Concentration-Dependent Thermochromism and Supramolecular Aggregation in Solution of Triblock Copolymers Based on Lengthy Oligothiophene Cores and Poly(benzyl ether) Dendrons

Joke J. Apperloo and René A. J. Janssen*

Laboratory for Macromolecular and Organic Chemistry, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

Patrick R. L. Malenfant and Jean M. J. Fréchet*

Department of Chemistry, University of California, Berkeley, California 94720-1460

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ABSTRACT: Self-complexation of triblock copolymers based on undeca- and heptadecathiophene cores attached to generation three Fréchet-type poly(benzyl ether) dendrons in solution at low temperature leads to the formation of relatively small but well-defined supramolecular assemblies. The formation of these aggregates is associated with a strong thermochromic effect. Upon cooling dilute solutions, minor concentration-*independent* changes in the optical absorption due to *intra*chain planarization precede significant concentration-*dependent* thermochromic changes that are shown to originate from *inter*molecular $\pi-\pi$ stacking interactions. The structurally well-defined nature of the substrates enables the determination of distinct temperature regimes for both intra- and intermolecular thermochromic changes. Furthermore, combining thermodynamic expressions for both the concentration and temperature dependence of aggregation allows a quantitative analysis of the self-assembly phenomenon. The results show that the supramolecular aggregates are relatively small, yet well-defined involving from 5 to 6 molecules in an average aggregate. The apparent size limitation of the aggregates is ascribed to steric constraints imparted by the dendritic wedges. Relatively high exothermicities accompany the aggregation process, increasing with conjugation length from −73.0 kJ/mol with the undecathiophene triblock (G3-T11-G3) to −85.8 kJ/mol for the heptadecathiophene analogue (G3-T17-G3), suggesting that $\pi-\pi$ stacking is the driving force for complexation.

Introduction

The study of compositional and architectural block copolymers is an emerging area of research in which the compatibility, or lack thereof, between the different blocks may be used to achieve self-organization on the nanometer scale.[1] As a result, a number of approaches have been explored in recent years that combine linear conjugated fragments with dendritic wedges. For example, dendritic wedges[2] have been used as side chains to solubilize and/or segregate conjugated polymer chains[3] or as the termini of well-defined conjugated oligomers to create AB- or ABA-type block copolymer architectures.[4]

Many π-conjugated polymers, including block copolymers incorporating π-conjugated segments, exhibit thermochromism or solvatochromism, i.e., change in their color as a function of temperature or the nature of the solvent.[5−8] For π-conjugated polymers in solution, thermochromism has been found to be concentration independent, and hence, thermochromic transitions have been attributed to an intrachain phenomenon.[5] The origin of the thermochromism rests with the increase in torsional strain along the main chain, as well as the coiling of the side chains that result from an increase in temperature. This translates into a decrease in effective conjugation length and a blue shift of the optical absorption. In addition, thermochromic changes reflect interchain interactions[5−8] and accompany the formation of small aggregates or microcrystallites. To date, no explicit answer has been provided on whether the thermochromic behavior is driven by *intra*chain conformational changes or by *inter*chain interactions and if aggregation or microcrystallization of the π-conjugated polymer chains takes place only after an intramolecular chain conformational change has occurred.[5−8]

We report on the use of well-defined, dendritic triblock substrates, to distinguish between *intra*- and *inter*molecularly driven thermochromic changes. We show that oligothiophenes having either 11 or 17 repeat units that are end-substituted with generation three (G3) Fréchet-type poly(benzyl ether) dendritic wedges,[2] G3-T11-G3 and G3-T17-G3, respectively, form supramolecular aggregates in solution at low temperature. The highly branched nature of the dendritic blocks ensures excellent solubility for the ABA triblock copolymers, despite the minimal substitution of the oligothiophene backbone. As the solubility of the triblocks is high, it is possible to study a considerable range of concentrations, and a clear concentration dependence of the thermochromic changes could therefore be uncovered, while distinct temperature ranges could be assigned to either intra- or intermolecular phenomena. The concentration dependence of the thermochromism gives strong support for the *inter*molecular origin of this effect.

