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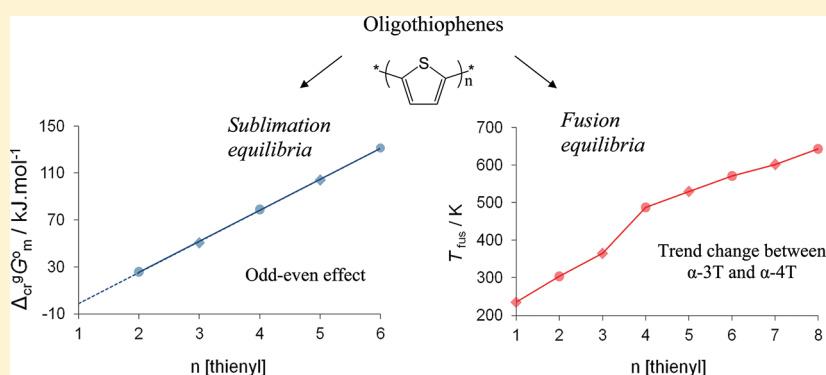
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Phase Stability Trend in Linear α -Polythiophene OligomersJosé C.S. Costa,[†] Carlos F.R.A.C. Lima,[†] Lígia R. Gomes,[‡] Bernd Schröder,[§] and Luís M.N.B.F. Santos^{†,*}[†]Centro de Investigação em Química, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre, 687, P-4169-007 Porto, Portugal[‡]CIAGEB, Faculdade de Ciências da Saúde, Escola Superior de Saúde da UFP, Universidade Fernando Pessoa, Rua Carlos da Maia, 296, P-4200-150 Porto, Portugal[§]CICECO, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal Supporting Information

ABSTRACT:



This work reports a thermodynamic study and structural analysis of a series of linear α -oligothiophenes to explore the effect of the successive increase of the number of thiophene rings on the thermodynamic properties related to solid–liquid and solid–gas equilibria. The compounds studied were α -quaterthiophene (α -4T), α -quinquthiophene (α -5T), and α -sexithiophene (α -6T). For each compound, the vapor pressures at different temperatures were measured using the Knudsen effusion method combined with a quartz crystal microbalance (KMBQ). From the obtained results, the standard molar enthalpies, entropies and Gibbs energies of sublimation were determined. For α -4T and α -5T (α -6T decomposes), the fusion temperatures and the standard molar enthalpies of fusion were determined in a power compensated differential scanning calorimeter (DSC). Standard molar entropies of fusion were derived accordingly. The obtained results for sublimation and fusion were compared with available data for the analogous thiophene (T), 2,2'-bitiophene (α -2T) and 2,2':5',2''-terthiophene (α -3T) compounds. To support the energetic study, a structural analysis was performed, based on the available X-ray crystallographic data for solid phase, and computational chemistry calculations, using density functional theory (DFT) with the hybrid exchange correlation functional (B3LYP) at the 6-311++G(d,p) level of theory, for gas phase. Entropic and enthalpic differentiations along the linear α oligothiophenes series were observed, suggesting a subtle odd–even effect and also a trend change in the series, centered at α -4T, which is probably related with the change in the supramolecular structure.

1. INTRODUCTION

The interest in physical properties of organic conjugated oligomers has intensified over the past few decades because of the ability of these compounds to act as organic semiconductors (OSCs). In terms of the polythiophenes (PTs), they were studied as conductive species in the last three decades and the earliest comprehensive review published on PTs dates from 1981.¹ Their semiconducting properties arise from the delocalization of the π molecular orbitals along the polymeric chain,² and thus, conjugated oligomers and polymers are of considerable interest as promising organic materials in electronic and optoelectronic devices.^{3–7} Among these compounds, oligothiophenes (OTs) and polythiophenes (PTs) have excellent electronic

properties such as stability under ambient conditions, structural versatility, simple and versatile synthesis, easy functionalization, and relatively low cost, which makes them one of the most studied and important classes of linear conjugated polymers.^{8–15} They have a wide range of applications, as for instance in conducting films,¹⁶ electrochromics,¹⁷ organic field-effect transistors (OFETs),¹⁸ electroluminescent devices,¹⁹ organic light-emitting diodes (OLEDs),²⁰ chemical sensors,^{21,22} laser microcavities,²³ and organic photovoltaic solar cells (OPVs).²⁴ In addition,

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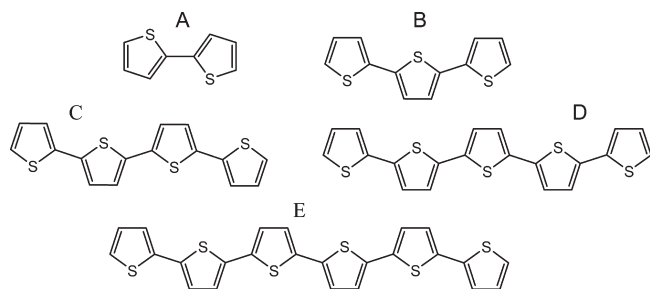


Figure 1. Schematic representation of α -bithiophene (A), α -terthiophene (B), α -quaterthiophene (C), α -quinquethiophene (D), and α -sexithiophene (E).

oligothiophenes and polythiophenes have recently found applications in areas of diagnostics, therapeutics and drug scanning.^{22,25} These materials are also considered to be a promising alternative to the traditional microelectronic devices based on typical inorganic semiconductors. Thiophene oligomers can easily be synthesized and characterized and provide interesting models for understanding the structural, electronic and thermochemical features that might control charge transport and optical properties in the corresponding polymers. As far as thiophene materials are concerned, unsubstituted α -oligothiophenes are the simplest compounds of this family. For instance, high charge mobility was found for α -sexithiophene (α -6T).²⁶ Because of their importance for the understanding of the conductivity properties of these materials and their behavior as charge carriers, the crystal structures of several thiophene oligomers have been reported in the literature.^{27,28} Thiophene-based materials exhibit a variety of intra- and intermolecular interactions such as van der Waals interactions, weak hydrogen bonds and π - π stacking.^{6,7}

This work is focused on the phase transitions (fusion and sublimation) of some thiophene conjugated oligomers: α -quaterthiophene (α -4T); α -quinquethiophene (α -5T), and α -sexithiophene (α -6T), as illustrated in Figure 1. The vaporization enthalpies were also derived by combining the thermodynamic parameters of fusion and sublimation. The importance of volatility studies in the manufacturing technology of thin films of these materials should be noted because one of the most common deposition methods is vacuum deposition.^{29,30}

This work aims to explore the origins of energetic and entropic differentiation in the condensed phases of α -oligothiophenes caused by the increase of the number of thiophene rings in the chain. The results obtained are compared and analyzed altogether with previous literature data for 2,2'-bithiophene (α -2T)^{31,32} and 2,2':5',2''-terthiophene (α -3T).³³

The literature thermodynamic parameters for α -2T and α -3T were measured using the same experimental conditions employed for the other members of the series measured in our work (α -4T, α -5T, and α -6T). The trends in the standard molar enthalpies and entropies of fusion and sublimation for this series of compounds are analyzed and related with the crystal phase and gas phase studies.

