

End Groups of Functionalized Siloxane Oligomers Direct Block-Copolymeric or Liquid-Crystalline Self-Assembly Behavior

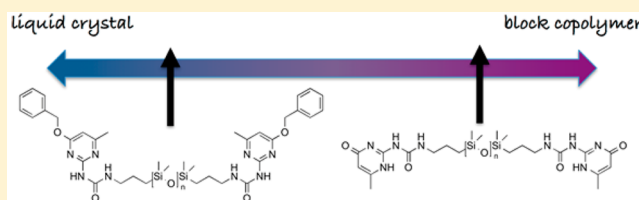
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S Supporting Information

ABSTRACT: Monodisperse oligodimethylsiloxanes end-functionalized with the hydrogen-bonding ureidopyrimidinone (UPy) motif undergo phase separation between their aromatic end groups and dimethylsiloxane midblocks to form ordered nanostructures with domain spacings of <5 nm. The self-assembly behavior of these well-defined oligomers resembles that of high degree of polymerization (N)–high block interaction parameter (χ) linear diblock copolymers despite their small size. Specifically, the phase morphology varies from lamellar to hexagonal to body-centered cubic with increasing asymmetry in molecular volume fraction. Mixing molecules with different molecular weights to give dispersity >1.13 results in disorder, showing importance of molecular monodispersity for ultrasmall ordered phase separation. In contrast, oligodimethylsiloxanes end-functionalized with an O-benzylated UPy derivative self-assemble into lamellar nanostructures regardless of volume fraction because of the strong preference of the end groups to aggregate in a planar geometry. Thus, these molecules display more classically liquid-crystalline self-assembly behavior where the lamellar bilayer thickness is determined by the siloxane midblock. Here the lamellar nanostructure is tolerant to molecular polydispersity. We show the importance of end groups in high χ –low N block molecules, where block-copolymer-like self-assembly in our UPy-functionalized oligodimethylsiloxanes relies upon the dominance of phase separation effects over directional end group aggregation.



INTRODUCTION

In an effort to overcome the size limitations facing top-down microelectronics fabrication, the bottom-up phenomenon of block copolymer nanophase separation is an attractive strategy for creating nanolithography templates.^{1–4} Numerous experimental and theoretical studies have shown that the morphology and domain spacing of nanophase-separated block copolymers can be predictably controlled by varying the degree of polymerization (N), the volume fraction (f), and the interaction parameter between blocks (χ).^{5–10} Block copolymers containing polydimethylsiloxane (PDMS) are particularly desirable, as the generally high incompatibility between siloxanes and many organic components facilitates ordered phase separation at low N , yielding correspondingly small features.^{11,12} For example, our group has utilized the high χ and etch contrast between blocks in PDMS-*b*-poly(lactic acid) to create ordered arrays of sub-20 nm features.¹³ However, while studies have shown that high χ –low N block copolymers can exhibit domain spacings as small as 9 nm,¹⁴ the structure size achievable by traditional block copolymers is still limited by the order–disorder transition at low molecular weight. Recent work with discrete dimethylsiloxane–lactic acid oligomers suggests that perfect monodispersity can help push ordered nanophase separation toward domain spacings as small as 6.8 nm.¹⁵ Siturel, Bates, and Hillmyer similarly expressed that features smaller than 5 nm may be better obtained by using

small, well-defined molecules that self-assemble instead of classical block copolymers.¹⁶ This class of low-molar-mass molecules is dominated by liquid crystals, which can exhibit ordered phases with domain spacings of a few nanometers in bulk.^{17–19} Here, self-assembly is strongly guided by directional interactions resulting from shape anisotropy and enthalpic forces (e.g., hydrogen bonding and π stacking). Thus, liquid crystal morphology generally depends on the molecular geometry rather than on the interplay between entropic and enthalpic forces to minimize the interfacial energy at a given volume fraction. For example, discotic mesogens predominantly exhibit columnar morphologies while calamitic mesogens are usually needed for nematic or smectic morphologies.¹⁸ Interestingly, molecules that bridge the gap between liquid crystals and block copolymers have been rarely studied. Hillmyer and co-workers showed that small (2.5–8.9 kg/mol) poly(ethylene oxide)–polyethylene block copolymers exhibit phase transition behavior resembling those of both high molecular weight block copolymers and low molecular weight nonionic lyotropic liquid crystals.²⁰ However, the ability of small, discrete molecules to exhibit block-copolymer-like self-assembly behavior has yet to be demonstrated.

