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Chirality and Supramolecular Copolymerizations – The Elusive Role of Subtle Solvation Effects

Marco D. Preuss,^[a] Stef A. H. Jansen,^[a] Ghislaine Vantomme,^[a] and E. W. Meijer*^[a]

This contribution is dedicated to the seminal contributions of Meir Lahav and Leslie Leiserowitz to science and to celebrate their 2021 Wolf Prize in Chemistry.

Abstract: Recent investigations of supramolecular polymers based on chiral triphenylene-2,6,10-tricarboxamides (TTAs) showed how temperature-induced changes in solvation can greatly influence the preferred helical conformation of the supramolecular polymers formed. Here, we combine chiral TTA with achiral copolymerization partners to further investigate temperature-dependent solvation effects. Systematic variation of the system's composition shows clear impacts on the temperature window where the conformational change occurs. Further, simple chain length variations in the

achiral comonomer greatly affect the ability to influence the conformational change in the copolymer, while the differences in the properties of the individual homopolymers are rather small. We herein highlight how subtle changes in the monomers can impact the observed copolymer properties drastically; an effect arising from the emerging complexity of multicomponent interactions in supramolecular copolymers with solvent-solute interactions being more important than typically thought.

Keywords: Chirality · Supramolecular Chemistry · Supramolecular Copolymers · Solvation Effects · Chainlength

Introduction

Detailed understanding of association thermodynamics in catalysis, biochemistry, medicinal chemistry, and supramolecular chemistry is of great importance to successfully design functional molecular systems. When enthalpically favourable contacts between two molecules result in association, the system often suffers from reduced conformational, translational, and rotational freedom.^[1,2] Therefore, binding only occurs if the enthalpic gain outweighs the entropic loss.^[3] As often exemplified in biomolecular recognition, stronger intermolecular interactions (larger ΔH) results in higher entropic penalties as more conformational restraints occur.^[4–6] This interdependency of enthalpy and entropy might result in no improvement of the association constants or, in the most extreme case, in no association at all. While enthalpic contributions are mostly related to the molecular structure and can be readily understood, such as functional groups that can undergo hydrogen bonding to stabilize intermolecular interactions, the origin of the equally important entropic contributions are more elusive.^[7–9] Further, weak intermolecular interactions involved in supramolecular associations allow many different factors to play a role and a precise knowledge of the different processes involved in the assembly of two moieties is necessary. As discussed in an excellent review by George Whitesides on protein-ligand interactions, protein-ligand complex formation in solution is always accompanied by changes in the solvation sphere of the protein, the ligand, and the forming protein-ligand complex. These solvation effects are influencing the thermodynamic landscape of

intermolecular interactions.^[3] The principles of monomer-monomer associations and the role of solvation are closely related to those discussed for protein-ligand interactions, and the aforementioned points are conferrable to supramolecular polymerization processes by translating *protein* into *polymer* and *ligand* into *monomer*.

The thermodynamic properties in supramolecular polymers can be greatly influenced by modifying the molecular structure of the monomers^[8–10] and various experimental and computational methods have been elaborated over the past decades to determine the thermodynamic parameters of supramolecular polymerizations.^[11–14] Our and other groups studied in great detail the supramolecular polymerization of benzene-1,3,5-tricarboxamides (BTA).^[15] Moderate changes such as increasing the chain length of solubilizing sidechains reduces the aggregate stability due to increased solubility of the monomers. More drastic structural variations, such as extending the

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π -surface of benzene-1,3,5-tricarboxamide to triphenylene-2,6,10-tricarboxamide, strongly increases the stability of the supramolecular polymers formed.^[7] Besides chemical modifications of the monomers, solvents and solvent mixtures have proven useful to influence the stability of supramolecular aggregates.^[16–18] Besides the stability also the morphology of the formed aggregates can be influenced using different solvents, with first examples by Lehn in 2007.^[19] By changing the solvent nature or by adding a cosolvent, morphological changes like branched or linear,^[19] H- or J- aggregates,^[20] *P* or *M* helicity^[21] as well as 1D fibers or circular polymers^[22] could be achieved. While many examples of solvation effects in supramolecular polymers have been reported, they are mostly empirical in nature. Only few examples systematically studied the molecular origins of solvation-dependent pathways of supramolecular polymers.^[17]