2. EXPERIMENTAL SECTION

2.1. Purification and Characterization of Thiophene Oligomers. The compounds α -quaterthiophene and α -sexithiophene

were obtained commercially from Sigma-Aldrich Chemical Co. The compound α -quinquethiophene was obtained commercially from TCI Europe N. V. Prior to its use, α -4T, α -5T, and α -6T were washed with acetone and subsequently purified by successive sublimations under reduced pressure (<10 Pa), at $T = 423$ K, $T = 483$ K, and $T = 563$ K, respectively. The final purity of the samples was verified by gas chromatographic analysis (GC), using an HP 4890 apparatus equipped with an HP-5 column, cross-linked, 5% diphenyl and 95% dimethylpolysiloxane. For α -4T the following mass fraction purity was obtained: 0.999. For α -5T and α -6T, a clean GC analysis was obtained, consistent with a mass fraction purity of 1.000. The relative atomic masses used in our work were those recommended by the IUPAC Commission in 2007.³⁴

2.2. Solid–Liquid Equilibrium–Differential Scanning Calorimetry. The temperatures and the standard molar enthalpies of fusion for α -4T and α -5T (α -6T decomposes when reaching the onset of fusion) were measured in a power compensation differential scanning calorimeter, SETARAM Model DSC 141, using a heating rate of $0.0333 \text{ K} \cdot \text{s}^{-1}$, hermetically sealed aluminum crucibles, and samples of about 5 mg in each experiment. A constant flow of nitrogen was applied. The standard molar entropies of fusion for each compound were derived. The temperature and heat flux scales were calibrated by measuring the temperature and the enthalpy of fusion of some reference materials:³⁵ *o*-terphenyl, benzoic acid, indium, 4-methoxy benzoic acid, tin, lead, and zinc. To measure their temperature and enthalpy of fusion, at least five concordant experiments for each reference compound were performed. The compounds studied were measured with the same experimental procedure used in the calibration runs.

2.3. Solid–Gas Equilibrium–Knudsen Effusion/Quartz Crystal Microbalance. Knudsen effusion based methods are the most widely used for measuring the vapor pressures of organic compounds for pressures lower than 1 Pa. The vapor pressures of α -quaterthiophene, α -quinquethiophene and α -sexithiophene as a function of temperature were measured by the combined Knudsen/Quartz crystal effusion apparatus.³⁶ This technique is based on the simultaneous gravimetric and quartz crystal microbalance mass loss detection. The technique has the advantages of requiring smaller sample sizes and results in shorter effusion times and the possibility of achieving temperatures up to 650 K.

2.4. Computational Thermochemistry. Quantum chemical calculations were performed with the Gaussian 03 software package.³⁷ The optimization of the geometries as well as the fundamental vibrational frequency calculations were performed for the compounds using the B3LYP/6-311++G(d,p) level of theory.^{38,39} The frequencies were scaled using the scaling factors of 0.9887 for the zero-point energy correction (ZPE), and of 0.9688, 1.0102, and 1.0161 for the fundamental vibrational frequencies when applied to the calculation of heat capacity, enthalpy and entropy, respectively.⁴⁰ A 1D-hindered rotor formalism was considered for the treatment of the thienyl–thienyl internal rotation. This treatment considers the formalism introduced by Broadbelt and co-workers using the program CALCTHERM.^{41–43} In this context, the torsional potentials were fitted by a Fourier series and the hindered rotor Schrödinger equations solved numerically. These calculations were used for the determination of gas phase heat capacities, enthalpies and entropies for all species at $T = 298.15$ K, corrected for hindered rotation.

2.5. Prediction of Vaporization Enthalpies with COSMO-RS. The standard procedure of COSMO-RS (conductor-like

Table 1. Experimental and Literature Data for the Temperatures, Standard Molar Enthalpies, and Standard Molar Entropies of Fusion, for Thiophene, 2,2'-Bithiophene, 2,2':5',2''-Terthiophene, α -Quaterthiophene, and α -Quinquethiophene and derived, entropies, and Gibbs energies of fusion at $T = 298.15\text{ K}^a$

compound	$T_{\text{fus}}\text{ (K)}$	$\Delta_{\text{cr}}^{\text{H}}_{\text{m}}(T_{\text{fus}})$ ($\text{kJ}\cdot\text{mol}^{-1}$)	$\Delta_{\text{cr}}^{\text{S}}_{\text{m}}(T_{\text{fus}})$ ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)	note	$\Delta_{\text{cr}}^{\text{H}}_{\text{m}}(298.15\text{ K})$ ($\text{kJ}\cdot\text{mol}^{-1}$)	$\Delta_{\text{cr}}^{\text{S}}_{\text{m}}(298.15\text{ K})$ ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)	$\Delta_{\text{cr}}^{\text{G}}_{\text{m}}(298.15\text{ K})$ ($\text{kJ}\cdot\text{mol}^{-1}$)
thiophene	235.0	5.0	21.4	ref 50	8.4 ± 1.3	34.3 ± 4.8	-1.8 ± 1.9
2,2'-bithiophene	304.2 ± 0.1	16.5 ± 0.1	54.2 ± 0.3	ref 32	16.2 ± 0.1	53.1 ± 0.4	0.3 ± 0.2
2,2':5',2''-terthiophene	365.3 ± 0.2	20.7 ± 0.3	56.6 ± 0.7	ref 33	17.0 ± 1.3	45.6 ± 4.1	3.5 ± 1.8
α -quaterthiophene	487.6 ± 0.4	42.5 ± 0.3	87.2 ± 0.6	this work	32.2 ± 3.8	60.4 ± 9.8	14.2 ± 4.8
α -quinquethiophene	529.4 ± 0.4	47.0 ± 0.3	88.8 ± 0.6	this work	34.4 ± 4.6	57.6 ± 11.5	17.3 ± 5.8

^a The values for T , α -2T, and α -3T were taken from the respective references. The uncertainties of the experimental results were assigned based on independent experiments as $t \times s/\sqrt{n}$, including the calibration uncertainty, where t is obtained from student's t -distribution, s is the standard deviation, and n is the number of independent experiments. From literature data,⁶⁴ melting points: α -sexithiophene, 571 K; α -septithiophene, 601 K; α -octithiophene, 643 K.

screening model for real solvents) calculations consists of two main steps: quantum chemical COSMO calculations for the molecular species involved, and COSMO-RS statistical calculations,⁴⁴ leading directly to the chemical potential in the liquid state; the chemical potential of the gaseous state contains additional empirical assumptions. The enthalpy of vaporization, for a given temperature T , is obtained directly from vapor pressure calculations.

COSMO-RS calculations were done with COSMOtherm, version C2.1 revision 01.10,⁴⁵ using the parameter file BP_TZVP_C21_0110.⁴⁶ Prior DFT/COSMO (density functional theory/conductor-like screening model) calculations were performed using Turbomole V6.2,⁴⁷ with the RI-DFT BP level using the def-TZVP basis set.