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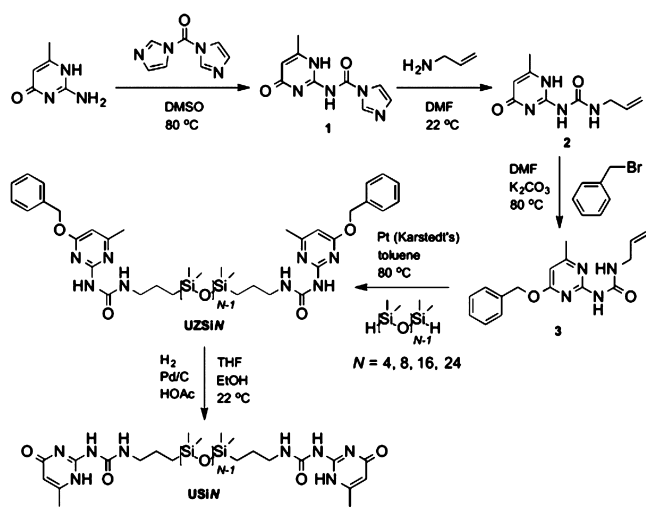
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Here we describe the synthesis and characterization of novel siloxane-based “block molecules” consisting of monodisperse dimethylsiloxane oligomers (ODMS) end-capped with ureidopyrimidinone (UPy), an aromatic motif capable of dimerizing via quadruple hydrogen bonds.^{21–23} Notably, we utilize a stepwise procedure to synthesize ODMS of perfectly defined length and thereby obtain oligomeric molecules with up to 24 dimethylsiloxane repeat units without any polydispersity. We show that these well-defined molecules exhibit phase separation between the dimethylsiloxane chain and the aromatic end groups into ordered morphologies with sub-5 nm domain spacings. By varying the molecule length and volume fraction, we further show data suggesting that the self-assembly of these UPy-functionalized ODMS resembles the behavior of block copolymers rather than liquid crystals. We investigate the role of end group interactions in facilitating this block-copolymer-like self-assembly by additionally studying O-benzylated UPy end groups.

RESULTS AND DISCUSSION

To synthesize well-defined UPy-functionalized siloxanes with varying molecular length and volume fraction, perfectly monodisperse ODMS with $N = 4, 8, 16,$ or 24 repeat units was utilized (Scheme 1). While monodisperse ODMS with four

Scheme 1. Synthesis of UZSiN and USiN



dimethylsiloxane repeat units can be commercially purchased, longer monodisperse ODMS are not readily available. Thus, we developed a stepwise procedure to synthesize ODMS in discrete lengths using chlorosilane and silanol building blocks. Synthetic details are presented in the Supporting Information as well as a recent paper,¹⁵ and the general strategy for the facile synthesis of monodisperse ODMS with various reactive or stable end groups will be reported in greater detail in further publications. UPy bearing a terminal olefin was synthesized for attachment to hydride-terminated ODMS chains via hydrosilylation (Scheme 1). However, in order to avoid attachment of ODMS to the oxygen atom of the enol tautomer of UPy, a benzyl protecting group was added prior to hydrosilylation. After purification, this benzyl group was removed by palladium-catalyzed reduction in hydrogen gas to give the final bis-UPy oligodimethylsiloxanes (USiN).