From the concentration and temperature dependence of the color changes, we find that rather well-defined supramolecular aggregates made up of a small number (4−7) of "dumbbell-shaped" oligothiophenes are formed with high reaction enthalpies. The driving force for this self-complexation is attributed to the strong $\pi-\pi$ interactions that result from the assembly of the conjugated blocks. Consistent with this view, the aggregation of the longest compound (G3-T17-G3) is more exothermic and

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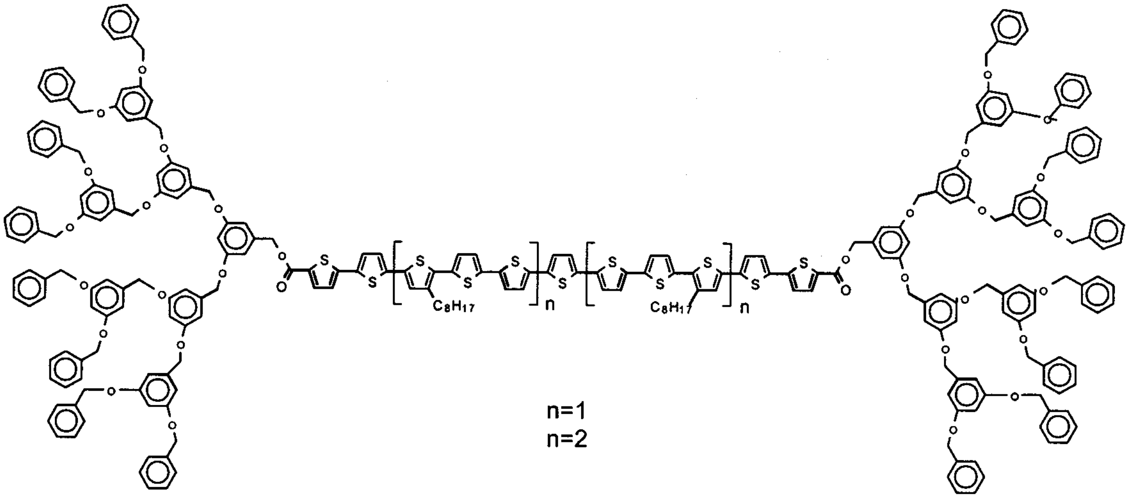
Chart 1



occurs at significantly higher temperature or lower concentrations. The $\pi-\pi$ interactions are favored by the highly planar conjugated configuration that can be attained as a consequence of minimal β-substitution and, to a lesser extent, the favorable van der Waals interactions between the dendritic fragments (Chart 1).

Experimental Section

The synthesis of G3-T11-G3 and G3-T17-G3 has been described in detail elsewhere.[4c,9] Solvents were distilled, dried, and deoxygenated before use. UV/vis/near-IR spectra were recorded using a Perkin-Elmer Lambda 900 spectrometer equipped with an Oxford Optistat cryostat for variable temperature experiments and 10 or 1 mm near-IR grade Suprasil quartz cells. Temperature was kept constant within ±0.3 K, and spectra were corrected for volume changes. For the temperature-dependent optical absorption experiments the concentration was in the range 10^{-6}–10^{-4} M.

Results and Discussion

Thermochromic Studies of G3-T11-G3 and G3-T17-G3 in Dichloromethane. Lowering the temperature of dilute solutions (10^{-6}–5×10^{-5} M) of G3-T11-G3 in dichloromethane initially results in a small red shift of the absorption band at 2.60 eV (477 nm). However, a sudden and pronounced transition to a much more resolved spectrum takes place at temperatures between 270 and 240 K (Figure 1a). At this point, the low-energy vibronics at 2.39 eV (519 nm) and 2.49 eV (498 nm, marked with an asterisk) become more pronounced, and a new low-energy band at 2.20 eV (0–0, 564 nm) appears in the spectrum (Figure 1a). Because of the excellent solubility of these “dumbbell-shaped” oligothiophene triblock copolymers, the thermochromic changes could be studied as a function of concentration over nearly 2 orders of magnitude. Figure 2a shows that the temperature at which the pronounced thermochromic transition occurs depends on the concentration and shifts to lower values for lower concentrations. For the lengthier system, G3-T17-G3, the spectral changes are stronger than in the case of G3-T11-G3 (Figure 1b). Also, at identical concentrations, the aggregation of G3-T17-G3 starts at temperatures that are 30–40 K higher than for G3-T11-G3 (Figures 1b and 2b), and the low-energy vibronics, especially the lowest energy (0–0) band, are much more pronounced. Furthermore, all transitions of G3-T17-G3 are slightly red-shifted compared to those of G3-T11-G3 (i.e., initial neutral transition at 2.58 eV (481 nm) and vibronics at 2.11 (0–0), 2.30, and 2.45 eV (588, 539, and 506 nm)) as a result of the increased effective conjugation length.