3. RESULTS

3.1. Fusion Temperatures, Enthalpies, Entropies, and Gibbs Energies of Fusion. For α -4T and α -5T, the experimental fusion temperatures, T_{fus} , and standard molar enthalpies of fusion at T_{fus} , $\Delta_{\text{cr}}^{\text{H}}_{\text{m}}(T_{\text{fus}})$, were measured in a power compensation differential scanning calorimeter, SETARAM Model DSC 141. The compound α -sexithiophene decomposes on melting, so it was not possible to obtain the thermodynamic parameters of fusion for this compound. For the α -3T compound, the fusion temperatures and enthalpies of fusion were remeasured by DSC and the results obtained are in full agreement with the literature data. The detailed experimental results respecting the fusion are given as Supporting Information (Tables S1 and S2 and Figures S1, S2, and S3).

The hypothetical molar enthalpies of fusion at $T = 298.15\text{ K}$ were calculated, according to eq 1

$$\Delta_{\text{cr}}^{\text{H}}_{\text{m}}(T) = \Delta_{\text{cr}}^{\text{H}}_{\text{m}}(T_{\text{fus}}) + \Delta_{\text{cr}}^{\text{C}}_{\text{p,m}}(T - T_{\text{fus}}) \quad (1)$$

The hypothetical molar entropy of fusion at $T = 298.15\text{ K}$ was calculated for each compound according to eq 2

$$\Delta_{\text{cr}}^{\text{S}}_{\text{m}}(T) = \Delta_{\text{cr}}^{\text{H}}_{\text{m}}(T_{\text{fus}})/T_{\text{fus}} + \Delta_{\text{cr}}^{\text{C}}_{\text{p,m}} \ln(T/T_{\text{fus}}) \quad (2)$$

where $\Delta_{\text{cr}}^{\text{C}}_{\text{p,m}} = C_{\text{p,m}}^{\circ}(\text{l}) - C_{\text{p,m}}^{\circ}(\text{cr})$. The value of $\Delta_{\text{cr}}^{\text{C}}_{\text{p,m}} = 54.4\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ was used according to the equation proposed

by Sidgewick⁴⁸ and recommended by Chickos,⁴⁹ and the uncertainty interval was taken as $\pm 20\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

The hypothetical molar Gibbs energies of fusion at $T = 298.15\text{ K}$ were calculated for each compound according to eq 3

$$\Delta_{\text{cr}}^{\text{G}}_{\text{m}}(298.15\text{ K}) = \Delta_{\text{cr}}^{\text{H}}_{\text{m}}(298.15\text{ K}) - 298.15 \times \Delta_{\text{cr}}^{\text{S}}_{\text{m}}(298.15\text{ K}) \quad (3)$$

Table 1 shows the experimental fusion temperatures, the values for the standard molar enthalpies and entropies of fusion at the fusion temperature, and the hypothetical standard molar enthalpies, entropies and Gibbs energies of fusion, at $T = 298.15\text{ K}$, for the compounds studied. The data for thiophene (T),⁵⁰ 2,2'-bithiophene (α -2T),³² and 2,2':5',2''-terthiophene (α -3T)³³ is also presented.

3.2. Heat Capacities of Crystalline and Gaseous Phases.

Table 2 presents the values of the standard molar heat capacities at $T = 298.15\text{ K}$ in the crystalline, $C_{\text{p,m}}^{\circ}(\text{cr}, 298.15\text{ K})$, and gas phases, $C_{\text{p,m}}^{\circ}(\text{g}, 298.15\text{ K})$, and of the standard molar heat capacities of sublimation, $\Delta_{\text{cr}}^{\text{C}}_{\text{p,m}}(298.15\text{ K})$, calculated as $\Delta_{\text{cr}}^{\text{C}}_{\text{p,m}} = C_{\text{p,m}}^{\circ}(\text{g}) - C_{\text{p,m}}^{\circ}(\text{cr})$ for the compounds studied. For α -quaterthiophene and α -quinquethiophene, $C_{\text{p,m}}^{\circ}(\text{cr}, 298.15\text{ K})$ was measured in this work, using a precise heat capacity drop calorimeter. The measurement procedure and the description of the apparatus have been described in detail elsewhere.⁵¹ Additional information concerning the experimental calibration procedure of the apparatus is available as Supporting Information (Tables S3 and S4). For 2,2'-bithiophene³² and 2,2':5',2''-terthiophene,³³ $C_{\text{p,m}}^{\circ}(\text{cr}, 298.15\text{ K})$ was obtained from the literature. For α -sexithiophene, $C_{\text{p,m}}^{\circ}(\text{cr}, 298.15\text{ K})$ was extrapolated from the plots of $C_{\text{p,m}}^{\circ}(\text{cr}, 298.15\text{ K}) = f[n(\text{thienyl})]$ for the α -(2T–5T) series. For 2,2'-bithiophene, $C_{\text{p,m}}^{\circ}(\text{g}, 298.15\text{ K})$ was calculated by computational chemistry considering the thienyl–thienyl 1D-hindered rotor correction in the frequencies calculations. For 2,2':5',2''-terthiophene, α -quaterthiophene, α -quinquethiophene and α -sexithiophene, $C_{\text{p,m}}^{\circ}(\text{g}, 298.15\text{ K})$ was computationally calculated using DFT with B3LYP/6-311++G(d,p) level of theory, considering an additive combination of 1D-hindered rotors taken from the 2,2'-bithiophene data with respect to the thienyl–thienyl internal rotations. For α -3T, α -4T, α -5T, and α -6T, two, three, four, and five 1D-hindered rotors were considered, respectively, and all of them were treated as the analogous rotor in α -2T. Additional information concerning the computational procedure is available as Supporting Information (Tables S5, S6, and S7 and Figure S4).

Table 2. Values of $C_{p,m}^{\circ}(\text{cr})$, $C_{p,m}^{\circ}(\text{g})$, and $\Delta_{\text{cr}}^{\circ}C_{p,m}^{\circ}$, Calculated at $T = 298.15$ K, for 2,2'-Bithiophene, 2,2':5',2''-Terthiophene, α -Quaterthiophene, α -Quinquethiophene, and α -Sexithiophene^a

compound	$C_{p,m}^{\circ}(\text{cr})$ ($\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)	note	$C_{p,m}^{\circ}(\text{g})$ ($\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)	$\Delta_{\text{cr}}^{\circ}C_{p,m}^{\circ}$ ($\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)
2,2'-bithiophene	205.5 ± 1.3	ref 32	150.0 ± 3.8	-55.5 ± 4.0
2,2':5',2''-terthiophene	267.5 ± 1.1	ref 33	225.7 ± 5.7	-41.8 ± 5.8
α -quaterthiophene	333.2 ± 1.3	this work	301.3 ± 7.6	-31.9 ± 7.7
α -quinquethiophene	402.8 ± 2.9	this work	377.1 ± 9.5	-25.7 ± 10.0
α -sexithiophene	466.7 ± 3.0	extrapolated value	452.7 ± 11.4	-14.0 ± 11.8