Previous studies have shown that PDMS functionalized with UPy exhibits phase separation between the polymer backbone

and the UPy motifs.^{24,25} High-molecular-weight supramolecular polymers were obtained, and the formation of UPy microdomains dramatically improved the elastic properties of the material. Thus, our well-defined USiN materials were expected to be polymeric in nature and contain nanoscale phase-separated domains. Indeed, we found that USiN molecules behave as high molecular weight copolymers instead of oligomers. When cast from chloroform, USi4 and USi8 are clear, brittle films while USi16 and USi24 are tacky, viscoelastic solids (Figure 1). Thermal analysis by differential scanning

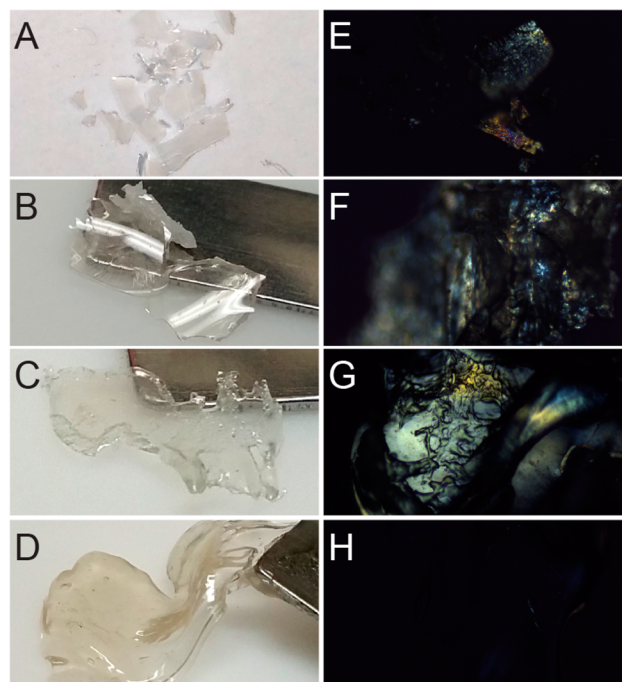


Figure 1. (A–D) Images of bulk (A) USi4, (B) USi8, (C) USi16, and (D) USi24. (E–G) Polarized optical microscopy images showing birefringence in (E) USi4, (F) USi8, and (G) USi16 materials. (H) USi24 lacks birefringence in polarized optical microscopy.

calorimetry (DSC) showed polymeric glass transition temperatures ranging from -14 to 64 °C depending on the number of dimethylsiloxane repeat units (Figure S1). An IR band at 1700 cm^{-1} characteristic of the pyrimidinone carbonyl stretch vibration indicates that UPy end groups exist in the strongly dimerizing keto form,^{21,24} and an IR band at 3216 cm^{-1} further confirms hydrogen bonding of the end groups to form supramolecular polymers (Figure S2).

In stark contrast to the liquid nature of unfunctionalized ODMS and even high molecular weight PDMS, the solidity of USiN suggests the existence not only of dimerized UPy end groups but also of phase-separated UPy “hard” domains. Interestingly, polarized optical microscopy (POM) showed USi4, USi8, and USi16 to be birefringent (Figure 1), presumably resulting from the presence of optically anisotropic material structures with periodic domains having one refractive index within a matrix having a second refractive index. This result further suggests that the UPy domains are well-ordered in these materials. Small-angle X-ray scattering (SAXS) confirmed that UPy and dimethylsiloxane moieties can phase separate into ordered structures with domain spacings (L_0) as small as 2.2 nm (Table 1 and Figure 2). Surprisingly, the phase morphology varies depending on the volume fraction. Specifically, USi4

Table 1. USiN Volume Fractions and Phase Characterizations^a

sample	f_{UPy}	L_0 (nm)	phase
USi4	0.52	2.2	LAM
USi8	0.35	3.2	HEX
USi16	0.21	4.8	BCC
USi24	0.15	–	DIS

^aThe domain spacing, L_0 , is the bilayer thickness for the lamellar (LAM) morphology and the center-to-center spacing for the cylindrical (HEX) and spherical (BCC) morphologies. The calculation of f_{UPy} is described in [Supporting Information](#).