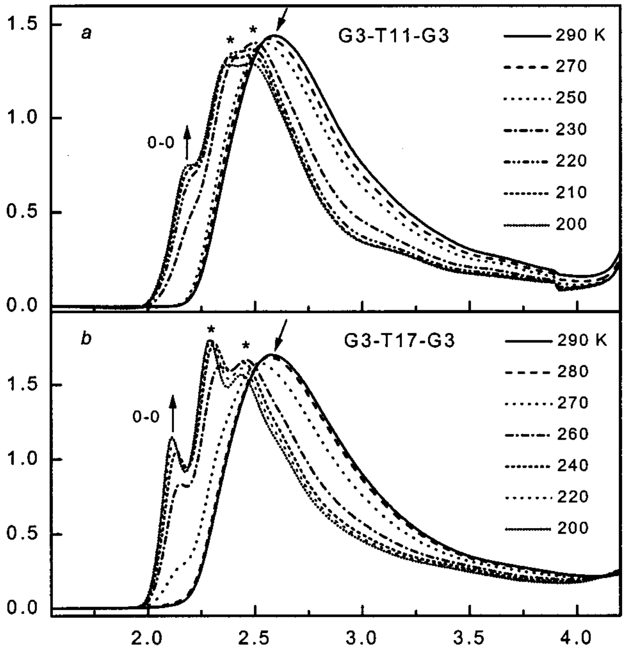


Figure 1. Optical absorption changes upon cooling dichloromethane solutions of (a) G3-T11-G3 and (b) G3-T17-G3.

The spectral changes that occur upon cooling can, in principle, originate from both *intra*- and *inter*molecular contributions, yet the concentration dependence of the thermochromic changes observed for these systems suggests an *inter*molecular mechanism. In accordance with the intermolecular nature of the effect, the new (0–0) band for G3-T11-G3 at 2.2 eV (564 nm) and for G3-T17-G3 at 2.11 eV (588 nm), which appears in the UV/vis spectrum at higher temperatures for more concentrated solutions (Figure 2), is ascribed to aggregated oligothiophenes subject to *inter*molecular ($\pi-\pi$) stacking interactions. As was previously observed for poly(diacetylene)s,[8e] the $\pi-\pi$ stacking might become significant once the oligothiophene backbone has achieved a relatively planar conformation, thus facilitating a favorable interchain alignment with much $\pi-\pi$ overlap. The *inter*molecular origin of the (0–0) band can also be

