Macromolecules

Liquid-Crystalline Phase Behavior in Polypeptoid Diblock Copolymers

Douglas R. Greer, Michael A. Stolberg, Sunting Xuan, Xi Jiang, Nitash P. Balsara, and Ronald N. Zuckermann

Materials Sciences Division and Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

College of Chemistry, University of California, Berkeley, Berkeley, California 94720, United States

Supporting Information

ABSTRACT: Polypeptoid homopolymers and block copolymers undergo thermal transitions in the solid state that can be detected by differential scanning calorimetry (DSC), but so far there is neither consensus on the underpinnings of the observed thermal transitions nor consensus on the expected number of transitions. We synthesized a series of polypeptoid diblock copolymers containing hydrophobic alkyl side chains and hydrophilic ethylene oxide side chains, systematically varying side-chain length (S), backbone main-chain length (N), block copolymer composition (n/m), and N-terminal group, and studied their thermal transitions by a combination of X-ray scattering and DSC. The thermal transitions are largely unaffected by S, N, and n/m but strongly affected by the N-terminal group. Block copolymers with an acetylated N-terminus exhibit two thermal transitions. The low temperature thermal transition is due to a transition from a crystalline phase to a sanidic liquid crystalline mesophase. The molecules adopt planar, boardlike conformations and are arranged in a rectangular crystal lattice with extended backbones that run parallel to each other. The side chains extend on either side and are located within the plane of the backbone. The liquid crystalline phase is characterized by conformational disorder in dimensions normal to the molecular plane. The high temperature thermal transition is due to melting of the liquid crystalline phase to give an isotropic phase. Block copolymers with a free N-terminus (non-acetylated) exhibit only one thermal transition and similar out-of-plane conformational disorder. This disorder appears to be due to a difference in the pendant side chain display angle of the terminal nitrogen atom.

INTRODUCTION

Poly(N-substituted glycine) polymers (polypeptoids) are a family of comb-like polymers that can be synthesized by either iterative solid-phase synthesis or conventional solution polymerization. Polypeptoids are structurally similar to polypeptides, but the absence of hydrogen bond donors along the polypeptoid backbone provides a simplified platform to study polymer melting behavior. A large number of polypeptoids are crystalline with accessible thermal transitions and exhibit well-defined X-ray diffraction peaks. The polypeptoids synthesized by submonomer solid-phase synthesis with sequence-defined and nearly monodisperse features are ideal systems for studying the relationship between molecular structure and crystalline behavior. Thermal transitions in crystalline polypeptoids have been probed by several investigators, but so far there is consensus neither on the underpinnings of the observed thermal transitions nor on the expected number of transitions. Rosales et al. studied the melting of alkyl-substituted polypeptoid homopolymers synthesized by solid-phase synthesis. They used differential scanning calorimetry (DSC) to show that these materials have a single thermal transition and that their melting temperature and enthalpy decrease as a function of increasing alkyl side chain length. Surprisingly, Lee et al. observed two melting transitions in high molecular weight alkyl-substituted polypeptoid homopolymers synthesized by solution polymerization. They attributed the first thermal transition to side chain melting and the second thermal transition to backbone melting. Fetsch et al. also observed two thermal transitions in the DSC measurements of poly(N-pentylglycine) and likewise attributed the first thermal transition to crystalline packing of the side chains. Sun et al. studied the melting of polypeptoid diblock copolymers synthesized by solid-phase synthesis containing an N-decylglycine block (Ndc) and a triethyleneoxy block (Nte). They also observed two thermal transitions, which were attributed to the melting of the separate Nte and Ndc blocks. It is evident that a comprehensive understanding of thermal transitions in polypeptoids is lacking.