Multicomponent systems have received increasing attention as a promising pathway in engineering systems of emerging complexity with new structures, properties, and functions.^[23,24] Examples presented in literature are dilution-induced supramolecular polymerizations,^[25] thermally bisignate supramolecular polymerizations^[26] or sequence-controlled supramolecular copolymerizations.^[27] Mixing experiments with chiral monomers, either with their enantiomeric counterpart (majority-rules experiment)^[28] or achiral counterparts with similar molecular frameworks (sergeant and soldiers experiment),^[29,30] resulted in many exciting fundamental insights about the transfer and amplification of asymmetry in

molecular systems. In the latter experiment, pioneered by Green and co-workers for chiral macromolecules, the overall chirality of a system can be dominated in a non-linear fashion by a small amount of chiral dopant (sergeant) in a pool of achiral monomers (soldier).

With the 2021 Wolf Prize for establishing fundamental reciprocal influences of three-dimensional molecular structures on structures of organic crystals, Lahav and Leiserowitz are awarded for their many seminal contributions to the chemical sciences. Amongst other scientific discoveries, they explained the role of solvents on crystal polymorphism and showed why the addition of alcohols to aqueous solutions induces the precipitation of the least stable β form of glycine.^[31] Moreover, chirality and stereochemical approaches have always dominated their research activities, as the role of minute amounts of added molecules that interact specifically with crystal interfaces can influence the observed overall morphology.^[32,33] These fundamental insights have stimulated many scientists and are a source of inspiration of the study presented here.

As previously published, homopolymers of chiral TTA show temperature-dependent inversion of the helical screw sense.^[7] Computational analysis revealed these conformational changes to be closely related to temperature-induced changes in the solvent-polymer interaction, with increasing solvation at lower temperatures (Figure 1). Due to the absence of strong directional interactions between solvent and solute, the differential solvation of the various helical states was reported to origin from entropic changes in the system.^[7] While previous