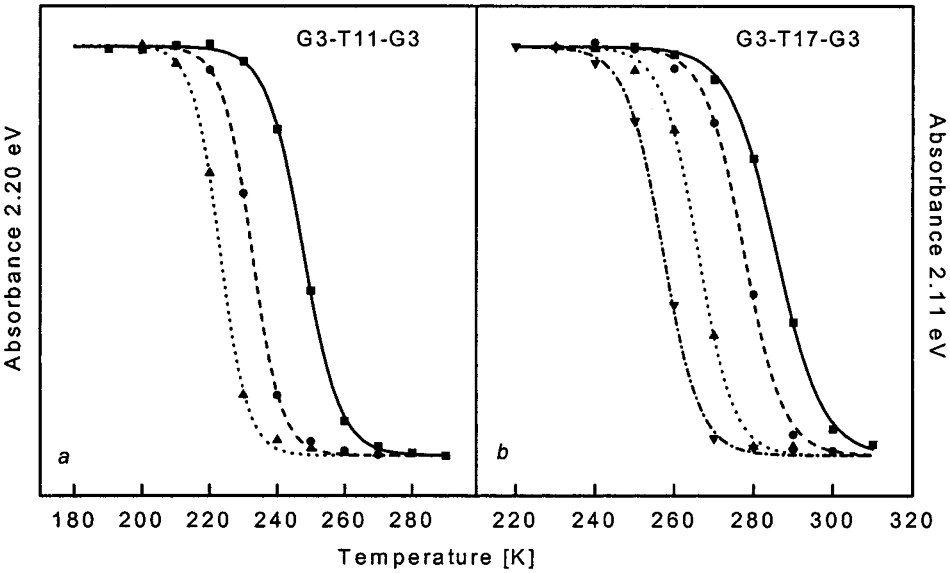


Figure 2. Normalized sigmoidal curves obtained on fitting the intensities of the absorbance at (a) 2.20 eV (564 nm) for G3-T11-G3 (1.0×10^{-6}, 5.2×10^{-6}, and 50×10^{-6} M solutions) and (b) 2.11 eV (588 nm) for G3-T17-G3 (1.0×10^{-6}, 4.5×10^{-6}, 2.0×10^{-5}, and 5.6×10^{-5} M solutions) as a function of the temperature. Down triangles, up triangles, circles, and squares represent increasing concentrations.

Table 1. S-Curve Characteristics

compd	$C_T \times 10^6$ [M]	T_m [K]	ΔT [K]
G3-T11-G3	1	223.1	4.09
	5.2	232.5	4.37
	50	247.7	5.43
G3-T17-G3	1	257.2	4.65
	4.5	266.0	4.50
	20	277.5	4.98
	56	285.6	5.88

inferred from the fact that it is observed at room temperature at very high concentrations (i.e., at the solubility limit), where interchain stacking processes are expected to occur. In contrast to what can be expected for longer π-conjugated polymers, it must be noted that an *intra*chain π-stacking interaction via bending of the conjugated segment is not possible in G3-T11-G3 and G3-T17-G3. This is due to the limited length of the oligothiophene and the presence of the bulky dendritic end groups. In contrast, bending of poly(3-alkylthiophenes) does occur for sufficiently long polymer chains with seven to eight units in all-cis conformations required for backfolding to occur.[10]

Because the aggregation band is initially absent and reaches a limiting value at a given temperature, plotting the normalized absorption intensity as a function of the temperature gives a sigmoidal curve (S-curve) that can be approximated with a Boltzmann distribution (eq 1) in which α is the fraction of aggregated chains.

$$\alpha = \frac{1}{1 + e^{(T - T_m)/\Delta T}} \tag{1}$$

In this equation, T_m is the temperature at which $\alpha = 0.5$ and ΔT relates to the width of the curve. Table 1 lists the characteristics for the different S-curves. The corresponding fits are shown in Figure 2, which clearly reveals that the temperature at which the onset of aggregation occurs decreases with increasing concentration. The aggregation process reaches completion (i.e., no more spectral changes observed below a certain temperature) within a relatively narrow temperature region (~30 K). The concentration dependence of this assembly process demonstrates that we are observing *inter*molecular interactions. The fact that a final ordered state is reached soon after the onset of aggregation suggests a limit to the degree of $\pi-\pi$ stacking that can be achieved. This can be rationalized by the presence of the relatively large dendritic wedges that prevent the formation of extended π-stacks.

In an attempt to quantify the aggregation results, we derived a thermodynamic model to determine the enthalpies of aggregation as well as the aggregation numbers n (where n is the number of molecules that make up the aggregate) by combining thermodynamic expressions that relate both the concentration and the temperature dependence of self-assembly processes.[11,12] For any association equilibrium, the equilibrium constant is

$$-\ln K = \frac{\Delta H^0}{RT} - \frac{\Delta S^0}{R} \tag{2}$$

Differentiation of eq 2 with respect to temperature yields

$$\Delta H = RT^2\left(\frac{\mathrm{d}\ln K}{\mathrm{d}T}\right) \tag{3}$$

For the self-complementary equilibrium reaction $nX \leftrightarrows X_n$, the equilibrium constant is written as

$$K(n) = \frac{\alpha}{n(1-\alpha)^n {C_T}^{n-1}} \tag{4}$$

In which C_T is the total molar concentration of X. At $T = T_m$ ($\alpha = 0.5$), differentiation with respect to temperature affords

$$\left(\frac{\mathrm{d}\ln K(n)}{\mathrm{d}T}\right)_{T=T_m} = (2 + 2n)\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{T=T_m} \tag{5}$$

Combining eqs 1, 3, and 5 gives

$$\Delta H^0 \underset{\text{eqs 3,5}}{=} RT_m^{\ 2}(2+2n)\left(\frac{d\alpha}{dT}\right)_{T=T_m} \underset{\text{eq 1}}{=} RT_m^{\ 2}(2+2n)\frac{-1}{4\Delta T} \quad (6)$$