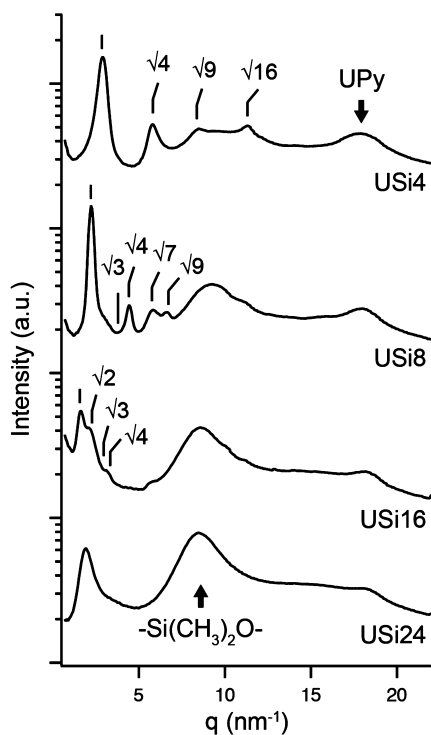


Figure 2. Small-angle X-ray scattering of USiN materials. Intensity is given in arbitrary units, and curves have been shifted for visual clarity. The siloxane backbone and the UPy interdisc scattering are marked with arrows.

exhibits a lamellar morphology, USi8 a hexagonally packed columnar morphology, and USi16 a body-centered cubic morphology. Highly asymmetric USi24 is disordered, as it exhibits a broad, low-intensity Lorentzian peak typical of correlation hole scattering in disordered block copolymer melts. This result agrees with the lack of birefringence of USi24 in POM. Stacking of UPy dimers with an interdisc distance of 3.5 Å can be seen in the SAXS spectra of USi4 and USi8, although there is no evidence for crystallization of the UPy domains. Such lateral aggregation is logical given the lamellar and columnar morphologies of USi4 and USi8, respectively. UPy stacking is less apparent in the spectrum of USi16 and is nearly absent in the spectrum of USi24. These results likely reflect both the constraints against significant lateral aggregation in body-centered cubic and disordered morphologies as well as the low UPy volume fraction contribution to the scattering intensity.

Our observations suggest that unlike conventional liquid crystal self-assembly, USiN self-assembly is not dominated by directional interactions. Indeed, previous studies of UPy-

functionalized poly(ethylene butylene) and polycaprolactone indicate that UPy dimers have relatively low propensity for ordered aggregation without additional directionality provided by adjacent hydrogen-bonding urea or urethane motifs.^{26,27}

Instead, the self-assembly of USiN into ordered nanoscale morphologies appears to be driven predominantly by phase separation and can be considered analogous to the self-assembly of a linear diblock copolymer in which one block is significantly more rigid than the other. In our USiN molecules, the UPy end groups represent short, rigid A blocks and the ODMS segments represent flexible B blocks. Studies of linear block copolymers suggest that the ABA topology exhibits identical phase behavior as an AB topology in the strongly segregated regime.^{28,29} However, conformational asymmetry of the blocks shifts the phase boundaries because of the tendency of the interface to curve toward the more flexible block.³⁰ Thus, the appearance of lamellar, hexagonal close packed, body-centered cubic, and disordered phases with varying USiN volume fraction is generally consistent with block copolymer theory. It is probable that the high chemical incompatibility of dimethylsiloxane and UPy is necessary for such ordered nanophase separation. The high conformational freedom of ODMS chains likely further facilitates the polymeric behavior of USiN on such molecular length scales, as the DSC data suggest even short ODMS segments to be amorphous on the basis of a lack of sharp dimethylsiloxane melting transitions ([Figure S1](#)). In other words, the unusual flexibility of dimethylsiloxane backbones³¹ may allow the USiN molecules to behave more like Gaussian polymer chains, which is an underpinning requirement in classical block copolymer mean-field theory.^{5,32}