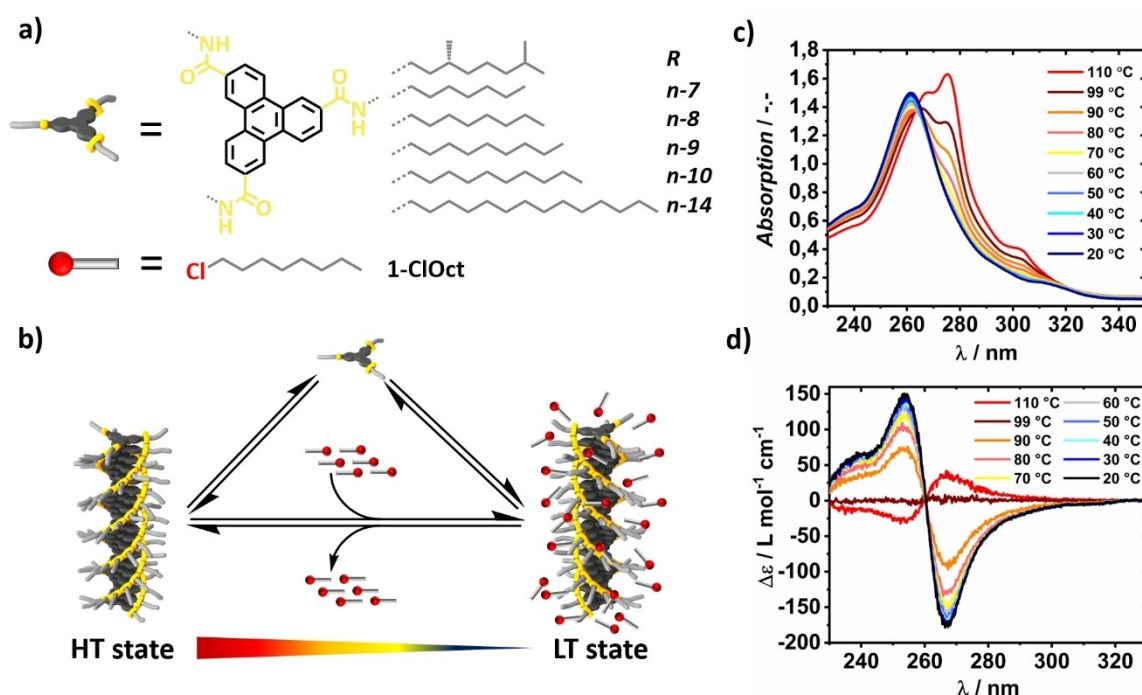


Figure 1. a) Overview of chiral *R* and achiral *n*-7, *n*-8, *n*-9, *n*-10 and *n*-14 TTA derivatives investigated in this study and molecular structure of the used solvent 1-ClOct, b) schematic illustration of the assembly into the high (HT) and low temperature (LT) states with different degree of solvation, c) UV-VIS and d) ECD spectra of *R* at variable temperatures.

studies achieve morphology changes by varying the solvent system, we herein aim to study solvation related morphology changes in chiral TTA based supramolecular polymers by adding an achiral comonomer, while keeping the solvent invariant. We anticipate that the achiral comonomer results in different solvent-solute interactions than observed in the homopolymerization of chiral TTA and therefore influences the helical inversion. We further investigate the impact of the chain length of the achiral comonomer on the copolymerization.

Results

The Homopolymerization of the Chiral TTA Monomer

The supramolecular polymerization of chiral TTA derivative **R** was studied using a combination of UV-VIS and electronic circular dichroism (ECD) experiments. All measurements were performed in 1-chlorooctane (1-ClOct) at a concentration of 250 μM . Chlorinated solvents were previously shown to enhance the dynamics of the supramolecular polymerizations of TTA, preventing kinetic trapping and facilitating reproducibility.^[7] At high temperatures, the UV-VIS spectrum shows an absorption maximum at 276 nm with two shoulders at 266 nm and 300 nm (Figure 1c). At a concentration of 250 μM , the monomeric state cannot be reached by increasing the temperature in our experimental setup ($\vartheta_{\text{max}} = 110^\circ\text{C}$) and the absorptions at 276 nm and 300 nm were assigned to the monomeric species by variable temperature UV (VT-UV) and variable temperature ECD (VT-ECD) measurements at lower concentrations (Figure S1). Upon cooling, the monomers further assemble, as evidenced by the hypsochromic shift of the shoulder at 266 nm to 262 nm, accompanied by a change in intensity (Figure 1c). The polymerization occurs via a cooperative mechanism, as indicated by the non-sigmoidal

shape of the VT-UV cooling curve (Figure S2). As previously mentioned, **R** displays two temperature-dependent helical conformations as shown by VT-ECD measurements, in the following described as less solvated high-temperature (HT) and more solvated low-temperature (LT) state. At high temperatures, the ECD spectrum displays a positive Cotton effect at 266 nm and a negative Cotton effect at 255 nm (Figure 1d). Upon cooling below 99°C , the ECD signal inverts in sign. The similar shape of the high- and low-temperature CD suggests an enantiomeric-like nature of the observed helical aggregates. At high temperatures, a fraction of monomer remains in solution as indicated by the stronger pronounced monomer absorption in the VT-UV, resulting in the lower intensity of the ECD signal at 110°C (Figure 1c). Further cooling results in a sharp transition to the low temperature state.