A combination of eqs 2 and 4 at $T = T_m$ shows the concentration dependence of the aggregation process:

$$\frac{1}{T_m} = \frac{(n-1)R}{\Delta H^0}\ln C_T + \frac{\Delta S^0 - (n-1)R\ln 2 + R\ln n}{\Delta H^0} \quad (7)$$

Hence, ΔH^0 can be obtained from the slope of the curve of $1/T_m$ as a function of $\ln C_T$:

$$\Delta H^0 = \frac{R(n-1)}{\text{slope}} \quad (8)$$

Combining the results for the temperature and the concentration dependence (eqs 3 and 8, respectively) provides the equation required to determine the aggregation number:

$$n = \frac{2(\text{slope}\cdot T_m^{\ 2}/4\Delta T) - 1}{2(\text{slope}\cdot T_m^{\ 2}/4\Delta T) + 1} \quad (9)$$

In agreement with eq 7, an excellent linear correlation is obtained upon plotting $1/T_m$ versus the natural logarithm of the concentration (Figure 3). The slopes obtained are -1.14×10^{-4} K^{-1} for G3-T11-G3 and -9.7×10^{-5} K^{-1} for G3-T17-G3, and the corresponding aggregation numbers are $n = 5.3 \pm 0.5$ and $n = 6.2 \pm 1$, respectively. The resulting average enthalpies of aggregation divided by the aggregation number minus 1 are $\Delta H°/(n-1) = -73.0$ kJ/mol for G3-T11-G3 and $\Delta H°/(n-1) = -85.8$ kJ/mol for G3-T17-G3. As expected, the aggregation is more exothermic in the case of G3-T17-G3 since it is less soluble than G3-T11-G3 with its shorter oligothiophene block. A possible explanation for the relatively high exothermicity observed for these materials can be ascribed to the substitution pattern of the compounds. Because the β-substitution along the oligothiophene backbone is minimal, the "dumbbells" can achieve highly planar conjugated configurations in solution at lower temperatures. Despite the rigidity that results upon aggregation, precipitation does not occur, since the dendritic wedges continue to provide adequate solubility, thus allowing the materials a large degree of energetically favorable interchain π-orbital overlap in the aggregated state. Additionally, van der Waals attractions between the dendritic segments could contribute to the high exothermicity; however, this contribution is expected to be small. Given the narrow temperature range within which the aggregation process reaches completion, it is not surprising that the aggregation number is limited ($n \sim 5$ and $n \sim 6$), and this can be rationalized by the steric constraints imparted by the dendritic wedges.

Identification of the role of the dendrons in the aggregation of the triblock copolymers in more detail is hampered by the absence of distinct spectroscopic changes associated with the end groups. However, it is clear that the dendrons serve to enhance the solubility of the oligothiophene cores. As an example, the same T17 oligomer, carrying two unsubstituted benzyl ester end groups, is only sparsely soluble in dicholoromethane, and its UV/vis spectrum indicates that it is in the aggregated form at room temperature.[9b] Given the enhanced solubility of G3-T17-G3, we consider it unlikely that the dendritic end groups favor an ordered structure in the same temperature regime as the oligothiophenes blocks. Therefore, we expect their ordering to be limited and consequently envision the nanoaggregates as being held together by oligothiophenes while the wobbling dendrons are sticking out, continuing to ensure solubility of the nanoaggregates.

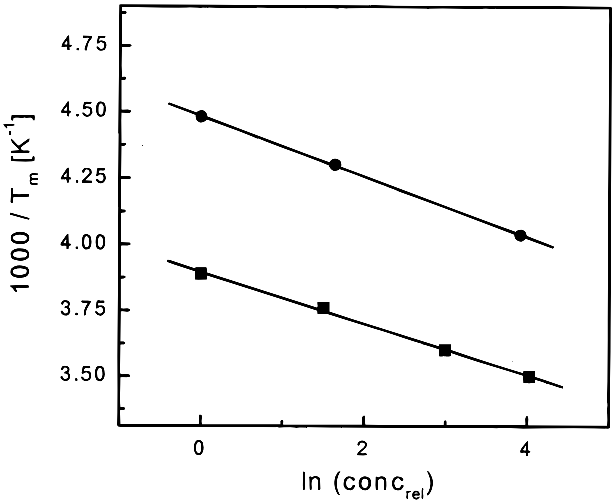


Figure 3. Linear fits obtained after plotting the natural logarithm of the concentration (relative values) of G3-T11-G3 (circles) and G3-T17-G3 (squares) versus the reciprocal T_m (determined from the sigmoidal fits of Figure 2).

