pronounced effect for P3HT₁₈. The high ring strain in this system and the steric hindrance of the alkyl chain of the two thiophene rings adjacent to the ethylene bridge induce a twist of consecutive rings, which decreases the orbital overlap and so the conjugation length on the macrocycle.

By addition of methanol to the chloroform solution ($V_{\text{CHCl}_3}:V_{\text{MeOH}} = 20:80$), all the polymers aggregate and the maximum absorption is bathochromically shifted. For linear systems, the increase of the molar mass induces a more pronounced shift to higher wavelengths (from 469 to 526 nm). A shoulder around 600 nm appears, indicating a small aggregation for small system P3HT₁₈ and P3HT₂₅. For longer system P3HT₃₃ and even more for P3HT₄₂, vibronic bands appear at 550 and 620 nm. In the latter case, the organized structure becomes predominant.

The cyclic systems present a completely different behavior upon aggregation when increasing the molar mass. For short chain length P3HT₁₈ and P3HT₂₅, the maximum absorption is higher than linear homologues of respectively 22 and 7 nm and a very small shoulder of vibronic band can be observed. This probably indicates a higher flatness of the macrocycle in the aggregated state which can be seen as a better π -conjugation. The aggregation of such cycle remains low since no vibronic bands are clearly observed. For longer system P3HT₃₃ and P3HT₄₂, the maximum absorption is lower than the linear equivalent of respectively 17 and 19 nm. This can be attributed to shorter effective conjugation length due to the bent conformation of the cyclic structure and probably to the steric hindrance of the regiodeflect. Moreover, the intensities of the

vibronic bands at 550 and 620 nm are clearly lower for P3HT₄₂, indicating a lower π - π interaction upon aggregation, coherent with the less organized giant cyclic structures. Those observations agree with the study of Seferos,³⁶ except for our smallest system, which is indeed shorter and did not contain aliphatic spacer that induces flexibility and probably better organization.

Since the aggregation behavior of a conjugated polymer is depending upon its molecular weight, the absorption of thin film of polymers deposited by drop-casting on a glass substrate has been compared with the absorption in the aggregated state. Figure 6 presents those results for P3HT₁₈ and P3HT₄₂ (see also Figure S7). For high molar masses, the addition of a poor solvent induces a strong aggregation identical to the solid state either for linear or cyclic systems. For short molar masses, the maximum of absorption is bathochromically shifted by 20 nm at the solid state because an important part of the chain remains in solution even with addition of poor solvent. The cyclic system presents a larger absorption spectrum with a more intense vibronic band as compared to its linear counterpart. This indicates a very high intermolecular interaction between cyclic structures in the film.

■ THERMAL PROPERTIES

The thermal analysis of linear and cyclic P3HT can give complementary information on their organization at the solid state and the crystallization and melting behavior can be probed by differential scanning calorimetry (DSC). Figure 7 represents the thermograms of the second heating and the first cooling at a rate of 10 °C/min of P3HT₃₃-H/H, -CHO/CHO, and -cyclic. Table 2 summarizes the temperature and the enthalpy of each thermal transition. The thermal transitions of P3HT₁₈ are not clearly defined due to the low molar mass and so are not reported here (Figure S8).

As classically observed, the increase in molecular weight of polymer induces an increase in thermal transition temperature and enthalpy, almost linearly⁵⁷ in the range of the studied molar mass (Figure 7B,C). Higher thermal transition (until P3HT₃₃) are observed for all P3HT-CHO/CHO compare to P3HT-H/H precursors, which can find the origin in the association by