Homopolymerization of Achiral Monomers of Variable Chain Length

As for the chiral monomer, the supramolecular polymerization of each achiral TTA derivative (Figure 1a) can be monitored by following the absorption change at 276 nm by VT-UV measurements (Figure 2a and S2). The thermodynamic parameters of the homopolymerizations were determined using Van't Hoff analysis (Table 1, Figure 2b and S3). For all monomers studied, the change of the enthalpy upon elongation is negative ($\Delta H < 0$), therefore enthalpically favouring supramolecular polymerization. From **n-7** towards **n-9** the absolute values of the enthalpy decrease from $-52.9 \text{ kJ mol}^{-1}$ to $-47.7 \text{ kJ mol}^{-1}$, followed by an increase to $-51.8 \text{ kJ mol}^{-1}$ for **n-14**. Compound **n-9** shows the smallest enthalpic contribution to the supramolecular polymerization of the studied monomers. For all derivatives, the determined changes in entropy are negative ($\Delta S < 0$). This entropic penalty upon polymerization is a consequence of the loss of rotational, translational, and

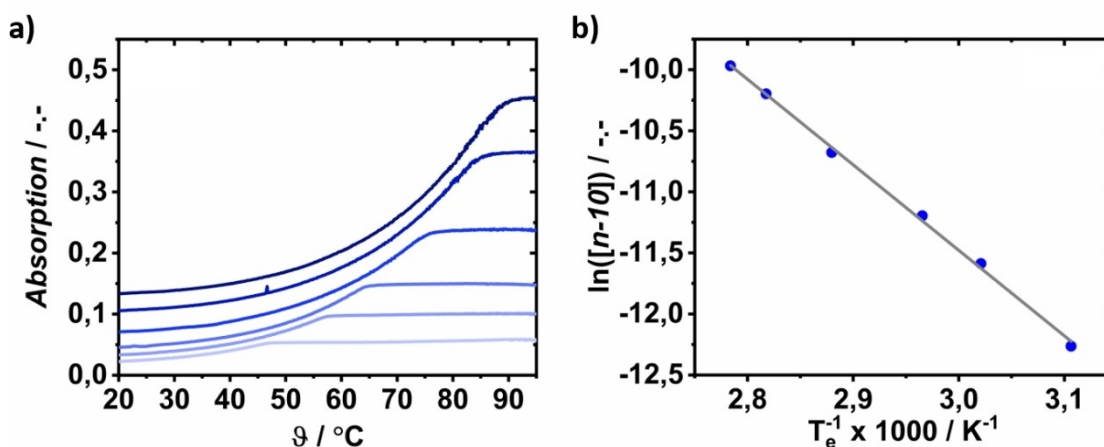


Figure 2. a) VT-UV cooling curves at 276 nm of **n-10** at 50 μM , 40 μM , 25 μM , 15 μM , 10 μM and 5 μM in 1-ClOct and b) experimental data (blue circles) and linear fit (grey line) for Van't Hoff analysis of **n-10**.

Table 1. Enthalpic ΔH and entropic ΔS parameters for homopolymerization derived from Van't Hoff analysis and calculated Gibbs free energy ΔG at 20 °C of **R**, **n-7**, **n-8**, **n-9**, **n-10** and **n-14**. All values are reported with their respective errors and the errors for ΔG were calculated using Gauss error propagation.

	ΔH [kJ mol ⁻¹]	ΔS [J mol ⁻¹ K ⁻¹]	ΔG at 20 °C [kJ mol ⁻¹]
R	-49.4 ± 0.7	-51.6 ± 2.1	-34.3 ± 1.0
n-7	-52.9 ± 1.3	-60.5 ± 3.8	-35.2 ± 1.7
n-8	-48.6 ± 1.2	-49.5 ± 3.4	-34.1 ± 1.5
n-9	-47.7 ± 4.0	-46.9 ± 11.6	-33.9 ± 5.2
n-10	-48.5 ± 1.0	-50.1 ± 2.9	-33.8 ± 1.3
n-14	-51.8 ± 0.7	-61.6 ± 1.9	-33.8 ± 0.9

