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Suppression of Mesoscopic Order by Complementary Interactions in Supramolecular Polymers

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Supporting Information

ABSTRACT: We show here that complementary interactions can suppress mesoscopic order and thus lead to a counterintuitive change in material properties. We present results for telechelic supramolecular polymers based on poly(propylene oxide) (PPO), thymine (Thy), and diaminotriazine (DAT). The self-complementary systems based on Thy exhibit lamellar order and 2D crystallization of Thy in the bulk. We show that the microphase segregation is inhibited by addition of DAT: the strong complementary Thy−DAT interaction inhibits crystallization of thymine in microdomains and lamellar structuration. As a result, the supramolecular polymer with only weakly self-complementary stickers is a solid, whereas the supramolecular polymer with strongly complementary stickers is a liquid.

Supramolecular interactions are employed to induce mesoscopic order by self-assembly, as in crystals,[1] liquid crystals,[2] bolaamphiphiles,[3] and polymer−surfactant systems.[4] We recently described the long-range order and order−disorder transition (ODT) of a homoditopic telechelic supramolecular polymer.[5] Homoditopic telechelic supramolecular polymers (A−spacer−A and B−spacer−B) consist of bifunctional molecular units linked together through directional and reversible noncovalent bonds (such as hydrogen bonds or π−π stacking) between the A and B stickers.[6] In our system,[5] the long-range order was driven by dispersion forces between the stickers and the spacer, crystallization of the stickers, and directional interactions between the stickers.

When only the directional interactions dictate their behavior, telechelic supramolecular polymers [(A−spacer−A═B−spacer−B)$_n$] are disordered. They may display reversible polymer-like properties in solution and in the bulk. Their viscosity increases with the average degree of polymerization (DP = n), which increases with the thermodynamic association constant (K_{AB}) of the A and B stickers.[6] For hydrogen-bonded supramolecular polymers, the viscosity decreases as the temperature increases because the hydrogen bonds are released and the association lifetime decreases.[6]

However, incompatibility between the spacers and the stickers and crystallization of the stickers can induce organization. Clusterization[7−11] (with[9] or without[8] crystallization of the stickers) as well as long-range order[5,11] have been evidenced in many supramolecular polymers based on self-complementary[12] associations (A = B). The organization controls the mechanical properties: sticker domains act as physical cross-links, causing behavior typical of thermoplastic elastomers.[5,9,10]

Organization has also been reported in supramolecular polymers based on complementary[13] associations (A ≠ B). Lehn, Rowan, and their co-workers obtained liquid crystals from telechelic supramolecular polymers where A and B are two different stickers that strongly associate with one another but weakly self-associate.[14] Liquid crystallinity was obtained in part because the spacers used were rigid.

Here we report that optimization of the directional interactions by strong complementary associations can paradoxically suppress mesoscopic order in telechelic supramolecular polymers with flexible spacers. This effect is due to modifications of the stickers' ability to crystallize and of the sticker−backbone dispersion forces. Consequently, supramolecular polymers having the same backbone but self-complementary or complementary stickers show very different mechanical behaviors (Figure 1). When the stickers are weakly self-complementary and mesoscopic order is absent, the material is a liquid (Figure 1a). When the stickers are weakly self-complementary and mesoscopic order is present, the material is a solid (Figure 1b). When the stickers are strongly complementary and mesoscopic order is absent, the material is a liquid (Figure 1c).

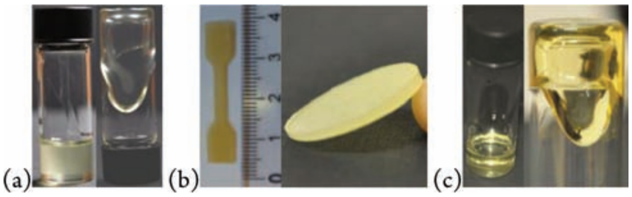

Figure 1. Pictures of: (a) a supramolecular polymer with weakly self-complementary stickers (DAT), DAT−PPO-2200−DAT, which is a liquid; (b) a supramolecular polymer with weakly self-complementary stickers (Thy) and mesoscopic order, Thy−PPO-2200−Thy, which is a solid; and (c) a supramolecular polymer with strongly complementary stickers (Thy and DAT), 50/50-M-2200 (i.e., a stoichiometric mixture of Thy−PPO-2200−Thy and DAT−PPO-2200−DAT), which is a liquid.