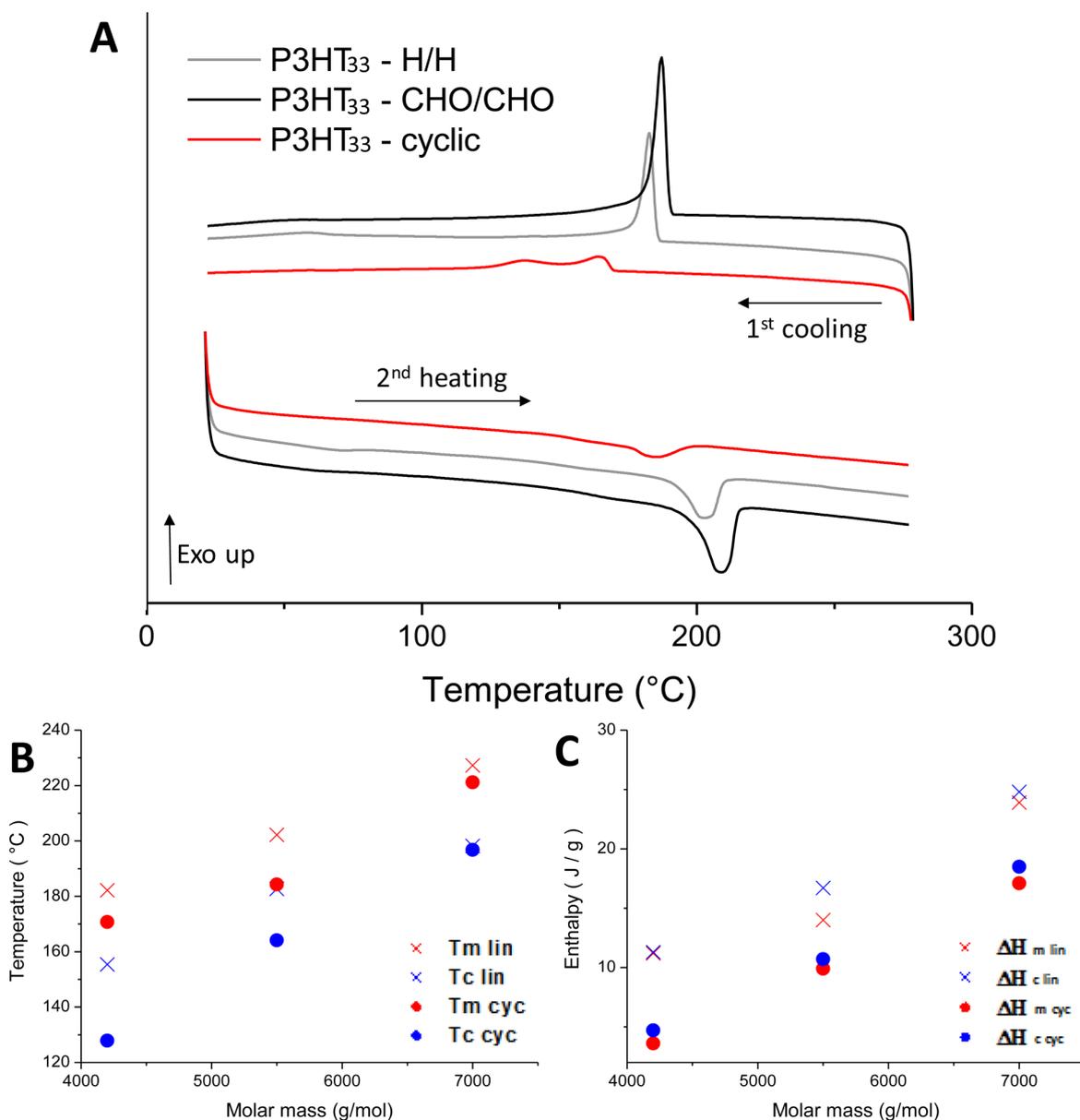


Figure 7. (A) DSC thermograms of P3HT₃₃-H/H (gray), P3HT₃₃-CHO/CHO (black), and P3HT₃₃-cyclic (red) recorded at 10 K/min. (B) Melting and crystallization temperatures of linear and cyclic P3HTs in function of molar mass. (C) Melting and crystallization enthalpy of linear and cyclic P3HTs as a function of molar mass.