conformational freedom of the monomer upon incorporation into the polymer. From **n-7** to **n-9** the entropic penalty decreases from -60.5 J mol⁻¹ K⁻¹ to -46.9 J mol⁻¹ K⁻¹. This decrease is unexpected since the entropic penalty due to loss of conformational and rotational freedom within the sidechains was expected to increase with increasing chain length. Further increasing the chain length results in a higher entropic penalty of -61.6 J mol⁻¹ K⁻¹ for **n-14**. In the series studied, **n-9** exhibits the smallest and **n-14** the largest entropic penalty upon polymerization. In general, it can be observed that a favourable enthalpic contribution results in a higher entropic penalty. A clear trend in the entropic penalty or the enthalpic contribution to the polymerizations upon increasing the chain length remains elusive, indicating additional effects to play a role as well. Despite the differences in the enthalpic and entropic values for each monomer, the overall stack stability at room temperature, as expressed by ΔG derived from the Gibbs

equation, shows only slight differences, indicating enthalpy-entropy compensations (Table 1). In view of the reported errors in the thermodynamic parameters as determined by Van 't Hoff analyses, we further validated the ΔG values with thermodynamic mass-balance models (Figure S4, Table S4).^[12] The most drastic change of about 1 kJ mol⁻¹ occurs between **n-7** and **n-8**, and further increasing the chain length from **n-8** to **n-14** only results in minor changes of polymer stability in the order of 0.3 kJ mol⁻¹. It is remarkable how small the changes in the stack stability are, even though the length of the solubilizing sidechains is doubled from **n-7** to **n-14**. To distinguish if the observed changes in the system result from variations in the monomer-monomer or in the monomer-solvent interactions, we further aimed to study the isolated monomer-monomer interactions in solid state using Fourier transform infrared spectroscopy (FTIR).^[11,34] Overall, the observed spectra indicate similar strength and nature of the intermolecular interactions, indicating that changing the chain length of the peripheral side chains hardly affects the monomer-monomer interplay (Figure S5). The variable length of the side chain might cause a small difference in solvation of the monomers and polymers and therefore influence the thermodynamic properties of the system in solution.

Copolymerization of **R** with Achiral Monomers of Variable Chain Length

To investigate the impact of a comonomer on the transition from the HT to the LT state, we mixed **R** with the achiral monomers. During all measurements the total sample concentration was kept constant at $c = 250 \mu\text{M}$. Figure 3 displays the