We also report that above the ODT temperature (T_{ODT}), where all of the supramolecular polymers are disordered, their

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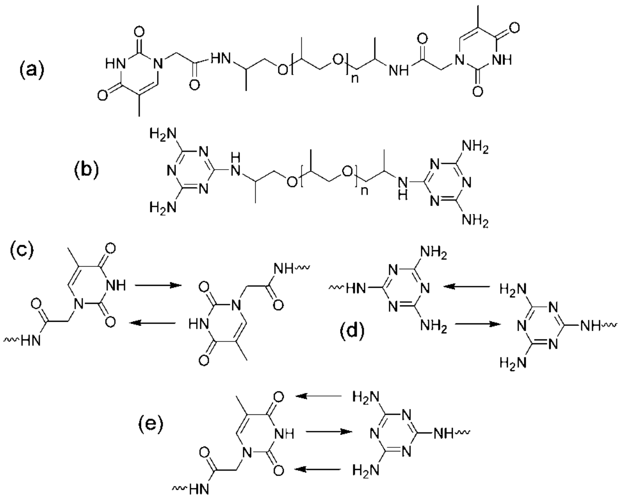
behavior is controlled by the directional interactions. In that case, the viscosities of the supramolecular polymers depend on the association constants.

The supramolecular polymers used in this study are based on noncrystalline and low-molecular-weight (460 and 2200 g mol^{-1}) poly(propylene oxide) (PPO) chains functionalized on both ends with thymine (Thy) or diaminotriazine (DAT) groups (Chart 1a,b). They are denoted as Thy−PPO-*X*−Thy, DAT−PPO-*X*−DAT, and $\phi/(100-\phi)$-M-*X*, where *X* is the molecular weight (in g mol^{-1}) of the PPO spacer and $\phi/(100-\phi)$-M-*X* indicates a mixture (M) of ϕ% Thy−PPO-X−Thy and $(100-\phi)$% DAT−PPO-*X*−DAT. The synthesis of Thy−PPO-X−Thy (*X* = 460, 2200) is described in ref 5. DAT−PPO-*X*−DAT (*X* = 460, 2200) were synthesized via aromatic nucleophilic substitution of diamine telechelic PPO-*X* with 2-chloro-4,6-diamino-1,3,5-triazine [see the Supporting Information (SI)]. $\phi/(100-\phi)$-M-*X* (*X* = 460, 2200) were prepared by separately solubilizing Thy−PPO-*X*−Thy and DAT−PPO-*X*−DAT in a good solvent (1:1 $CHCl_3$/MeOH blend or CH_2Cl_2) and then mixing the two solutions. $\phi/(100-\phi)$-M-*X* (*X* = 460, 2200) were then obtained in the bulk by solvent casting and annealing under vacuum at 100 °C for 3 h.

Chart 1. (a) Thy−PPO-*X*−Thy; (b) DAT−PPO-*X*−DAT; (c) Thy−Thy Self-Association; (d) DAT−DAT Self-Association; (e) Thy−DAT Complementary Association



Thy and DAT can associate with one another through self- and heterocomplementary hydrogen bonding (Chart 1c−e).[15] Thy−DAT complementary association is much stronger than either Thy−Thy or DAT−DAT self-association, as evidenced by the differences in the thermodynamic binding constants: $K_{Thy-DAT} = 890\ M^{-1}$ versus $K_{DAT-DAT} = 2.2\ M^{-1}$ and $K_{Thy-Thy} = 4.3\ M^{-1}$ (as determined by ^1H NMR spectroscopy in $CDCl_3$).[15] Thy and DAT are very polar groups, while the PPO chain is much less polar. Thymine derivatives readily crystallize, while DAT derivatives are known for their tendency to form glasses instead of crystallizing. Indeed, they form hydrogen-bonded aggregates that pack poorly because of their multiple nonequivalent hydrogen-bonding sites.[16] Therefore, three different phenomena can concur and compete in the bulk: hydrogen bonding between the stickers, phase segregation between the PPO chains and the stickers, and crystallization of the thymines into microdomains. This system can then be used to underline the respective effects of hydrogen bonding, phase segregation, and the ability of the sticker to crystallize on the structure. The bulk behaviors of our homoditopic compounds Thy−PPO-*X*−Thy and DAT−PPO-*X*−DAT and their mixtures 50/50-M-*X* (*X* = 460, 2200) were investigated by structural (X-ray scattering, polarized optical microscopy), thermal [differential scanning calorimetry (DSC)], rheological, and mechanical characterizations.