^a The values for α -2T and α -3T were taken from the respective references. The uncertainties in $C_{p,m}^{\circ}(\text{g})$ are based on the observed difference between the value obtained with quantum chemical calculations and experimental literature value for the gaseous heat capacity of thiophene at $T = 298.15$ K ($72.4 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$).⁶⁵

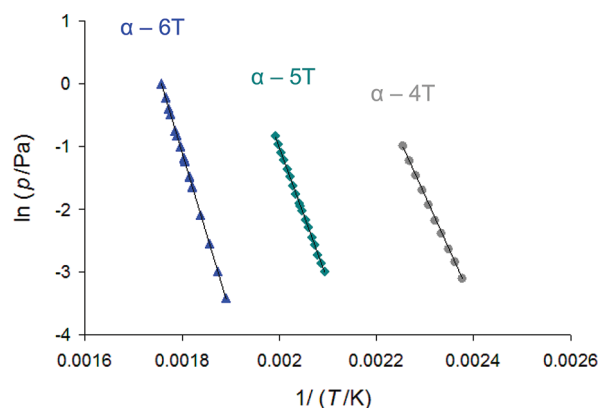


Figure 2. Plots of $\ln p$ against $1/T$ for α -quaterthiophene (α -4T), α -quinquethiophene (α -5T), and α -sexithiophene (α -6T).

3.3. Vapor Pressures, Enthalpies, Entropies, and Gibbs Energies of Sublimation. The standard molar enthalpies of sublimation at the mean temperature of the sublimation experiments, $\langle T \rangle$, were derived for α -quaterthiophene, α -quinquethiophene, and α -sexithiophene, using the integrated form of the Clausius–Clapeyron eq 4

$$\ln(p/\text{Pa}) = a - b \times (K/T) \quad (4)$$

where a is a constant and $b = \Delta_{\text{cr}}^{\circ}H_m^{\circ}(\langle T \rangle)/R$. The plots of $\ln p = f(1/T)$ for α -4T, α -5T and α -6T are presented in Figure 2.

The detailed experimental results of sublimation are given as Supporting Information (Tables S8, S9, and S10).

Table 3 presents the global results obtained in the sublimation studies for α -4T, α -5T, and α -6T. The data for α -2T³¹ and α -3T³³ is also presented.

The standard molar enthalpies of sublimation at the mean temperature were determined by the parameter b of the Clausius–Clapeyron equation, and the molar entropies of sublimation at $\langle T \rangle$ and $p(\langle T \rangle)$, $\Delta_{\text{cr}}^{\circ}S_m(\langle T \rangle, p(\langle T \rangle))$, were calculated by eq 5

$$\Delta_{\text{cr}}^{\circ}S_m(\langle T \rangle, p(\langle T \rangle)) = \Delta_{\text{cr}}^{\circ}H_m^{\circ}(\langle T \rangle)/\langle T \rangle \quad (5)$$

The standard molar enthalpies of sublimation, at $T = 298.15$ K, $\Delta_{\text{cr}}^{\circ}H_m^{\circ}(298.15 \text{ K})$, were determined by eq 6

$$\Delta_{\text{cr}}^{\circ}H_m^{\circ}(T) = \Delta_{\text{cr}}^{\circ}H_m^{\circ}(\langle T \rangle) + (T - \langle T \rangle) \times \Delta_{\text{cr}}^{\circ}C_{p,m}^{\circ} \quad (6)$$

The standard molar entropies of sublimation, at $T = 298.15$ K, $\Delta_{\text{cr}}^{\circ}S_m(298.15 \text{ K})$, were calculated using the eq 7

$$\Delta_{\text{cr}}^{\circ}S_m^{\circ}(T) = \Delta_{\text{cr}}^{\circ}S_m(\langle T \rangle, p(\langle T \rangle)) + \Delta_{\text{cr}}^{\circ}C_{p,m}^{\circ}(T) \times \ln(T/\langle T \rangle) - R \times \ln(p^{\circ}/p(\langle T \rangle)) \quad (7)$$

where $p^{\circ} = 10^5$ Pa.

The standard molar Gibbs energies of sublimation were calculated through eq 8, where the parameters are referenced to $T = 298.15$ K

$$\Delta_{\text{cr}}^{\circ}G_m^{\circ}(T) = \Delta_{\text{cr}}^{\circ}H_m^{\circ}(T) - T \times \Delta_{\text{cr}}^{\circ}S_m^{\circ}(T) \quad (8)$$

The vapor pressures at $T = 298.15$ K were calculated through eq 9

$$p(T) = p^{\circ} \times \exp\left(-\frac{\Delta_{\text{cr}}^{\circ}G_m^{\circ}(T)}{R \times T}\right) \quad (9)$$

where $p^{\circ} = 10^5$ Pa.

Table 4 lists the derived standard ($p^{\circ} = 10^5$ Pa) molar enthalpies, entropies, and Gibbs energies of sublimation and the vapor pressures, at $T = 298.15$ K, for α -2T, α -3T, α -4T, α -5T, and α -6T. For thiophene, $\Delta_{\text{cr}}^{\circ}H_m^{\circ}$ and $\Delta_{\text{cr}}^{\circ}S_m^{\circ}$ were derived using eqs 10 and 11, respectively:

$$\Delta_{\text{cr}}^{\circ}H_m^{\circ}(T) = \Delta_{\text{cr}}^{\circ}H_m^{\circ}(T) + \Delta_{\text{l}}^{\circ}H_m^{\circ}(T) \quad (10)$$

$$\Delta_{\text{cr}}^{\circ}S_m^{\circ}(T) = \Delta_{\text{cr}}^{\circ}S_m^{\circ}(T) + \Delta_{\text{l}}^{\circ}S_m^{\circ}(T) \quad (11)$$

Table 5 lists the standard ($p^{\circ} = 10^5$ Pa) molar enthalpies, entropies, and Gibbs energies of vaporization, at $T = 298.15$ K, for the compounds studied, derived from the combined experimental results for the sublimation and fusion, using eqs 10 and 11. For thiophene, $\Delta_{\text{f}}^{\circ}H_m^{\circ}$ was taken from the literature⁵² and $\Delta_{\text{f}}^{\circ}S_m^{\circ}$ was calculated as $S_m^{\circ}(\text{g}) - S_m^{\circ}(\text{l})$. The predicted values for the enthalpies of vaporization obtained with COSMO-RS are presented, as well.