In this study, we synthesized a systematic series of diblock copolypeptoids, varying side-chain length (S), backbone main-chain length (N), block copolymer composition (n/m), and N-terminal capping group to elucidate the relationship between...
thermal transitions and molecular structure. The thermal transitions in these materials were studied by a combination of temperature-dependent X-ray scattering and DSC. We show that most of the crystalline polypeptoids in this study are in fact liquid crystalline, exhibiting a sanidic mesophase, a phase previously found in polymers with flexible alkyl side chains emanating from an extended, rigid aromatic backbone. This sanidic mesophase is characterized by the parallel stacking of boardlike molecules, with different spatial arrangements of the stacks. This finding suggests a general framework for understanding thermal transitions in a wide range of polypeptoid materials and nanoassemblies.

### EXPERIMENTAL SECTION

**Synthesis of Polypeptoids.** The mPEG amine submonomers 2-(2-methoxyethoxy)ethylamine and 2-(2-(2-methoxyethoxy)ethoxy)-ethylamine, for Ndc and Nte (mPEG₂-NH₂ and mPEG₂-NH₃), were purchased from PurePEG (98% purity) and Peptide Solutions, Inc. (98% purity), respectively. Linear alkylamines and 4-methylpiperidine were purchased from TCI (>98% purity). (98% purity). Bromoacetic acid was purchased from ACROS Organics (99% purity). Trifluoroacetic acid was purchased from Sigma-Aldrich (99% purity). All other solvents (HPLC grade) used in this study were purchased from Millipore. All polypeptoids in this study were synthesized using automated solid-phase submonomer synthesis on a Symphony X peptide synthesizer at a scale of 200 mg Rink amide resin (0.64 mmol/g) by adapting reported procedures. Bromoacetylation reactions were performed with bromoacetic acid (0.8 M) and N,N′-diisopropylcarbodiimide (0.8 M) in DMF for 20 min at room temperature. Displacement reactions were performed at 1 M amine concentrations in DMF for 30 min at room temperature. The N-terminal acetylation of the polypeptoids was performed on the crude, cleaved polypeptoids (∼200 mg) in 2 mL of DMF/THF (1:1, v/v) followed by the addition of 100 µL of acetic anhydride and 100 µL of pyridine, and allowed to stir at room temperature for 20 min. The solvents were then removed under vacuum, and the crude product was lyophilized from acetonitrile/water (1:1, v/v) to afford a fluffy white powder. The final product was analyzed by MicroTOF electrospray mass spectrometry and reverse phase HPLC equipped with an analytical cyano column. 50 mg of final product with 80–90% molecular purity was obtained in most cases.

**X-ray Scattering.** Wide-angle X-ray scattering (WAXS) and small-angle X-ray scattering (SAXS) measurements were performed at ALS beamline 7.3.3 and SSRL beamline 1-5. Prior to measurement, lyophilized polypeptoids were placed between Kapton windows separated by a rubber gasket spacer, annealed at 125 °C for half an hour, and cooled slowly (cooling rate is <1 °C/min) to remove thermal history. All polypeptoids synthesized for this study are known to be isotropic above 100 °C.

**Differential Scanning Calorimetry (DSC).** DSC was performed on a TA Instruments Q2000 series with a nitrogen purge rate of 50 mL/min. The calorimeter was calibrated with an indium reference. Samples of between 2 mg and 10 mg of lyophilized peptoid were loaded into aluminum T-Zero series pans and compressed with standard lids. An unloaded pan with lid of the same type was used as reference for all samples. To erase thermal history, all samples were first heated from room temperature to 150 °C. The samples were then put through two cycles of cooling to 0 °C and heating to 150 or 180 °C at a rate of 10 °C/min. All data shown are from the second heating cycle with exothermic being up. Labels near each melting peak display the temperature in °C of the enthalpy extrema and the integrated melting enthalpy in J/g of total polymer. Peaks were integrated using a linear method.

### RESULTS AND DISCUSSION

The crystal structure of the N-acetylated diblock copolypeptoid family, Ac-Ndc₃₋₅-Nte₃₋₅, has been previously studied at room temperature. It was shown that these molecules adopt boardlike configurations in the crystalline state as shown in Figure 1a. X-ray scattering data from these samples contain peaks corresponding to the dimensions a, b, and c shown in Figure 1a. It was shown that b is a linear function of backbone length, c is a linear function of side chain length, and a is independent of these parameters. All of the block copolymers exhibited microphase separation in the crystalline state. Here we seek a molecular level understanding of how the chains become disordered upon melting for both N-acetylated polypeptoid crystals and their non-acetylated counterparts.