Thy−PPO-*X*−Thy (*X* = 460, 2200) exhibit two distinct orderings below T_{ODT} (67 °C for *X* = 2200, 109 °C for *X* = 460): a crystalline ordering and a lamellar ordering (with *d* spacings of 60 Å for *X* = 2200 and 28 Å for *X* = 460).[5] The lamellar structure consists of alternating two-dimensional crystallized thymine planes and amorphous PPO layers. This microphase segregation seems to be crystallization-driven. As a result, these materials are solid below T_{ODT} (Figure 1a), even above their glass transition temperatures (T_g = 24 °C for *X* = 460 and −62 °C for *X* = 2200). At T_{ODT}, a transition to a disordered state occurs, and these materials become liquid. Dynamic mechanical analysis (DMA) and tensile tests of Thy−PPO-2200−Thy confirmed these observations (see the SI).

In contrast, DAT−PPO-*X*−DAT (*X* = 460, 2200) show no order. Indeed, they display a glass transition step only in DSC (Figure 2a) and show no birefringence in polarized optical microscopy images. Their X-ray scattering spectra at 25 °C (see the SI) are composed of a broad band between 11 and 2 Å characteristic of nearest-neighbor correlations in amorphous phases. This broad halo does not contain any sharp peaks characteristic of crystallinity. These results indicate that DAT−PPO-*X*−DAT (*X* = 460, 2200) are amorphous. This confirms the ability of DAT derivatives to form glasses because of their lack of efficient packing.[16] A low-intensity peak that scales with the chain length was also observed in the X-ray spectra of DAT−PPO-*X*−DAT (*X* = 460, 2200). We interpret this peak as resulting from the correlation hole effect.[17,5] It reflects the typical distance between the strongly scattering polar stickers separated by the PPO chain (resulting in the chain length scaling) but does not indicate mesoscopic organization.[18] Therefore, DAT−PPO-*X*−DAT (*X* = 460, 2200) are in a disordered state. The rheology of DAT−PPO-2000−DAT from

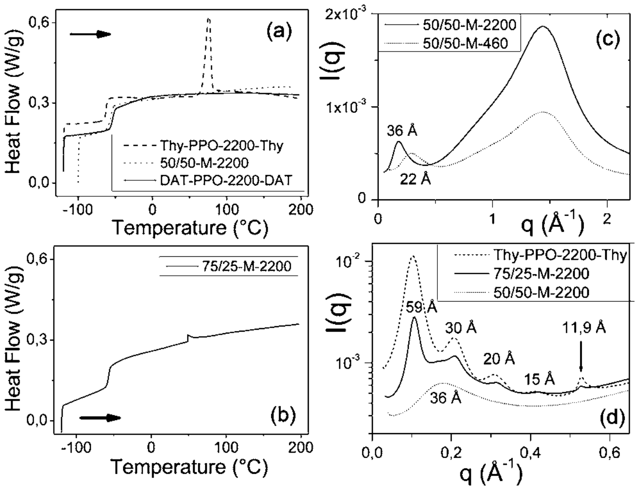


Figure 2. (a, b) DSC at 10 °C/min (exo down) of (a) DAT−PPO-2200−DAT, 50/50-M-2200, and Thy−PPO-2200−Thy and (b) 75/25-M-2200. (c, d) X-ray scattering at 25 °C of (c) 50/50-M-*X* (*X* = 460, 2200) and (d) 75/25-M-2200, 50/50-M-2200, and Thy−PPO-2200−Thy.