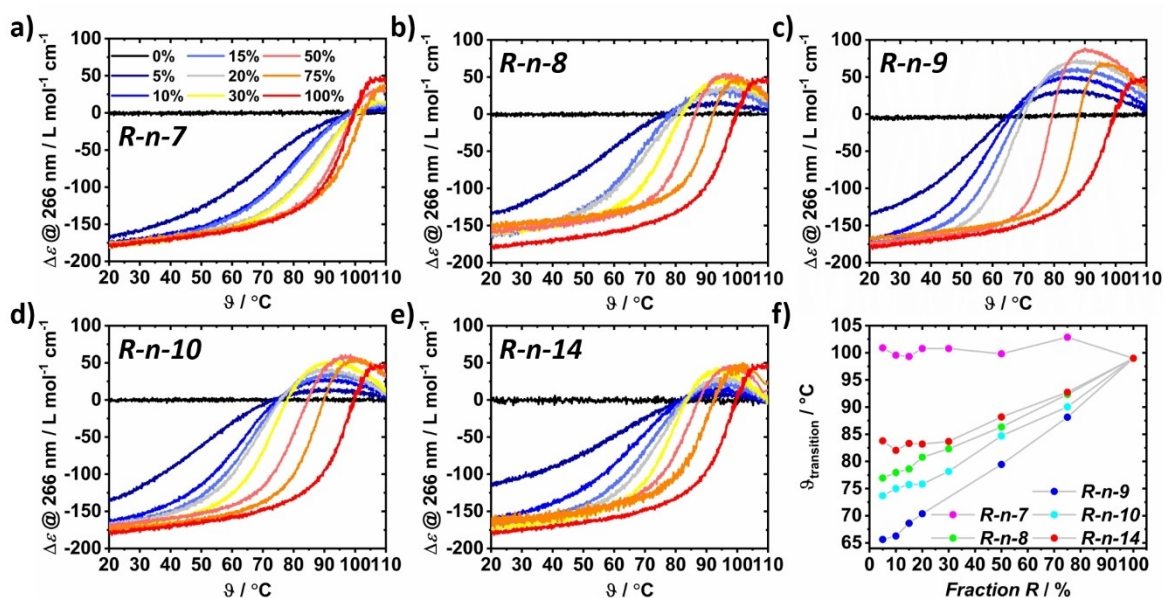


Figure 3. VT-ECD measurements at 266 nm of copolymerizations a) **R-n-7**, b) **R-n-8**, c) **R-n-9**, d) **R-n-10**, e) **R-n-14** and f) the observed transition temperatures $\theta_{\text{transition}}$ from HT to LT state of the copolymerizations in dependence on fraction **R**; the grey lines are displayed to guide the eye.

cooling curves for the copolymerizations **R-n-7**, **R-n-8**, **R-n-9**, **R-n-10**, and **R-n-14**. Regardless of the content of the achiral comonomer, the multicomponent systems undergo copolymerization as evidenced by the expressed helical bias in the VT-ECD curves. Despite for **R-n-7**, a positive ECD signal is observable over a broader temperature regime upon decreasing the amount of **R** (Figure 3f). In the most extreme case, the transition temperature can be significantly shifted from 99 °C for 100% **R** to 66 °C for 5% **R** by copolymerizing **R** with **n-9**. Please note that experimental pipetting inaccuracies become more significant at low contents of **R**, which might result in the observed fluctuations of the transition temperature at **R**-contents below 20%. Considering the similar homopolymer properties of the achiral monomers, the impact of the different monomers on the transition temperature in the copolymerizations are surprisingly large. Two potential correlations can be found comparing the properties of the individual homopolymers to the observations made in the corresponding copolymers. Firstly, it is intriguing that copolymerizations of **R** with **n-8**, **n-9**, **n-10**, and **n-14** show the HT state over a broader temperature window, in contrast to **n-7** (Figure 3). This coincides with the observations in the ΔG values for the homopolymers, where **n-7** is the only achiral comonomer that shows higher stack stability than the chiral monomer **R** (Table 1). As previously discussed, the homopolymer stability in this study is mainly influenced by solvation effects, therefore indicating that mixing of **R** with better solvated monomers results in the presence of the HT state over a broader temperature window. Secondly, the most significant shift of the transition temperature was observed for the copolymerization of **R** with **n-9**. The ΔH and ΔS values of **n-9** present a turning point in the series of the achiral compounds studied, showing the lowest entropic penalty as well as the lowest enthalpic contribution to the polymerization (Table 1). Besides these findings, no clear correlation between the individual homopolymer properties and the impact on the transition temperature between HT and LT state can be found.

Discussion

As discussed in the introduction, the change in helical conformation of the homopolymer of **R** is the result of a difference in solvation between the HT and LT state, expressed in lower and higher degree of solvation. By adding a comonomer, the solvation properties change and impact the competition between HT and LT state. To support this assumption, we further performed qualitative simulations (Figure 4). At first, we fitted a model for two competitive, cooperative polymerizations as outlined by Zhao and Moore to ECD and UV/VIS cooling curves to determine the thermodynamic parameters of **R**.^[12] The different solvation was implemented in the system analogous to our previous report on TTA polymerization.^[7] Subsequently, the solvation difference between the HT and LT state was changed, while keeping the other thermodynamic parameters constant. The results of