To date, no explicit relation has been established between thermochromic behavior and interchain phenomena in the literature.[5-8] It has been argued that torsion of the main chain is the cause of the thermochromic observations and that the size of the side chain substituents is of major importance in determining the character of the thermochromic effect.[7h,13] As a result, thermochromism is often discussed exclusively in terms of *intra*molecular phenomena. In the case of 3,4-dialkyl-substituted polythiophenes, the steric interactions are maximized; thus, the polymer is always torsionally strained and absorbs at high energies, without any thermochromic observations.[13] The materials studied herein are unique in that they have a low degree of β-substitution with only two and four alkyl substituents for G3-T11-G3 and G3-T17-G3, respectively, but still possess excellent solubility due to the incorporation of G3 dendritic end groups. It must be noted that the absorption maxima of the molecularly dissolved "dumbbells" at room temperature are at lower energy compared to that of oligothiophenes of comparable length having a slightly higher degree of β-substitution (one alkyl chain per three thiophene units).[14] This suggests that, in these cases, less torsion of the oligothiophene backbone is required to provide solubility, thus indicating a relatively large degree of planarity already at room temperature for G3-T11-G3 and G3-T17-G3.

Distinction between *Intra*- and *Inter*molecular Phenomena via UV/vis Spectroscopy. Until now, we have used the concentration dependence of the growing 0−0 transition as a measure of the degree of intermolecular organization. We assume that an intrachain planarization (preorganization) precedes the interchain stacking. To distinguish between intra- and intermolecularly driven thermochromism, the energy shifts of the initial maximum absorption wavelength upon cool-

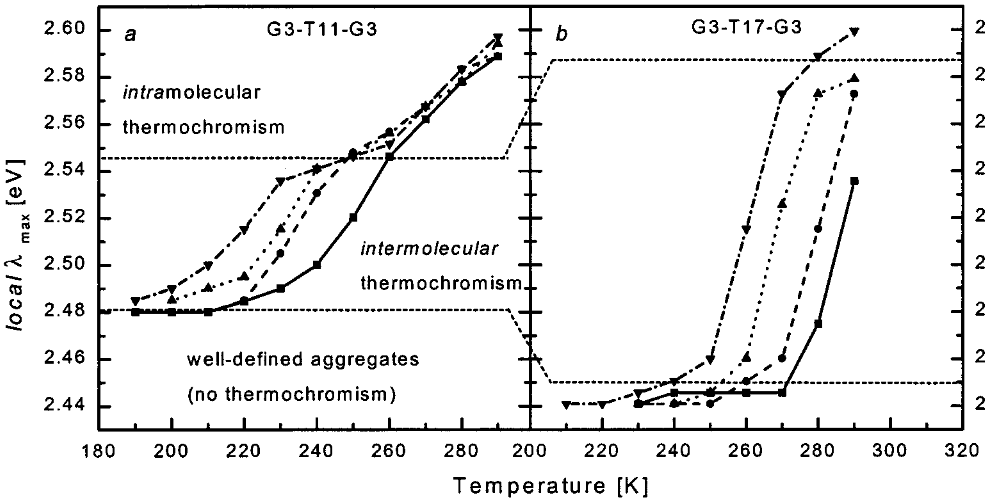


Figure 4. Shifts of the high-energy absorption maxima as a function of the temperature for different concentrations of (a) G3-T11-G3 (0.3×10^{-6}, 1.0×10^{-6}, 5.2×10^{-6}, and 50×10^{-6} M) and (b) G3-T17-G3 (1.0×10^{-6}, 4.5×10^{-6}, 2.0×10^{-5}, and 5.6×10^{-5} M). Down triangles, up triangles, circles, and squares represent the increasing concentrations. The three areas, representing regimes of different thermochromic behavior, are separated by a dashed line.

ing were plotted as a function of temperature (Figure 4). We assume that the initial red-shifting transition evolves into the high-energy vibronic transition of the later, more resolved, absorption spectrum obtained upon further cooling (Figure 1).