hydrogen bonding of the aldehyde chain ends. The P3HT-H/H (P3HT₁₈ to P3HT₃₃, see [Supporting Information](#)) presents two thermal transitions during the cooling step, one around 60 °C, independent of the molar mass, and one ranging from 120 to 183 °C, dependent on the molar mass. The first one is attributed to a crystal–crystal phase transition with the disordering of the CH₃ of the alkyl side chain inducing a change in the π - π stacking of the thiophenic backbones.^{58,59}

The cyclic polymers present a completely different behavior upon heating and cooling. Both temperature and enthalpy of melting and crystallization ([Figures 6B,C](#)) are lower, indicating a decrease in the crystalline part of the samples. All the four cyclic polymers present upon cooling two close thermal transition differing by ca. 30 °C. The low transition observed around 60 °C for linear P3HT-H/H is absent. This suggests

that the alkyl chains are probably already interdigitated, which could explain the low temperature transition. Since the intermolecular interaction by π - π stacking has already been demonstrated to be quite low by UV–vis absorption, the temperature of the second transition is lower than the one of linear homologue.

The case of P3HT₄₂-cyclic is slightly different. At this molar mass, several studies have demonstrated that linear P3HT tends to fold itself.⁶⁰ We can therefore estimate that the organization of long cyclic chains is similar to linear ones. And so, the melting and crystallization temperatures are close to the linear homologues. The lower enthalpy still suggests a lower crystalline proportion.

To the best of our knowledge, this is the first time that cyclic poly(3-hexylthiophene) has been compared to the linear

Table 2. Thermal Properties of Linear P3HT_x-H/H, P3HT_x-CHO/CHO, and P3HT_x-Cyclic

sample	T_m (°C)	ΔH_{melt} (J/g)	T_c (°C)	ΔH_{cryst} (J/g)
P3HT ₂₅ -H/H	182.2	11.2	155.4	11.3
P3HT ₂₅ -CHO/CHO	192.9	11.5	172.8	12.9
P3HT ₂₅ -cyclic	149.8, 170.7	3.6	100.7, 127.9	4.7
P3HT ₃₃ -H/H	202.2	14.0	182.7	16.7
P3HT ₃₃ -CHO/CHO	209.0	16.6	187.1	19.7
P3HT ₃₃ -cyclic	184.3	9.9	137.4, 164.1	10.7
P3HT ₄₂ -H/H	227.3	23.9	198.2	24.8
P3HT ₄₂ -CHO/CHO	229.6	23.5	200.0	24.5
P3HT ₄₂ -cyclic	221.2	17.1	177.3, 196.8	18.5

counterpart, and since the precise determination of crystal nature remains quite complex, further structural investigations will be carried out and will be the scope of a future communication.

CONCLUSION

The cyclization of linear homotelechelic bis-aldehyde polythiophene has been performed for different chain lengths (from average DP of 18 to 42) via an intramolecular McMurry coupling reaction. The efficiency of this reaction in pseudo high dilution conditions leads to high yielded macrocyclic samples with very low contamination by linear precursor or cyclic dimer, as confirmed by complementary SEC, MALDI-ToF, and NMR characterizations. This allows for a direct comparison of the properties of macrocyclic and linear P3HT as well as a comparison for different size of polymers. For shorter systems, the ring strain induces in solution a twist between adjacent thiophene rings leading to lower wavelength absorption. On the contrary, at solid state, those macrocycles present an “infinite” conjugation and, so, higher wavelength absorption. For longer cyclic systems, when chains are aggregated, a higher disorder is observed compared to linear counterparts, even if the thermal transitions, as probed by DSC, are very close to linear equivalent systems.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.6b02599.

Supplementary figures, experimental protocols, SEC, DSC, MALDI-ToF, and ¹H NMR characterizations (PDF)

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Notes

The authors declare no competing financial interest.

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