Interestingly, narrow dispersity of the ODMS segment is vital for ordered morphologies. Mixtures of USiN molecules of various lengths to create artificial dispersity suggested that structures become disordered with increased dispersity, with all order lost by $M_w/M_n = 1.14$ ([Figure S3](#)). Therefore, unlike conventional block copolymers, which may in some cases form ordered morphologies even with $M_w/M_n > 1.3$,^{33–35} the nanodomain ordering of USiN is sensitive to polydispersity. The thermal phase behavior of USiN molecules and extraction of an effective χ value are interesting topics for further investigation.

To understand the self-assembly of USiN molecules, the intermolecular interactions of the end groups must be carefully considered. We thus further investigated the self-assembly of O-benzylated USiN molecules (UZSiN), which were synthetic precursors originally designed to avoid improper attachment of ODMS chains to UPy during hydrosilylation ([Scheme 1](#)). SAXS showed that UZSiN molecules form lamellar layers regardless of volume fraction ([Figure 3A](#) and [Table 2](#)), which is additionally evident from the highly birefringent circular focal conic and fan textures seen in POM ([Figure 4](#)). Diffraction peaks of O-benzylated UPy end groups can be observed in the SAXS spectra of samples with high f_{UPy} . Accordingly, UZSiN molecules have liquid-crystalline rather than polymeric attributes. UZSi4 and UZSi8 are white powders, while UZSi16 and UZSi24 are waxy solids ([Figure 4](#)) that may be deformed by shear at room temperature in order to align crystallographic orientations ([Figure S4](#)). DSC showed sharp order–disorder transitions rather than glass transitions ([Figure S1](#)). In context, previous research suggested that liquid crystal molecules incorporating just two or three dimethylsiloxane units prefer smectic phases because of phase separation of the dimethylsiloxanes.^{36–39} However, ODMS segments longer than

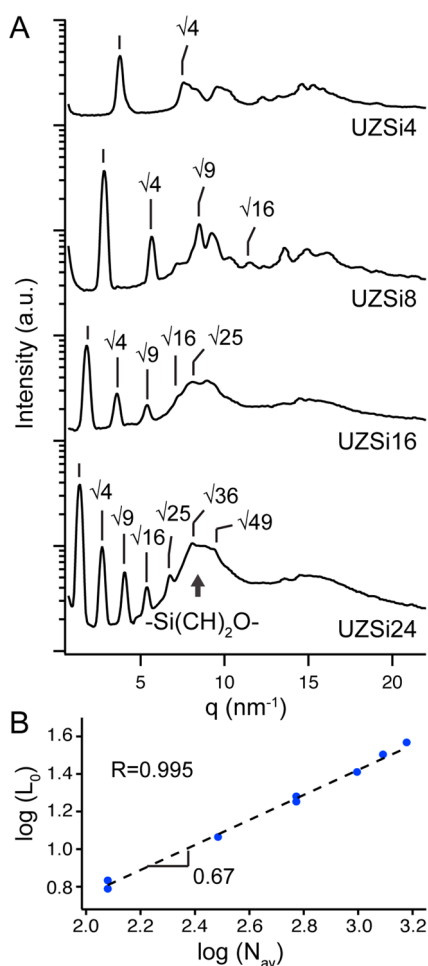


Figure 3. (A) Small-angle X-ray scattering of UZSiN materials. Intensity is given in arbitrary units, and curves have been shifted for visual clarity. The siloxane backbone scattering is marked with an arrow. (B) Fit of the lamellar spacing (L_0) vs the average number of dimethylsiloxane units in pure and mixed UZSiN.