Table 6 presents the molar entropies in crystalline, liquid and gas phases, at $T = 298.15$ K, for the compounds studied. Total gas phase entropies were obtained from ab initio calculations, corrected for hindered rotation. Entropies in the crystal and liquid phases were derived from the sublimation and fusion results using eqs 12 and 13, respectively. For thiophene, $S_m^{\circ}(\text{l})$ was obtained from the literature.⁵⁰

$$S_m^{\circ}(\text{cr}, T) = S_m^{\circ}(\text{g}, T) - \Delta_{\text{cr}}^{\circ}S_m^{\circ}(T) \quad (12)$$

$$S_m^{\circ}(\text{l}, T) = \Delta_{\text{cr}}^{\circ}S_m^{\circ}(T) + S_m^{\circ}(\text{cr}, T) \quad (13)$$

Table 3. Experimental Sublimation Results Obtained for 2,2'-Bithiophene, 2,2':5',2''-Terthiophene, α -Quaterthiophene, α -Quinquethiophene, and α -Sexithiophene Where a and b are from the Clausius–Clapeyron Equation, $\ln(p/Pa) = a - b \times (K/T)$ and $b = \Delta_{cr}^{\circ}H_m(\langle T \rangle)/R$; $R = 8.314472 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ^a

compound	a	b (K)	r^2	$\langle T \rangle$ (K)	$p(\langle T \rangle)$ (Pa)	$\Delta_{cr}^{\circ}H_m(\langle T \rangle)$ (kJ·mol ⁻¹)	$\Delta_{cr}^{\circ}S_m(\langle T \rangle, p(\langle T \rangle))$ (J·K ⁻¹ ·mol ⁻¹)	note
2,2'-bithiophene	37.73 ± 0.18	10348 ± 50	0.99997	283.14	0.442	86.0 ± 0.4	303.7 ± 1.4	ref 31
2,2':5',2''-terthiophene	36.60 ± 0.12	13527 ± 42	0.99991	351.01	0.144	112.5 ± 0.3	320.5 ± 1.0	ref 33
α -quaterthiophene	37.97 ± 0.29	17289 ± 127	0.9996	432.02	0.129	143.8 ± 1.1	332.9 ± 2.4	this work
α -quinquethiophene	41.72 ± 0.06	21370 ± 29	0.99997	489.94	0.149	177.7 ± 0.2	362.7 ± 0.5	this work
α -sexithiophene	45.19 ± 0.18	25709 ± 97	0.9998	552.38	0.260	213.8 ± 0.8	387.0 ± 1.4	this work

^aThe values for α -2T and α -3T were taken from the respective references.

Table 4. Values of the Standard ($p^{\circ} = 0.1 \text{ MPa}$) Molar Enthalpies, $\Delta_{cr}^{\circ}H_m^{\circ}$, Entropies, $\Delta_{cr}^{\circ}S_m^{\circ}$, and Gibbs Energies, $\Delta_{cr}^{\circ}G_m^{\circ}$, of Sublimation, and Vapour Pressures, at $T = 298.15 \text{ K}$, for 2,2'-Bithiophene, 2,2':5',2''-Terthiophene, α -Quaterthiophene, α -Quinquethiophene, and α -Sexithiophene

compound	$\Delta_{cr}^{\circ}H_m^{\circ}$ (kJ·mol ⁻¹)	$\Delta_{cr}^{\circ}S_m^{\circ}$ (J·K ⁻¹ ·mol ⁻¹)	$\Delta_{cr}^{\circ}G_m^{\circ}$ (kJ·mol ⁻¹)	$p(298.15 \text{ K})$ (Pa)	$d(\Delta_{cr}^{\circ}G_m^{\circ})/dn$ (kJ·mol ⁻¹)
2,2'-bithiophene ^a	85.2 ± 1.3	198.3 ± 1.4	26.0 ± 1.3	2.8×10^0	
2,2':5',2''-terthiophene	114.7 ± 1.8	215.5 ± 1.4	50.5 ± 1.8	1.4×10^{-4}	24.4
α -quaterthiophene	148.1 ± 2.6	231.9 ± 3.7	78.9 ± 2.8	1.5×10^{-9}	28.5
α -quinquethiophene	182.6 ± 3.0	263.9 ± 4.6	103.9 ± 3.3	6.2×10^{-14}	25.0
α -sexithiophene	217.4 ± 3.6	288.8 ± 7.4	131.3 ± 4.2	1.0×10^{-18}	27.3

^aValues recalculated from original literature data using the $\Delta_{cr}^{\circ}C_{p,m}$ derived in this work.

Table 5. Values of the Standard ($p^{\circ} = 0.1 \text{ MPa}$) Molar Enthalpies, $\Delta_f^{\circ}H_m^{\circ}$, Entropies, $\Delta_f^{\circ}S_m^{\circ}$, and Gibbs Energies, $\Delta_f^{\circ}G_m^{\circ}$, of Vaporization, Calculated at $T = 298.15 \text{ K}$, for Thiophene, 2,2'-Bithiophene, 2,2':5',2''-Terthiophene, α -Quaterthiophene, α -Quinquethiophene, and α -Sexithiophene

compound	$\Delta_f^{\circ}H_m^{\circ}$ (kJ·mol ⁻¹)	$\Delta_f^{\circ}H_m^{\circ}$ COSMO-RS (kJ·mol ⁻¹)	$\Delta_f^{\circ}S_m^{\circ}$ (J·K ⁻¹ ·mol ⁻¹)	$\Delta_f^{\circ}G_m^{\circ}$ (kJ·mol ⁻¹)
thiophene	34.7 ⁵³	37.2	102.5 ± 5.0	4.3 ± 5.0
2,2'-bithiophene	69.0 ± 1.3	64.4	145.2 ± 1.5	25.7 ± 1.3
2,2':5',2''-terthiophene	97.7 ± 2.2	91.1	169.9 ± 4.3	47.0 ± 2.6
α -quaterthiophene	115.9 ± 4.6	118.2	171.5 ± 10.5	64.7 ± 5.5
α -quinquethiophene	148.2 ± 5.5	144.7	206.4 ± 12.4	86.7 ± 6.6
α -sexithiophene		171.0		

Table 6. Values of the Entropies in Crystalline, $S_m^{\circ}(\text{cr})$, Liquid, $S_m^{\circ}(\text{l})$, and Gas, $S_m^{\circ}(\text{g})$, Phases, at $T = 298.15 \text{ K}$, for Thiophene, 2,2'-Bithiophene, 2,2':5',2''-Terthiophene, α -Quaterthiophene, α -Quinquethiophene, and α -Sexithiophene^a

compound	$S_m^{\circ}(\text{cr})$ (J·K ⁻¹ ·mol ⁻¹)	$S_m^{\circ}(\text{l})$ (J·K ⁻¹ ·mol ⁻¹)	$S_m^{\circ}(\text{g})$ (J·K ⁻¹ ·mol ⁻¹)
thiophene		181.2 ± 0.4 ⁵⁰	283.6 ± 5.0
2,2'-bithiophene	186.7 ± 5.2	239.8 ± 5.2	385.0 ± 5.0
2,2':5',2''-terthiophene	284.5 ± 5.2	330.0 ± 6.6	500.0 ± 5.0
α -quaterthiophene	377.2 ± 6.2	437.7 ± 11.7	609.2 ± 5.0
α -quinquethiophene	455.8 ± 6.8	513.4 ± 13.3	719.7 ± 5.0
α -sexithiophene	539.8 ± 8.9		828.6 ± 5.0

^aThe uncertainty in $S_m^{\circ}(\text{g})$ was considered as $\pm 5 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$.