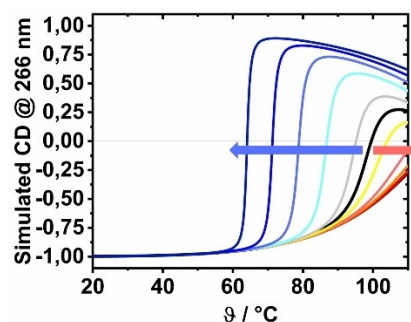


Figure 4. Simulated CD cooling curves at 266 nm upon changing the solvation difference between HT and LT state in the homopolymerization of **R**. The blue arrow shows a larger and the red arrow a lower solvation difference compared to the fit of the experimentally obtained cooling curve of **R** (black line).

the simulated ECD curves are displayed in Figure 4. The black curve represents the fitted ECD curve of **R**. When the solvation difference between the HT and LT state is increased, the simulated cooling curves show a shift to lower transition temperatures (as indicated by the blue arrow). On the other hand, if the solvation difference between the HT and LT state decreases, the simulated cooling curves show a shift to higher transition temperatures (indicated by the red arrow). This observation implies that the transition temperature is sensitive to changes in the solvation properties of the system.

As mentioned in the introduction, the different solvation of the two helical states is of entropic nature.^[7] During the assembly process of the copolymers, changes in the solvation occur between the monomer-solvent and the polymer-solvent interaction. Each addition step of a monomer to the end of a polymer releases solvent molecules from the polymer end as well as from one side of the monomer. This change in solvation is entropically favourable and in a homopolymerization, the entropic gain for each addition step is the same. In copolymerizations however, the copolymerizing monomers might exhibit different solvation properties. Therefore, the individual entropic gain for each addition step is no longer constant and varies with the composition of the copolymerizing system. In this particular system, the homopolymerizations indicate that the monomer solubility of **n-8** to **n-14** is slightly higher than the one of **R**. In these cases, the transition between HT and LT state is shifted to lower temperatures, indicating a larger solvation difference between the two states. If the achiral monomers exhibit higher solvation compared to **R**, the average entropic gain in each addition step to the polymer is increased and favourable for the polymerization process. The more solvent is freed upon polymerization into the HT state, the higher the relative entropic penalty for the transition into the more solvated LT state. The entropic contributions become less significant upon further cooling and at the transition temperature the enthalpic favourable solvent-polymer interaction dominates and the transition into the LT state occurs. Therefore, we conclude that better solvated comonomers

might increase the entropic penalty upon transition into the LT state, making the HT state more favourable and result in lower temperatures for the transition. Even though the previous discussion gives a possible explanation for the observed properties, the individual impact of the chain length on the conformational change remains elusive.

Conclusion

The systematic change from heptyl to tetradecyl of the peripheral side chains showed little impact on the assembly properties in solution of triphenylene-2,6,10-tricarboxamide (TTA) based supramolecular homopolymers. Even though significant variations in the individual enthalpic and entropic parameters have been observed, the overall thermodynamic stability stayed mostly invariant, indicating enthalpy-entropy compensation. Mixing of such achiral TTA monomers with chiral TTA, significantly influenced the occurrence of the previously described helical inversion in homopolymers of chiral TTA. Qualitative computational analysis suggests that the achiral comonomers change the solvation properties of the system and therefore influence the transition temperature. Nonetheless, no clear relation between the chain length of comonomer, solvent-solute interactions and the observed properties in the copolymer is apparent from the studied series. Regarding the small differences in the homopolymer properties, the impact on the copolymerization is surprising. This observation highlights how subtle changes in the individual components can drastically influence the properties of multi-component systems, an effect not foreseeable from studying the individual components. We address these findings to be a result of emerging complexity due to multicomponent interactions in molecular aggregation, as beautifully shown in the past for crystals by Meir Lahav and Leslie Leiserowitz.

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Conflict of Interests

The authors declare no conflict of interests.

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