In the acetylated polymers, the N-terminal nitrogen atom is sp²-hybridized (trigonal planar) as are the other nitrogen atoms in the chain. The angle between the N-terminal side chain and the backbone is thus expected to be nearly identical to that between internal side chains and the backbone (Figure 1d). In the non-acetylated polymer, the terminal nitrogen atom is sp³-hybridized (tetrahedral). In this case, the angle between the N-
terminal side chain and the backbone is distinct from that between internal side chains and the backbone (Figure 1e). As we describe below, this small molecular difference has a large impact on the crystallization properties.

A series of N-acetylated and non-acetylated polypeptoid block copolymers composed of alkane and ether-containing N-substituted glycine monomers were synthesized by an iterative solid-phase method for this study (Figure 1 and Table 1). In most cases, the polymers were synthesized as matched pairs: each acetylated block copolymer has a non-acetylated counterpart. In block copolymers 1–5, the acetyl group is directly adjacent to the block with the alkyl side chains. Block copolymers 6–9 are non-acetylated matched pairs of these polymers (except for Ac-Ndc$_9$-Nte$_2$ in 4). The length of the block with alkyl side chains, $n$, and the length of the block with ethylene oxide side chains, $m$, and side chain length, $S$, were varied over a considerable range (Table 1). The number of monomers in each block is used to define $n$ and $m$, while the number of non-hydrogen atoms in the side chain is used to define $S$. In the final four columns of Table 1 are the thermal transition data compiled from our DSC studies.

We first examined the thermal behavior of these polymers in the solid state by DSC. For all these polymers, we found that the acetylated block copolymers (1–5) exhibit two thermal transitions at around 45 and 90 °C, while the non-acetylated block copolymers (6–9) exhibit one thermal transition at around 90 °C (Figures S1–S3). Surprisingly, a subtle change in the end group structure of the diblock copolypeptides (N-acetylated vs non-acetylated) results in a significant difference in their thermal behavior. This unexpected phenomenon inspired us to further investigate the impact of the N-terminus on the crystal structures of the diblock copolypeptides and their thermal transitions.

We next used X-ray scattering to study the structural underpinnings of these thermal transitions. The melting of Ac-Ndc$_9$-Nte$_9$ (1) crystals, as seen by DSC, exhibited two thermal transitions across different $q$ values (Figure 2). At temperatures above the second melting point, 1 is an isotropic liquid with no discernible X-ray scattering features. We thus focused on the low temperature thermal transition (Figure 2). In Figure 3, we show the results of three separate X-ray scattering experiments across different scattering angles wherein 1 was heated across the first thermal transition. The small-angle X-ray scattering (SAXS) profiles (Figure 3a), which reflect the $b$ dimension of the crystal (corresponding to the length of the main chain, Figure 1a), are insensitive to temperature. We thus conclude that the first thermal transition does not affect the length of the polymer chain ($b \approx 52$ Å). The intermediate-angle X-ray scattering profiles (Figure 3b), which reflect the $c$ dimension of the crystal (corresponding to the side-chain width, Figure 1a), are also insensitive to temperature. In contrast, wide-angle X-ray scattering (WAXS), which reports on the closest packing dimension, $a$, reveals significant changes as a function of temperature (Figure 3c). At 30 °C, we see the (100) peak corresponding to the $a$ dimension at $q \approx 1.36$ Å$^{-1}$. We also see higher order scattering peaks corresponding to (101), (102), and (103) reflections. The presence of these reflections indicates the long-range correlation between the $c$ direction and a direction, detailed in ref 22. With increasing temperature, the (101), (102), and (103) peaks become less pronounced while the (100) peak broadens. At 50 °C, only a single broad peak corresponding to the $a$ dimension at $q \approx 1.36$ Å$^{-1}$ is visible in Figure 3c. The average spacing between molecules along the $a$ direction remains unchanged as the temperature changes from 30 to 50 °C. The primary signature of the lower thermal transition is thus due to an increase in disorder along the $a$ direction.