In the case of G3-T11-G3, a concentration-*in*dependent red shift of the transition is initially observed, from 2.60 eV (477 nm) to about 2.55 eV (486 nm), implying that an *intra*molecular ordering process is occurring. The minor deviations are a consequence of the 1 nm resolution of the UV/vis spectrophotometer. Subsequently, the continuing red-shift becomes concentration dependent (from 2.55 eV (486 nm) to 2.48 eV (500 nm)) until no further thermochromic changes are observed. It is noticeable that the temperature ranges where the concentration-dependent changes occur are identical to those of the steep region of the sigmoidal curves presented in Figure 2, which is related to the intensity of the “aggregation” band. This is in agreement with the notion that, when the oligothiophene has reached a certain degree of planarity, with concomitant decrease in solubility, it is “preorganized” for favorable interchain interactions. It has been argued that torsion versus planarization provides the basis for thermochromism without any consideration for interchain interactions. The concentration dependence of the appearance of the well-resolved red-shifted spectrum (Figure 2) provides unambiguous evidence that it represents an interchain aggregated species, as opposed to an *intra*molecularly ordered species. In the G3-T11-G3 system, only a small red shift, without any increase in vibronic resolution in the absorption spectrum, relates to *intra*molecular organization. Subsequently, the processes of aggregation and further *intra*molecular planarization occur simultaneously. This is probably the result of “assisted planarization” in which interchain stacking forces the participating oligothiophene chains into a more rigid conformation.

Interestingly, for G3-T17-G3, a concentration dependence of the changes in $\lambda_{\max}$ is already observed at the highest temperatures, without any evidence for a prior intramolecular planarization of the backbone (Figure 4b). This suggests that the more limited solubility of the lengthier oligomer is in fact the driving force for aggregation. Once part of an aggregate, the “assisted planarization” continues to a significantly higher degree than in the case of G3-T11-G3 (2.44 eV vs 2.48 eV), until the aggregation limit ($n \sim 5$) has been reached and no further thermochromic changes are observed.

Very similar spectral changes are observed upon cooling solutions of neutral poly(3-alkylthiophene)s.[15] It is highly probable that for polymers the well-resolved red-shifted spectra obtained upon cooling correspond to $\pi-\pi$ stacked aggregated chain segments that can originate from both inter- and intrachain stacking interactions. Extensive *intra*chain stacking resulting from folded polymer chains[10] can be thought to originate from a high (local) concentration of independent chain segments. This *intra*chain stacking contribution can explain the previously observed concentration independence of the thermochromic transitions.

In our opinion the observation of distinct thermochromic changes in solution, and to some extent also in the solid state, strongly depends on the presence of a fine balance between solubility (or some motional freedom in the solid state) and a tendency of conjugated chains to form aggregates via $\pi-\pi$ interactions. In this view the varying degree of thermochromism exhibited by differently substituted polythiophenes[7] is a consequence of solubility differences and the extent to which π-stacking can occur, rather than intrachain conformational disorder alone.

Conclusions

We have shown that the self-assembly of structurally well-defined “dumbbell-shaped” oligothiophene triblock copolymers end-substituted with G3 poly(benzyl ether) dendritic wedges, G3-T11-G3 and G3-T17-G3, occurs in solution at reduced temperatures and leads to the formation of well-defined supramolecular assemblies. The size of the supramolecular aggregates is small ($n = 5.3 \pm 0.5$ for G3-T11-G3 and $n = 6.2 \pm 1$ for G3-T17-G3) due to steric constraints caused by the dendritic wedges. Furthermore, the incorporation of poly(benzyl ether) dendrons provides materials with excellent solubility, thus allowing the study of concentration-dependent thermochromism. The concentration dependence of the organizing process confirms that the major thermochromic changes observed for G3-T11-G3 and G3-T17-

G3 result from *inter*molecular interactions, while an intramolecular "preorganization" results in a small concentration-independent red-shift in the UV/vis spectrum. This result contrasts with previous reports for π-conjugated polymers for which a concentration dependence could not be observed.[5] The differences can be explained by the additional *intra*molecular stacking process that can take place in the longer polymer systems. The driving force for assembly is attributed to the strong $\pi-\pi$ interactions of the oligothiophene units, and hence, the aggregation is more exothermic for the longer oligothiophene T17 than for T11. The present study of "dumbbell-shaped" oligothiophenes constitutes the first instance in which intra- and intermolecular phenomena have been distinguished in aggregated conjugated systems.

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