−10 to 120 °C (see the SI) is characteristic of a viscous fluid in the terminal flow regime, with a complex viscosity that is independent of the angular frequency ω and a loss modulus G'' that is higher than the storage modulus G' $[G''(\omega) \sim \omega$ and $G'(\omega) \sim \omega^2]$.

To understand why long-range ordering is found for Thy−PPO-*X*−Thy but not for DAT−PPO-*X*−DAT (*X* = 460, 2200), estimates of the Flory−Huggins interaction parameters (χ) for PPO/DAT ($\chi_{\mathrm{PPO/DAT}} = 3.5$) and PPO/Thy ($\chi_{\mathrm{PPO/Thy}} = 10.6$) can be compared. χ reflects the affinity between two molecules. It can be estimated from the Hildebrand solubility parameters determined by Fedor's method.[19] PPO appears to have a weaker affinity for Thy than for DAT, so the microphase segregation driving force is stronger in Thy−PPO-*X*−Thy than in DAT−PPO-*X*−DAT. This could explain why Thy−PPO-*X*−Thy is ordered and DAT−PPO-*X*−DAT is not (*X* = 460, 2200). Another important explanation is that the crystallization driving force is not present in DAT−PPO-*X*−DAT as it is in Thy−PPO-*X*−Thy (*X* = 460, 2200). In addition, Thy crystallization could be promoted by hydrogen bonding between the amide junctions, which are present in Thy−PPO-*X*−Thy but absent in DAT−PPO-*X*−DAT.

DSC (Figure 2a; also see the SI), polarized optical microscopy, and X-ray-scattering of 50/50-M-X (*X* = 460, 2200) show that these mixtures behave exactly as neat DAT−PPO-*X*−DAT. The X-ray scattering spectra of 50/50-M-X (*X* = 460, 2200) at 25 °C (Figure 2c) display a broad halo between 11 and 2 Å resulting from nearest-neighbor correlations, without any sharp peak characteristic of crystallinity. They also display a low-intensity peak resulting from the correlation hole effect that scales with the chain length. Thus, 50/50-M-X (*X* = 460, 2200) are amorphous and do not present well-ordered structures, in contrast to Thy−PPO-*X*−Thy. The presence of the DAT groups seems to inhibit the crystallization of thymine and the subsequent formation of the lamellar structure of crystallized thymine planes and PPO layers. This underlines the existence of a selective Thy−DAT interaction in the bulk state. In fact, the disorder in 50/50-M-X (*X* = 460, 2200) stems from the strong directional interactions between the Thy and DAT stickers: Thy no longer crystallizes when it is linked to DAT, and the dispersion interactions are weaker because DAT has a stronger affinity than Thy for PPO ($\chi_{\mathrm{DAT/PPO}} < \chi_{\mathrm{Thy/PPO}}$).

Again, DSC (see the SI), polarized optical microscopy, and X-ray-scattering (see the SI) of 25/75-M-2200 (the mixture containing 25% Thy−PPO-2200−Thy and 75% DAT−PPO-2200−DAT) indicated that this mixture behaves like DAT−PPO-2200−DAT and 50/50-M-2200. Thus, 25/75-M-2200 is amorphous, as expected since the DAT moieties are in excess relative to the Thy moieties.

In contrast, 75/25-M-2200 (the mixture containing 75% Thy−PPO-2200−Thy and 25% DAT−PPO-2200−DAT) displays in the heating cycle of DSC (Figure 2b) a "melting" endotherm, in addition to a glass transition step. This "melting" endotherm has a very low intensity but is reproducible. Its enthalpy of fusion (∼2 J/g) is quite low compared with that of Thy−PPO-2200−Thy (15 J/g).[5] Polarized optical microscopy images of 75/25-M-2200 show that it is birefringent, with Maltese crosses and spherulites (see the SI). The X-ray scattering spectrum of 75/25-M-2200 at 25 °C (Figure 2d) reveals a sharp peak at 11.9 Å characteristic of the Thy crystallinity in Thy−PPO-2200−PPO. It also reveals peaks corresponding to a lamellar structure at the same positions as for Thy−PPO-2200−Thy.[5] Moreover, the X-ray scattering spectrum of 75/25-M-2200 shows what seems to be a correlation hole peak at the same position as the one for 50/50-M-2200. These results suggest that 75/25-M-2000 is semicrystalline as a result of crystallization of the excess Thy moieties. While DAT groups are available, Thy groups associate with them, but when there is an excess of Thy functionalities, that excess is free to crystallize in 2D planes and form a lamellar structure, with the PPO chains in between the crystallized thymine planes.