Our interpretation of the temperature-dependent X-ray scattering data is depicted in Figure 4. At 30 °C, we obtain a simple periodic crystal with aligned molecules as shown in Figure 4a. At 50 °C, beyond the first thermal transition, the disappearance of the (101), (102), and (103) reflections indicates that the periodicity along the $a$ dimension is diminished. Because the $a$ dimension represents the closest packing between adjacent molecules (Figure 1a), this implies that the planes of the molecules along the $a$ dimension are disordered as shown schematically in Figures 4b and 4c. Thus, excursions of the molecules are restricted to the single $ab$

### Table 1. Polypeptoid Diblock Copolymers Synthesized and Their Chemistry and Heating Thermal Transitions

<table>
<thead>
<tr>
<th>Peptoid Nomenclature</th>
<th>Side chain 1 (R$_1$)</th>
<th>Side chain 2 (R$_2$)</th>
<th>$N$</th>
<th>$S$</th>
<th>$m$</th>
<th>$T_{m,1}$ (°C)</th>
<th>$T_{m,2}$ (°C)</th>
<th>$\Delta H_{m,1}$ (J/g)</th>
<th>$\Delta H_{m,2}$ (J/g)</th>
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<tr>
<td>Ac-Ndc$_9$-Nte$_9$</td>
<td>$\times_{1/3}$</td>
<td>$\times_{1/3}$</td>
<td>18</td>
<td>10</td>
<td>9</td>
<td>45.6</td>
<td>95.0</td>
<td>11.9</td>
<td>20.0</td>
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<tr>
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<td>$\times_{1/3}$</td>
<td>14</td>
<td>10</td>
<td>9</td>
<td>44.0</td>
<td>87.0</td>
<td>9.2</td>
<td>17.4</td>
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<tr>
<td>Ac-Ndc$<em>9$-Nte$</em>{15}$</td>
<td>$\times_{1/3}$</td>
<td>$\times_{1/3}$</td>
<td>25</td>
<td>10</td>
<td>9</td>
<td>45.8</td>
<td>96.2</td>
<td>7.2</td>
<td>14.9</td>
</tr>
<tr>
<td>Ac-Ndc$<em>9$-Nte$</em>{27}$</td>
<td>$\times_{1/3}$</td>
<td>$\times_{1/3}$</td>
<td>36</td>
<td>10</td>
<td>9</td>
<td>41.1</td>
<td>92.1</td>
<td>4.1</td>
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<td>Ac-Nhpe$_9$-Nde$_9$</td>
<td>$\times_{1/3}$</td>
<td>$\times_{1/3}$</td>
<td>18</td>
<td>7</td>
<td>9</td>
<td>41.9</td>
<td>96.6</td>
<td>11.3</td>
<td>21.7</td>
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<td>$\times_{1/3}$</td>
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<td>10</td>
<td>9</td>
<td>-</td>
<td>89.9</td>
<td>-</td>
<td>16.5</td>
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<tr>
<td>H-Ndc$_9$-Nte$_3$</td>
<td>$\times_{1/3}$</td>
<td>$\times_{1/3}$</td>
<td>14</td>
<td>10</td>
<td>9</td>
<td>-</td>
<td>83.3</td>
<td>-</td>
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<td>H-Ndc$<em>9$-Nte$</em>{15}$</td>
<td>$\times_{1/3}$</td>
<td>$\times_{1/3}$</td>
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<td>10</td>
<td>9</td>
<td>-</td>
<td>87.4</td>
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<td>$\times_{2/3}$</td>
<td>18</td>
<td>7</td>
<td>9</td>
<td>-</td>
<td>87.2</td>
<td>-</td>
<td>25.3</td>
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* denotes not observed.
plane. This restricted disorder gives rise to variability in the $a$ dimension and a loss of higher order scattering peaks, seen in the X-ray scattering data (Figure 3c). We posit that the polymer exhibits a sanidic liquid crystalline mesophase at around 50 °C. This mesophase was first discovered in melts of polymers with alkyl side chains emanating from an aromatic backbone. The distinct signature of this mesophase in our diblock copolypeptoids is a broad X-ray scattering peak characterizing a loss of order along the $a$ dimension with no loss of order along the $b$ and $c$ dimensions (Figure 3, 50 °C).

