

Self-Assembly through Stepwise Crystallization

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One of the most challenging problems in materials synthesis is the design of solid polymers with pre-defined secondary and tertiary structures. A large body of current research has addressed this problem, primarily through two approaches: the self-assembly of low molar mass molecules that have strong intermolecular interactions,¹ and the manipulation of the phase structures formed by segregated block copolymers.² These strategies have limitations. In the block copolymer case, the structures that can be obtained are limited to the spheres, lamellae, rods, and cubic phases characteristic of phase-separated block copolymers. Thus, the size of the structures that can be prepared by this method correspond to the characteristic domain sizes of the phases that form upon phase separation, typically 10–50 nm. Preparing block copolymers where one^{3–5} or both^{6,7} of the blocks are crystallizable can extend the range of structures and morphologies that can be obtained from block copolymers.

In recent work, we borrowed from small molecule chemistry as well as the tendency for block copolymers to phase-separate to build materials with defined conformations. For building blocks, we incorporate exact length segments of polyethylene (PE) and poly(ethylene oxide) (PEO) into polymers in a regular (AB)_n pattern. The PEO and PE segments strongly phase-separate, and unlike most block copolymers, both segments crystallize to form a rich variety of crystalline phases. One particularly interesting feature of PE/PEO microblock polymers is that the PE and PEO blocks normally adopt strikingly different crystal structures. PE typically crystallizes in an orthorhombic unit cell with the chains aligned along the *c*-axis in a planar zigzag conformation, while PEO crystallizes as a 7₂ helix,⁸ although a stress-induced metastable phase which contains planar zigzag chains has been reported.^{9,10}

To understand the structure of the (AB)_n polymers, we prepared a family of ABA oligomers that have the generic formula H(CH₂)_n(OCH₂CH₂)_mO(CH₂)_nH (where *n* = 6, 8, 10, 12, 14, 16 and *m* = 2–8, 10, 14) by coupling the appropriate alkyl bromides

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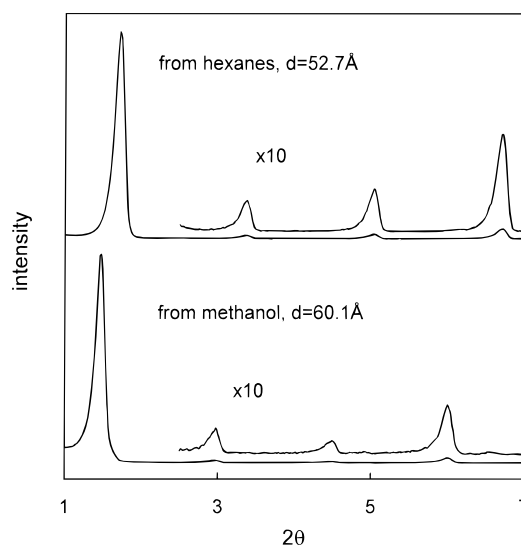


Figure 1. Powder XRD patterns for samples crystallized from different solvents.

with sodium alkoxides derived from exact length ethylene glycols. A number of analogous ABA oligomers have been prepared including compounds that contain PEO^{11,12} and thioether¹³ cores, as well as semifluorinated *n*-alkane oligomers.^{14,15} Because the degree of crystallinity of the oligomers is sensitive to having an exact number of ethylene oxide units in the chain, the ethylene glycols used in our syntheses were prepared by an iterative procedure that yields a single glycol product.^{16,17} Each compound was characterized by DSC measurements as well as by X-ray diffraction. All oligomers with *m* < 7 crystallized to form layered structures as evidenced by the well-defined series of *00l* lines seen in their X-ray diffraction patterns. The layer spacing calculated from the *00l* lines was compared with the results from the end to end distances of oligomers calculated by a molecular mechanics routine. Various chain conformations and packings were considered, but the XRD results agree best with fully extended chains oriented normal to the layers with the ethylene oxide core in a planar zigzag conformation.

Samples with seven ethylene oxide units were the most interesting since XRD (Figure 1) and DSC data (Figure 2) depend on sample history. For example, a 14–7–14 (*n–m–n*) oligomer crystallized from methanol has a melting point of 41.0 ± 0.5 °C and a ΔH_{fus} of 169 ± 1 J/g. The same oligomer crystallized from hexane melts at 39.0 ± 0.5 °C and has nearly the same ΔH_{fus} , 164 ± 1 J/g. We estimate that the degree of crystallinity for both samples is near 100% since these values correspond well to those we calculated based on the weight fraction of PE and PEO in the oligomer and the literature values for the ΔH_{fus} for the pure polymers. The XRD results, however, show that these two compounds have distinctly different packing arrangements in the solid state. For the sample crystallized from methanol, the XRD results give a layer spacing of 60.1 Å, while the corresponding