Table 2. UZSiN Volume Fraction and Phase Characterizations

sample	f_{UPy}	L_0 (nm)	phase
UZSi4	0.62	1.7	LAM
UZSi8	0.44	2.2	LAM
UZSi16	0.28	3.5	LAM
UZSi24	0.20	4.8	LAM

a few repeat units have not been previously studied, and long aliphatic chains tend to give a nematic morphology in conventional liquid crystals.^{40,41} Thus, the propensity for lamellar morphology in UZSiN can likely be attributed to the packing preference of the O-benzylated UPy end groups. The X-ray crystal structure of O-benzylated UPy alone (compound 3; Figure S5) shows that this moiety dimerizes through two hydrogen bonds rather than the four hydrogen bonds seen in UPy dimerization (Figure S6). Dimers of O-benzylated UPy can further interact through slipped stacking of phenyl and pyrimidine rings as well as $\text{CH}\cdots\pi$ interactions (Figure S7). This arrangement results in a planar crystal structure in which ODMS chains can extend away from the plane formed by the end group motifs (Figure 5). The overall nanostructure of UZSiN thus consists of alternating layers of amorphous ODMS

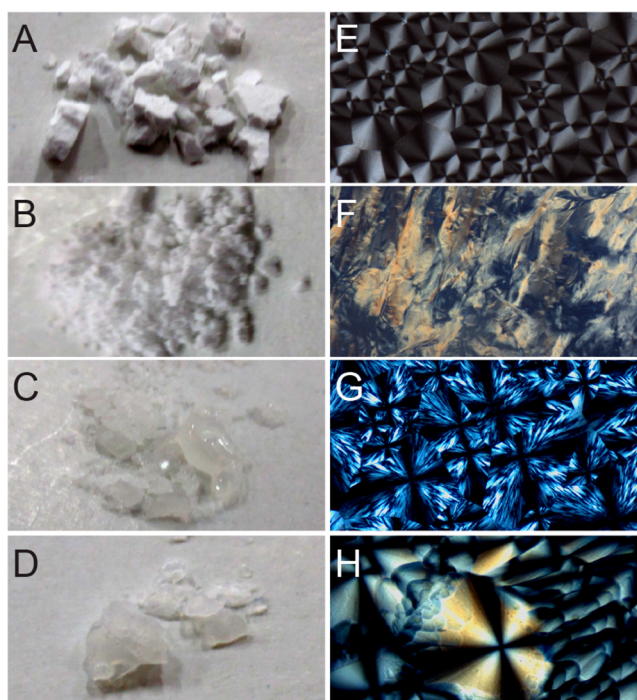


Figure 4. (A–D) Images of bulk (A) UZSi4, (B) UZSi8, (C) UZSi16, and (D) UZSi24. (E–H) Polarized optical microscopy images showing strongly birefringent smectic textures in (E) UZSi4, (F) UZSi8, (G) UZSi16, and (H) UZSi24.

and crystalline O-benzylated UPy. The incorporation of a benzyl group provides an additional source of directional intermolecular interaction that leads to crystallization of the UZSiN end groups in a planar geometry, thereby driving a lamellar morphology regardless of volume fraction.

Even though UZSiN molecules generally exhibit properties characteristic of thermotropic liquid crystals, some comparisons to block copolymer self-assembly can still be made. Mixing UZSiN molecules to create artificial polydispersity yields lamellae with L_0 that scales as $N_{\text{av}}^{2/3}$ (Figures S3 and 3B), where N_{av} is the average number of dimethylsiloxane repeat units. This mirrors the scaling law between L_0 and the degree of polymerization in a strongly segregated block copolymer,^{3,42–44} suggesting that benzylated UPy and siloxane domains are compositionally pure with narrow interface widths. However, mixtures containing >25% UZSi4 deviate from this trend, suggesting that UZSi4 molecules are too short to exhibit the conformational freedom needed to give freely jointed polymeric behavior.