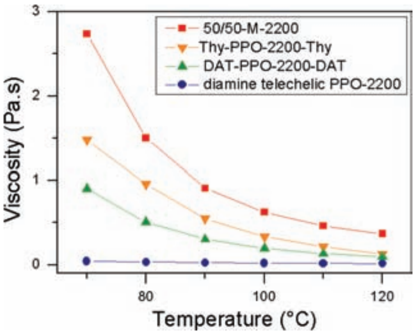


Figure 3. Viscosity as a function of temperature for diamine telechelic PPO-2200, DAT−PPO-2200−DAT, Thy−PPO-2200−Thy, and 50/50-M-2200.

At high temperatures, when crystallization and mesoscopic structuration are no longer present in Thy−PPO-2200−Thy, the viscosity of 50/50-M-2200 is higher than those of Thy−PPO-2200−Thy and DAT−PPO-2200−DAT (Figure 3). This viscosity effect can be attributed to the higher DP of the mixture because of the larger association constant between Thy and DAT than between Thy and Thy or DAT and DAT. Since the chain extension is due to hydrogen bonding, the viscosity decreases as the temperature increases, as observed in Figure 2. Indeed, the hydrogen bonds are released as the temperature increases, in agreement with FT-IR data (see the SI). These effects are traditional supramolecular polymer effects.

To conclude, contrary to Thy−PPO-*X*−Thy, DAT−PPO-*X*−DAT (*X* = 460, 2200) show no long-range organization because the crystallization driving force is not present in DAT derivatives and the phase segregation is weaker. In the 50:50 Thy−PPO-*X*−Thy/DAT−PPO-*X*−DAT mixtures (*X* = 460, 2200), the complementary association between Thy and DAT is strong enough to control the structure by inhibiting the Thy crystallization and the lamellar organization. The impact on the mechanical properties is crucial.

For amorphous and flexible spacers, the main factor to take into account for long-range order seems to be the crystallization of the stickers. Indeed, if it takes place, the ordering can appear whatever the segregation force between the spacer and the stickers. However, if there is no crystallization of the stickers, long-range order may also occur if the segregation is strong enough. Binder and his co-workers evidenced the long-range order of a supramolecular amphiphile consisting of monofunctional poly(isobutylene) (PIB) bearing a diaminotriazine chain end (PIB-3500−DAT).[11] $\chi_{\mathrm{PPO/DAT}} = 3.5$ is less than $\chi_{\mathrm{PIB/DAT}} = 6.1$,[19] illustrating that DAT has a weaker affinity for PIB than for PPO and possibly justifying why PIB-3500−DAT is ordered while DAT−PPO-*X*−DAT (*X* = 460, 2200) are not.[20] Hence, for polar functional groups, when the backbone is also rather polar, little tendency for long-range mesoscopic organization is expected in comparison with less polar backbones such as PPO.

To complete the understanding of the interplay between mesophase formation and thermomechanical behavior, it will be interesting to explore the structure and dynamics of systems in which incompatibility between the spacer and the stickers can induce long-range order but the stickers do not crystallize.

■ ASSOCIATED CONTENT

Supporting Information

Synthesis; ^{1}H and ^{13}C NMR data; DSC; X-ray scattering; FT-IR; rheology; DMA; and tensile tests. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(20) The control paramater actually is $(\chi\cdot n)/z$, where n is the DP and z is the functionality: $n \approx 70$, $z = 1$ for PIB-3500−DAT; $n \approx 35$, $z = 2$ for DAT−PPO-2200−DAT; $n \approx 8$, $z = 2$ for DAT−PPO-460−DAT.