Going back to the DSC data in Figure 2, the first thermal transition at around 50 °C is attributed to the transition from a crystalline structure to a sanidic liquid crystalline mesophase. The second thermal transition at 90 °C is attributed to the melting of the sanidic mesophase into an isotropic liquid.

We next examined the impact of $N$-terminal acetylation. The melting of H-Ndc$_9$-Nte$_9$ (6) crystals, as seen by DSC, is shown in Figure 5. Unlike its acetylated matched pair, melting in this sample occurs primarily in one step at around 90 °C. The X-ray scattering profiles obtained from the sample at temperatures between 30 and 50 °C are shown in Figure 6. The X-ray scattering profiles of H-Ndc$_9$-Nte$_9$ (6) are very similar to those of Ac-Ndc$_9$-Nte$_9$ (1) (compare Figures 3 and 6) in spite of the dramatic differences in the DSC data (compare Figures 2 and 5). Figures 6a and 6b indicate that the $b$ and $c$ dimensions of the crystal are unaffected by temperature changes between 30 and 50 °C. In Figure 6c, we see the disappearance of the (101), (102), and (103) peaks as temperature increases and the appearance of a single broad (100) peak. There is no difference between the crystal structures of H-Ndc$_9$-Nte$_9$ (6) and Ac-
Ndc₉-Nte₉ (1) at 50 °C (compare Figures 6c and 3c). There is, however, a subtle difference between the crystal structures of H-Ndc₉-Nte₉ (6) and Ac-Ndc₉-Nte₉ (1) at 30 °C: the (101), (102), and (103) peaks of H-Ndc₉-Nte₉ (6) are superposed on the broad scattering peak obtained at 30 °C, while those of Ac-Ndc₉-Nte₉ (1) are not. It therefore appears that the disorder of the molecular planes along the a dimension (Figure 4c), a characteristic of the sanidic liquid crystalline mesophase, seen in Ac-Ndc₉-Nte₉ (1) at 50 °C, is present in H-Ndc₉-Nte₉ (6) at 30 °C. The disorder of the molecule planes along the a dimension at 30 °C suppresses the first thermal transition in H-Ndc₉-Nte₉ (6). The qualitative difference in the crystal structure of H-Ndc₉-Nte₉ (6) and Ac-Ndc₉-Nte₉ (1) described above is seen in most of the matched pairs. This is shown in Figure 7, where we show WAXS data from all of the matched pairs at room temperature. The non-acetylated samples (6–8) all exhibit WAXS peaks superposed on a broad sanidic peak, and they exhibit only one thermal transition in the vicinity of 90 °C. Their acetylated counterparts (1–3) all exhibit WAXS peaks that are not superposed on a broad sanidic peak and exhibit two thermal transitions in the vicinity of 40 and 90 °C. Samples 5 and 9 are exceptions. While the WAXS and DSC data from 5 are consistent with the above observations, the WAXS data from the non-acetylated 9 shows one thermal transition but no evidence of a broad sanidic peak, perhaps due to their shorter side chains which are known to be more highly ordered.

It is clear from the discussion above that the two thermal transitions that are sometimes observed in polypeptoid block copolymers are not associated with the melting of individual blocks; all of the non-acetylated diblock copolymers exhibit only one thermal transition. Instead, the first thermal transition is associated with the selective loss of order along the a dimension while the second thermal transition is associated with the complete loss of order along all dimensions. This phenomenology was only previously observed in branched aromatic polymers with stiff backbones. The origin of backbone stiffness in polypeptoids remains an interesting open question. We recently showed that nearly all known crystalline polypeptoids adopt an all-cis backbone conformation, suggesting there is a universal low-energy conformation preferred by the peptoid backbone. The stiffness and extended structure may arise due to interchain interactions along the backbone, or it may be induced by packing constraints from the side chains. 