4. DISCUSSION

4.1. Solid–Gas Equilibrium. Figure 3 presents the trends of the heat capacities for the crystal and gas phases (at $T = 298.15 \text{ K}$) for the α -oligothiophene series. A linear relation between α -(T-6T) was obtained with a constant increase in $C_{p,m}^{\circ}(\text{g})$ per thienyl group ($75.7 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ per ring). For $C_{p,m}^{\circ}(\text{cr})$, a

linear relation from α -2T was observed ($r^2 = 0.9993$), with a constant increase per thienyl group ($65.8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ per ring), allowing the extrapolation of $C_{p,m}^{\circ}(\text{cr})$ for larger crystalline polythiophenes.

On the basis of the experimental results of sublimation and some literature data, Figure 4 shows the plots of $\Delta_{cr}^{\circ}H_m^{\circ} = f[n(\text{thienyl})]$, $\Delta_{cr}^{\circ}S_m^{\circ} = f[n(\text{thienyl})]$, and $\Delta_{cr}^{\circ}G_m^{\circ} = f[n(\text{thienyl})]$,

for the α -oligothiophene series, where $[n(\text{thienyl})]$ denotes the number of thiophene rings in the molecule. A linear relation in $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}$ at $T = 298.15$ K, was obtained for the α -3T, α -4T, α -5T, and α -6T, as shown in Figure 4 (A) ($r^2 = 0.99991$). The value of $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}$ for α -2T was not considered since it is an outlier relative to the α -(3T–6T) correlation. α -2T does not present central rings as the other members of this series. From α -3T the correlation is linear with a constant increase in $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}$ per thienyl moiety ($34.3 \text{ kJ} \cdot \text{mol}^{-1}$ per ring), allowing the extrapolation of $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}$ for larger polythiophenes. The larger than expected $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}$ for α -2T (relative to the α -(3T–6T) correlation) can be because the central rings are less able to interact via intermolecular forces than peripheral ones, which may be related with S–H intermolecular contacts.

Figure 4B presents the plot of standard molar entropies of sublimation against the number of thienyl units. Two different trends in the series are clearly observed: α -(2–4)T and

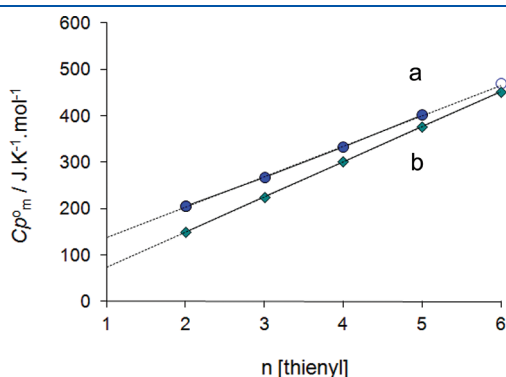


Figure 3. Trends of the heat capacities, $C_{p,m}^{\circ}$, at $T = 298.15$ K, for the crystal (a) and gas (b) phases for the α -oligothiophene series.

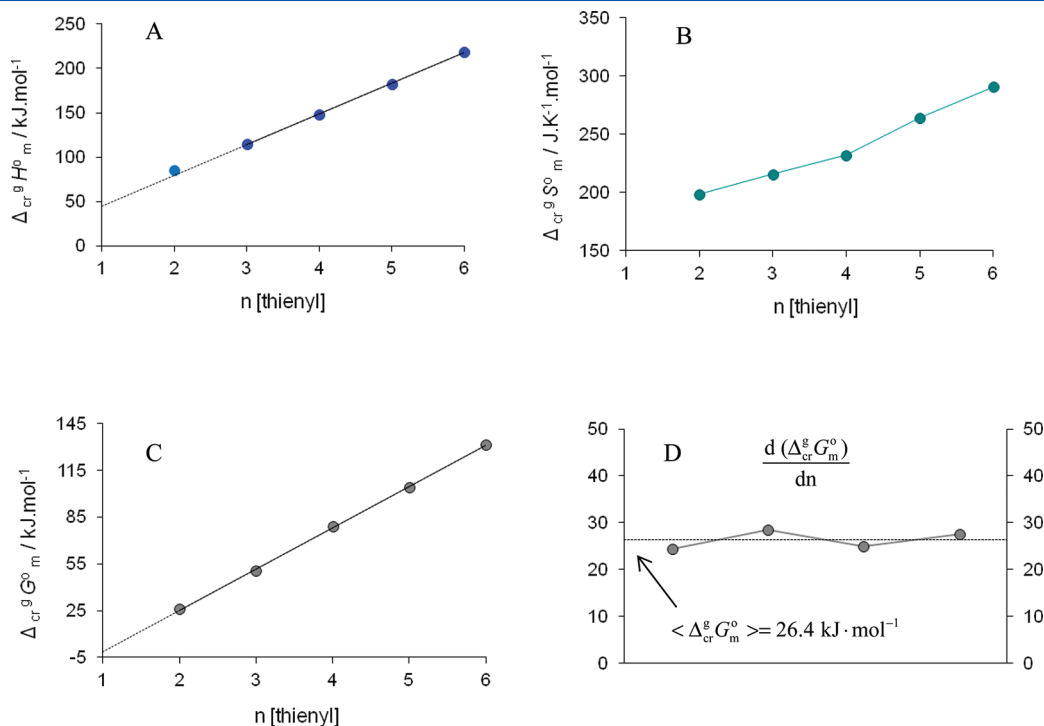


Figure 4. Trends of $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}$ (A), $\Delta_{\text{cr}}^{\text{g}}S_{\text{m}}^{\circ}$ (B), and $\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\circ}$ (C), at $T = 298.15$ K, for the α -oligothiophene series and representation of the second derivative values of Gibbs energies, $d(\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\circ})/dn$ (D).

α -(4–6)T, which may be related with a change of the crystalline structure before and after the α -4T.

Figure 4C presents a plot of $\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\circ}$ at $T = 298.15$ K, for the α -(2T–6T) series as a function of $n(\text{thienyl})$. A linear relation in the series was observed ($r^2 = 0.9995$). Due to the entropic compensation in $\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\circ}$, 2,2'-bithiophene fits well in this series. The plot of $\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\circ}$ indicates a subtle odd–even effect, with the even number of thiophene rings characterized slight by stability increase in crystal packing, hence reducing their volatility. The analysis of the second derivative of $\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\circ}$, Figure 4D, shows a clearly odd–even effect for this thermodynamic parameter and from the data observed for the α -(2–6)T series, the contribution per thienyl group in $\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\circ}$ for linear thiophene oligomers can be estimated (average value of $26.4 \text{ kJ} \cdot \text{mol}^{-1}$ per ring).