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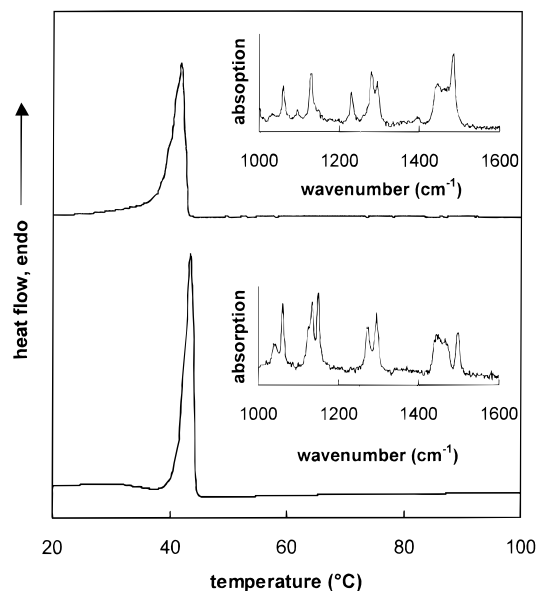


Figure 2. DSC first heating scans and the corresponding Raman spectra for samples crystallized from hexanes (top) and methanol (bottom).



Figure 3. Oligomer structure obtained by crystallization from methanol (top) and hexanes (bottom).

value for samples crystallized from hexanes is 52.7 Å. Thus, layered crystals of comparable stability are formed, but the individual molecules in the layers have different conformations.

The nature of the difference between the two structures can be seen in Figure 2. Shown are the DSC heating scans for samples crystallized from hexanes (top) and methanol (bottom), while the insets show a portion (1000–1600 cm^{-1}) of the Raman spectra for each sample. The sample recrystallized from methanol has bands at 1498 (CH_2 bending), 1150 (CH_2 rocking), and 1041 cm^{-1} (CC stretching), a pattern that is identical to that of highly oriented PEO held under tension.^{9,10} Such samples have been shown by X-ray diffraction to have a planar zigzag backbone conformation. The spectra also match the data from a 14–3–14 oligomer that has a planar zigzag conformation. Thus, the chain conformation for samples crystallized from methanol must be the fully extended trans conformation shown at the top of Figure 3. The same conclusion is reached from an analysis of the IR data and by comparing the layer spacing measured by XRD (60.1 Å) with the calculated length of the oligomer in its planar zigzag conformation (60.2 Å).

To assign the chain conformation of samples crystallized from hexanes, we again focused on the Raman and IR data. The spectra

show the bands characteristic of helical PEO, and the structure that best fits the data has a PEO core axis with the conformation of a 7_2 helix flanked by alkyl groups in their usual planar zigzag conformation. The calculated length of the linear structure (54.6 Å) is larger than the layer spacing observed by XRD (52.7 Å), but by tilting the alkyl chains 21° relative to the PEO core (see bottom structure in Figure 3), the overall length fits the layer spacing and provides more efficient packing for the alkyl groups. Similar conformations also have been proposed for AB nonionic surfactants^{18–20} and for a series of ABA oligomers where $m = 9$.^{11,12}

To understand why we obtain either a helical or a trans conformation for the PEO core under different crystallization conditions, it is reasonable to consider a stepwise process for the crystallization of the ABA oligomers. In particular, we believe that given the amphiphilic nature of the oligomers, the A and B subunits pre-organize before crystallization. Thus, the outcome of the crystallization process should be governed by the relative solubilities of the A and B segments in a given solvent. In hydrophobic solvents the alkyl portions of the oligomers should be more soluble than the PEO core, and the less soluble PEO core should crystallize first and choose its most stable conformation, the 7_2 helix. When the alkyl fragments crystallize, they adopt their normal planar zigzag conformation, but tilt with respect to the PEO core axis to accommodate the helical structure of the PEO core and to increase the packing density. This situation should be reversed when hydrophilic solvents are used for crystallization. For example, crystallization from methanol should yield a pre-organized structure where the alkyl portions are poorly solubilized. Thus, the alkyl portions of the oligomers should crystallize first in a trans zigzag conformation. When the PEO segments crystallize, they must conform to the structure defined by the alkyl segments and thus adopt a trans conformation. We note that this mechanism is not unlike that of protein folding, where the hydrophobic residues associate and help define the structure of the protein.

Even though spectral data show that ABA oligomers with PEO cores shorter than seven repeat units all have planar zigzag conformations, the abrupt formation of a helical unit in these oligomers at $m = 7$ should not be surprising. To insert a stable helix into a polyethylene chain and retain high crystallinity requires that the junctions between the PEO and PE chains have similar symmetries, a condition satisfied when the length of the PEO helix corresponds to one unit cell. This result points to a general strategy for incorporating stable crystalline polymer subunits into materials. By using segment lengths that correspond to multiples of the polymer unit cell, such segments can be expected to self-assemble into crystalline subunits that have the same structure as the parent polymer.

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Supporting Information Available: Experimental procedures and full characterization data for reaction products (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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