Figure 5. Second heating DSC trace of H-Ndc₉-Nte₉ (6). Enthermic maxima temperatures and transition enthalpies are displayed.

Figure 6. X-ray scattering measurements of H-Ndc₉-Nte₉ (6) through the first thermal transition. (a) SAXS measurements showing the (010) peak corresponding to the b dimension. (b) WAXS measurements showing the (001) and (002) peaks corresponding to the c dimension. The peak at q = 0.4 Å⁻¹ is due to the Kapton windows. (c) WAXS measurements showing the broadening of the (100) peak at q = 1.36 Å⁻¹ corresponding to the a dimension and the loss of the (101), (102), and (103) peaks at higher q.
The (100) peak corresponding to the a dimension.

chains. Direct evidence for this stiffness has been reported using temperature-dependent resonant soft X-ray scattering measurements on similar peptoid diblock copolymers.\(^{26}\) One of the dominant factors for inducing disorder of the molecular planes along the a dimension appears to be the orientation of the N-terminal side chain as depicted in Figure 1d,e. We propose that the increase disorder along the a dimension in the non-acetylated peptoid crystals is due to a difference in hybridization of the N-terminal nitrogen, resulting in a display angle mismatch of the N-terminal side chain (sp\(^3\)) relative to the internal side chains (sp\(^2\)). Interestingly, the number of thermal transitions (one versus two) and the thermal transition temperatures in the peptoids studied here are mainly affected by the N-terminal group, not the other parameters that define molecular structure: S, N, and n/m.

**CONCLUSION**

We present a systematic study of the thermal transitions of peptoid diblock copolymers with alkyl and ethylene oxide side chains using DSC and X-ray scattering. We explored the relationship between molecular structure and thermal transitions by varying the side chain length (S), backbone main-chain length (N), block copolymer composition (n/m), and the N-terminal group. Surprisingly, the \(T_m\) and \(\Delta H\) of the thermal transitions are largely unaffected by \(S\), \(N\), and \(n/m\). The nature of the thermal transitions is mainly affected by the N-terminal group. Block copolymers with an acetyl N-terminal group exhibit two thermal transitions. The low temperature thermal transition is due to a transition from a crystalline phase to a sanidic liquid crystalline mesophase. The polypeptoids adopt boardlike molecular conformations in the crystalline phase. The cis backbones of polypeptoids in the crystal are extended and parallel to each other. The liquid crystalline phase is characterized with the selective loss of planar order along the a dimension. The high temperature thermal transition is due to melting of the liquid crystalline phase. A broad X-ray scattering peak in the vicinity of \(q = 1.4\) Å\(^{-1}\) is a signature of the sanidic liquid crystalline phase in these diblock copolypeptoids. Block copolymers with a hydrogen atom at the N-terminus exhibit only one thermal transition. At low temperatures, the higher order scattering peaks corresponding to the crystalline phase in these block copolymers are superposed on the broad scattering peak that is the signature of the sanidic phase. This indicates that the molecular conformations in these crystals are characterized by planar disorder along the a dimension. We posit that the difference in the angle between the N-terminal side chain and the backbone and that between the internal side chains and the backbone cause conformational disorder of the molecules along the a dimension.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.8b01952.

DSC traces of homopolypeptoid Ac-Ndc\(_{20}\) and diblock copolypeptoids, WAXS and SAXS measurements of diblock copolypeptoids as a function of increasing temperature, and characterization data of diblock copolypeptoids (PDF)

**AUTHOR INFORMATION**

Corresponding Authors
*E-mail nbalsara@berkeley.edu.*
*E-mail rmzuckermann@lbl.gov.*

ORCID

Douglas R. Greer: 0000-0002-7664-6241
Xi Jiang: 0000-0002-9589-7513
Nitash P. Balsara: 0000-0002-0106-5565
Ronald N. Zuckermann: 0000-0002-3055-8860

Notes
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