4.2. Solid–Liquid Equilibrium. In Figure 5, the trends of T_{fus} , $\Delta_{\text{cr}}^{\text{l}}G_{\text{m}}^{\circ}(298.15 \text{ K})$, $\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ}(298.15 \text{ K})$, and $\Delta_{\text{cr}}^{\text{l}}S_{\text{m}}^{\circ}(298.15 \text{ K})$ along the α -oligothiophene series are presented. The thermodynamic parameters of fusion refer to the hypothetical values corrected to $T = 298.15$ K, thus allowing a direct comparison of the fusion parameters for this series. To compare the phase stability of different oligothiophenes, the analysis of melting points becomes important. Fusion temperatures are related to enthalpic and entropic contributions, as indicated by the relation $T_{\text{fus}} = \Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ}(T_{\text{fus}})/\Delta_{\text{cr}}^{\text{l}}S_{\text{m}}^{\circ}(T_{\text{fus}})$. The analysis of Figure 5A indicates a subtle odd–even effect, with an even number of thiophene rings favoring the stability of the crystal phase (leading to relatively higher melting point). This effect corroborates the results observed for $\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\circ}$. The analysis of the melting point temperatures shows a clear trend change from α -3T to α -4T. This suggests different supramolecular packing in solid oligothiophenes at this point. Considering the odd–even effect, the melting points of larger oligothiophenes may be estimated from the correlation shown in Figure 5A, according to the

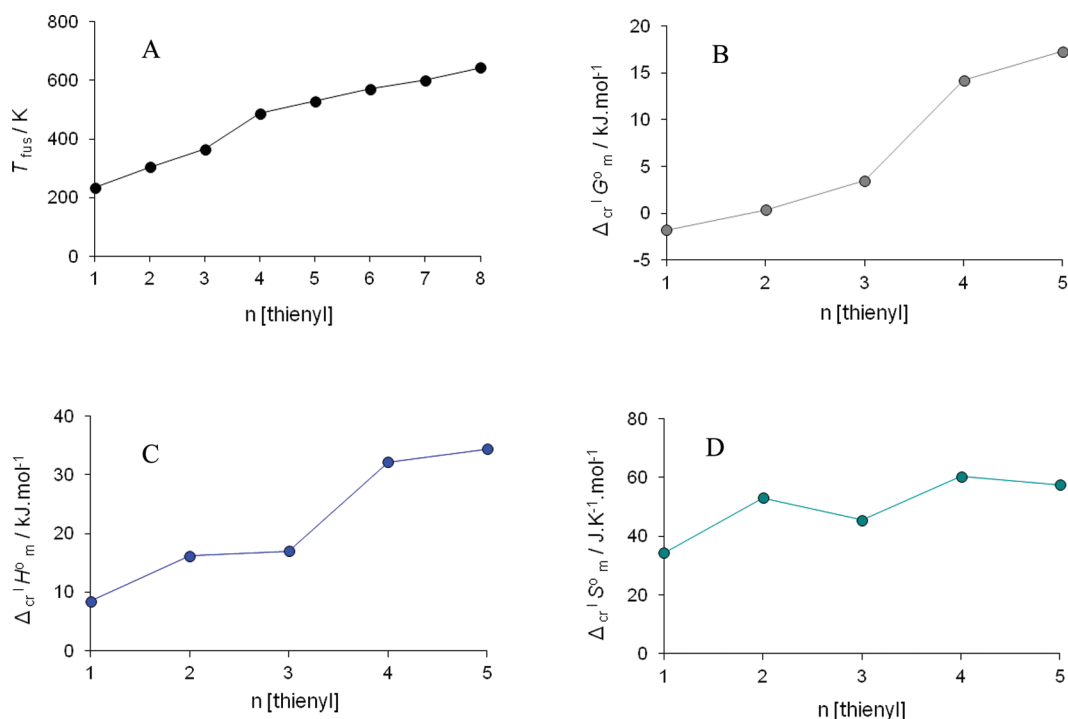


Figure 5. Trends of the fusion temperatures, T_{fus} (A), $\Delta_{\text{cr}}^1 G_m^0$ (B), $\Delta_{\text{cr}}^1 H_m^0$ (C), and $\Delta_{\text{cr}}^1 S_m^0$ (D), at $T = 298.15$ K, for the α -oligothiophene series. The derived uncertainties are expected to be partially canceled out if a differential analysis is considered and for this reason were not included in the plots.

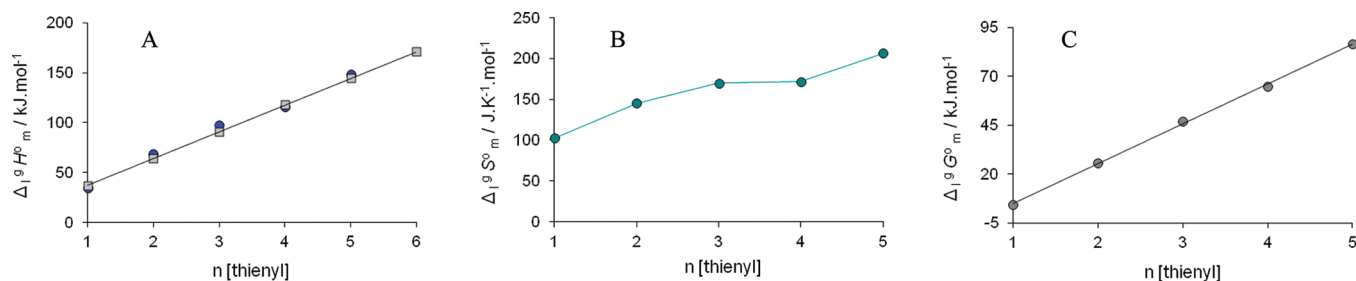


Figure 6. Trends of $\Delta_{\text{vap}}^0 H_m^0$ (●, derived experimental values; □, predicted values by COSMO-RS) (A), $\Delta_{\text{fus}}^0 H_m^0$ (B), and $\Delta_{\text{sub}}^0 H_m^0$ (C), at $T = 298.15$ K, for the α -oligothiophene series.

correlation obtained with odd α -oligothiophenes, or with even α -oligothiophenes.

Figure 5B represents the plot of the hypothetical $\Delta_{\text{cr}}^1 G_m^0$ at $T = 298.15$ K. The conclusions drawn from the plot of $\Delta_{\text{cr}}^1 G_m^0(298.15 \text{ K})$ as a function of the number of thienyl units in the molecule are the same as those presented before from the plot of fusion temperatures, Figure 5A: beyond α -4T a different trend is observed, and a small odd–even effect is present.

Figure 5C and D indicate that both the trends in $\Delta_{\text{cr}}^1 H_m^0$ (298.15 K) and $\Delta_{\text{cr}}^1 S_m^0$ (298.15 K) are also consistent with an odd–even effect along this series.