The balance between secondary interactions and phase separation in our functionalized siloxanes plays a crucial role in directing the morphology. As shown by UZSiN molecules, when the strong planar packing preference of end group motifs dominates structure formation, lamellae are formed regardless of the molecular volume fraction and dispersity. However, as shown by USiN molecules, when end groups lack a strong propensity for directional aggregation, block-copolymer-like phase separation behavior becomes more apparent. In this case, the molecules exhibit volume-fraction-dependent phase behavior reminiscent of linear diblock copolymers, where the volume fraction is readily related to the molecular weights of the individual blocks. In contrast to amphiphilic surfactants, our USiN “block molecules” are entirely hydrophobic and do not require solvent as a driving force for aggregation and interface

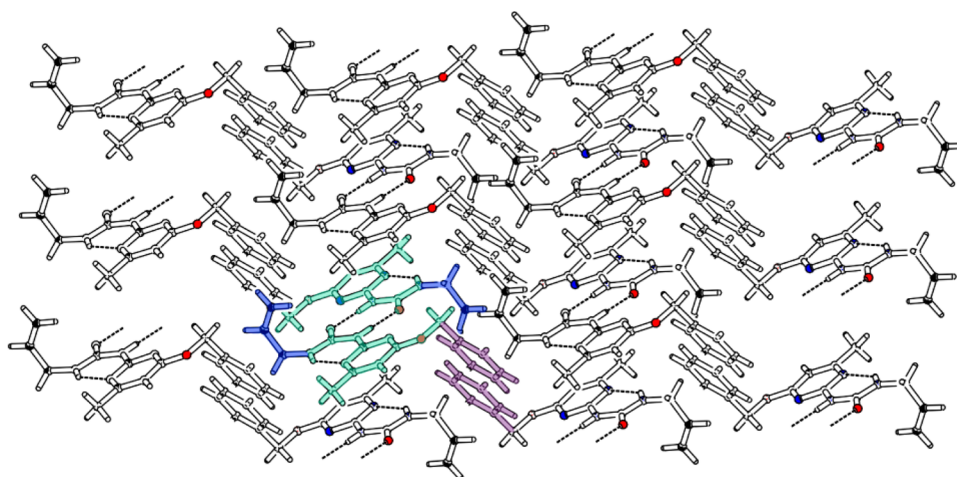


Figure 5. Planar geometry of crystallized compound **3** as seen by viewing unit cells lying in the XZ plane. Dotted lines are hydrogen bonds. Purple shading highlights a pair of phenyl rings in slipped stacking, green shading highlights a pyrimidine dimer, and blue shading highlights olefin terminals, where ODMS chains are attached by hydrosilylation. The planar geometry can also be viewed in the crystallography data included in the [Supporting Information](#).

minimization. However, in some aspects they may be regarded as similar to surfactants,^{17,45} which are frequently described by a packing parameter.⁴⁶ While the essence of a packing parameter does reflect volume fraction, it is designed to use aspects of molecular geometry such as headgroup size or tail branching to define the interfacial curvature. Calculations of packing parameter require estimates of molecular volume, hydrocarbon chain length, and effective headgroup area. Because these parameters must be determined empirically^{47,48} and are not readily applicable to our functionalized siloxanes, the ability to describe our molecules using accessible and well-established block copolymer concepts opens attractive avenues for understanding and predicting their self-assembly behavior.

CONCLUSION

We have presented a class of well-defined monodisperse end-functionalized siloxane oligomers that can exhibit ordered nanodomains with sub-5 nm spacings. Depending on the balance between directional interactions of the aromatic end groups and phase separation of the siloxane midblock from the end groups, the self-assembly behavior of these molecules can be similar to that of liquid crystals or linear diblock copolymers. Thus, these functionalized siloxane oligomers bridge the gap between classical liquid crystals and block copolymers.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/jacs.6b02172](https://doi.org/10.1021/jacs.6b02172).

Synthetic details, experimental methods, DSC data, POM images, SAXS spectra of polydisperse mixtures, and X-ray crystal structure of O-benzylated UPy ([PDF](#))
Crystallographic data for **3** ([CIF](#))

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Notes

The authors declare no competing financial interest.

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