4.3. Liquid–Gas Equilibrium. For the thiophene series, the hypothetical vaporization data, at $T = 298.15$ K, derived from the combination of the experimental sublimation and fusion results, are presented in Figure 6. Figure 6A also presents the correlation obtained for the enthalpies of vaporization predicted by the COSMO-RS approach. The prediction for the enthalpies of vaporization with COSMO-RS is in reasonable agreement with the derived experimental results. It is worth noting that the increment in the enthalpy of

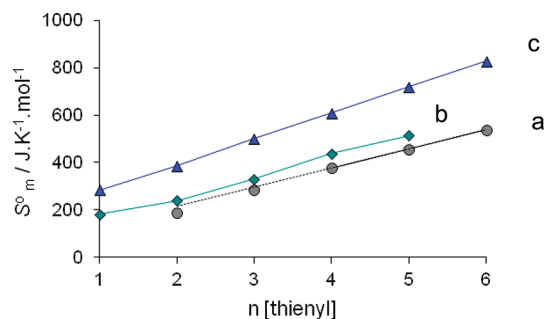


Figure 7. Entropy, S_m , at $T = 298.15$ K, for the crystal (a), liquid (b), and gas (c) phases, of the α -oligothiophene series.

vaporization per thienyl group is nicely reproduced by the COSMO-RS results.

Figure 6 (B) presents a plot of $\Delta_{\text{fus}}^0 H_m^0(298.15 \text{ K})$ as a function of the number of thienyl units, and suggests a trend change from α -3T to α -4T, which had already been observed in other

thermodynamic parameters. Figure 6 (C) presents the plot for $\Delta^{\circ}_{\text{cr}}G_{\text{m}}(298.15 \text{ K})$ showing a good linear correlation ($r^2 = 0.999$).

Figure 7 presents the trends in S_{m}° at $T = 298.15 \text{ K}$, for the crystal, liquid and gas phases of the α -oligothiophene series. According to this representation, two different linear trends representing the crystal phase can be observed: α -(2–4)T and α -(4–6)T. Assuming that the relation observed for the α -(4–6)T series holds for larger molecules ($r^2 = 0.9996$), it is possible to extrapolate the values of $S_{\text{m}}^{\circ}(\text{cr}, 298.15 \text{ K})$ for larger thiophene oligomers, based on an incremental value for $S_{\text{m}}^{\circ}(\text{cr}, 298.15 \text{ K})$ of $81.3 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ per ring. It is interesting to note that the odd–even effect is more pronounced in $S_{\text{m}}^{\circ}(\text{l}, 298.15 \text{ K})$, and can be related to some structural differentiation in the liquid phase.

4.4. Structural Analysis. From the analysis of the thermodynamic parameters obtained for these systems two main aspects can be highlighted: (i) T_{fus} , $\Delta^{\circ}_{\text{cr}}H_{\text{m}}(298.15 \text{ K})$, $\Delta^{\circ}_{\text{cr}}G_{\text{m}}(298.15 \text{ K})$, and $\Delta^{\circ}_{\text{cr}}G_{\text{m}}$ values indicate a subtle odd–even effect, and (ii) a trend change is observed in the T_{fus} , $\Delta^{\circ}_{\text{cr}}H_{\text{m}}(298.15 \text{ K})$, $\Delta^{\circ}_{\text{cr}}G_{\text{m}}(298.15 \text{ K})$ and $S_{\text{m}}^{\circ}(\text{cr}, 298.15 \text{ K})$ plots versus $n(\text{thienyl})$ for $n = 4$. To explore how structural aspects can be related to solid–gas and solid–liquid equilibria, an analysis of the crystal structures of the compounds studied was carried out.

Odd–even effects were already observed in some thermodynamic properties of paraffins,⁵³ fatty acids,⁵⁴ liquid crystals,⁵⁵ and long-chain amphiphiles.⁵⁶ It was observed that the odd–even effect can be noted in some physical properties, such as the melting points⁵³ and carrier mobility.⁵⁷ Concerning the linear oligothiophenes, the results obtained show that even oligothiophenes present relatively higher $\Delta^{\circ}_{\text{cr}}G_{\text{m}}$ values, indicating a reduced volatility and increased crystal packing stability. The most stable structure of the thiophene oligomers should correspond to the one that has the most efficient packing and can be related with the $\pi \cdots \pi$, $\text{CH} \cdots \pi$, $\text{S} \cdots \text{S}$, and $\text{S} \cdots \text{H}$ interactions. Because the periphery of the oligothiophenes consists of hydrogen and sulfur atoms, the packing will be influenced to a large extent by interactions involving those H and S atoms. However, an analysis of the H bond interactions on the available structures^{27,28} does not indicate any significant differentiation between even or odd oligothiophenes. All of them show a supramolecular herringbone arrangement stabilized by weak $\text{CH} \cdots \pi$ interactions. Nevertheless, crystal density is also a consequence of packing efficiency and, according to literature data,²⁷ the calculated densities of α -5T and α -7T are lower than the densities observed for even-numbered thiophene oligomers, suggesting a less efficient packing for the former cases, in agreement with the odd–even effect in this work.

Concerning the second highlighted aspect, conformational structure analysis revealed that all α -T, with the exception of α -2T and α -3T, form a planar chain. In α -3T, there is a slight deviation of 7 – 9° from planarity, while in α -2T, the rings are disordered across the C–C single bond.²⁸ In α -2T and α -3T, the thienyl rings are twisted while in α -(4–8)T they are planar. This contributes to a higher symmetry in the oligomers belonging to the latter group, and it has been observed by various authors that higher symmetry can be associated with lower $\Delta^{\circ}_{\text{cr}}S_{\text{m}}$ and $\Delta^{\circ}_{\text{cr}}S_{\text{m}}^{\circ}$ ^{58–63} which is in nice agreement with the experimental results obtained in this work for fusion and sublimation. It should be noted however, that differentiation due to symmetry can either be ascribed to an increase of $S_{\text{m}}^{\circ}(\text{cr})$, or to a decrease of $S_{\text{m}}^{\circ}(\text{l})$ and $S_{\text{m}}^{\circ}(\text{g})$ or to a combination of both. Regardless of what the correct interpretation is, more symmetry is associated with lower entropies of sublimation and fusion.

5. CONCLUSIONS

This study evaluated the structural and energetic effects associated with the number of thiophene rings on the thermodynamic properties related to solid–liquid and solid–gas equilibria in some linear α -oligothiophenes. The thermodynamic results obtained for sublimation and fusion are consistent with the information obtained by X-ray crystal structure analysis. According to the results obtained for the series of polythiophenes studied in this work, it seems possible to extrapolate the various thermodynamic parameters for a polymer whose number of thiophene rings is larger, and for which the measurement of some of these properties would be practically impossible. For the series of oligothiophenes studied, we have verified the occurrence of a subtle odd–even effect and that even-numbered oligomers possess greater stability in the crystalline phase, which agrees well with the crystallographic structures. A trend change in the series between α -3T and α -4T was also observed, which is probably related with the change in the supramolecular structure.

Although the structural study is important by itself, this work has demonstrated that experimental knowledge of the properties associated with thermodynamic equilibrium is essential for interpretation and understanding of the structure and phase stability of organic compounds, important information for the development of new organic semiconductors and materials.

■ ASSOCIATED CONTENT

S Supporting Information. Tables showing experimental results, optimized geometries, potential profiles, electronic energies, heat capacities, and enthalpies and figures showing thermograms and a potential profiles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*Tel: +351 220402536. Fax: +351 220402520. E-mail: lbsantos@fc.up.pt

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