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Constrained/Directed Crystallization of Nylon-6. I. Nonstoichiometric Inclusion Compounds Formed with Cyclodextrins

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ABSTRACT: Noncovalently bonded crystalline inclusion compounds (ICs) have been formed by threading host cyclic starches, cyclodextrins (CDs), onto guest nylon-6 (N-6) chains. When excess N-6 is employed, nonstoichiometric (n-s)-N-6-CD-ICs, with partially uncovered and "dangling" N-6 chains, result. While the host crystalline CD lattice is stable to ~300 °C, the uncovered, yet constrained, portions of the N-6 chains emanating from the CD-IC surfaces may crystallize below or be molten above ~225 °C. We have been studying the constrained crystallization of the unthreaded N-6 chains "dangling" from (n-s)-N-6-CD-ICs, with comparison to bulk N-6 samples, as functions of N-6 molecular weights, lengths of uncovered N-6 chains (N-6:CD stoichiometry), and the CD host used. In the IC channels formed with host α- and γ-CDs containing 6 and 8 glucose units, respectively, single and pairs of side-by-side N-6 chains are threaded and included. In α-CD-ICs, the ~0.5 nm channels produced by stacked α-CDs are separated by ~1.4 nm, while in γ-CD-ICs the ~1 nm channels are ~1.7 nm apart, with each stacked γ-CD channel including two N-6 chains. N-6 chains in the bulk and in the dense (n-s)-N-6-α-CD-IC brushes, with a protruding chain density of ~0.60 chains/nm^2, show distinctly different kinetic and thermodynamic crystallization behaviors. The constrained protruding chains in the dense (n-s)-N-6-α-CD-IC brushes do not in fact "dangle", but are apparently highly extended from the α-CD-IC crystal surfaces. This causes them to crystallize faster and to a much greater extent than those in bulk N-6 melts, and this behavioral distinction is enhanced as the molecular weights/lengths of the unincluded protruding N-6 chains are increased. On the other hand, the N-6 chains protruding from (n-s)-N-6-γ-CD-ICs do not show nearly as large a propensity for crystallization. It is suggested that this may be the result of strong interactions between each pair of N-6 chains included in and emerging from each of the γ-CD-IC channels. Furthermore, when added at low concentrations, the nontoxic, biodegradable (n-s)-N-6-CD-ICs serve as effective nucleating agents for the bulk crystallization of N-6 from the melt. This is a consequence of the ability of the N-6 chains protruding from their (n-s)-CD-ICs to crystallize more rapidly at higher temperatures than bulk N-6 chains when their molten mixture is cooled, thereby providing finely dispersed crystalline nuclei for the subsequent crystallization of the bulk N-6 chains.

Introduction

Cyclodextrins (CDs) are cyclic starches formed by the α-1,4-linking of six (α-CD), seven (β-CD), and eight (γ-CD) glucose units, with internal hydrophobic cavities of ~0.5−1.0 nm in diameter (Figure 1a). Harada and Kamachi first demonstrated in 1990,[1] using poly(ethylene oxide) oligomers, that noncovalently bonded crystalline ICs could be formed between guest polymers and host CDs. This is accomplished by threading of the guest polymers through the narrow CD cavities to form polymer threaded crystalline stacks, as illustrated in Figure 1b and c.

More recently[2−7] it has been demonstrated that crystalline nonstoichiometric (n-s)-polymer-CD-ICs can be obtained if an excess of the guest polymer is used during their formation. Note in Figure 2 that incomplete coverage of the threaded guest polymers results in the "dangling" of unincluded portions of the polymer chains from the (n-s)-polymer-CD-IC crystalline surfaces. If the guest polymer is crystallizable, then those portions of the chains "dangling" from (n-s)-polymer-CD-ICs may also crystallize. As a consequence, it has been demonstrated[2−7] that when small amounts of (n-s)-polymer-CD-ICs are added to the same neat bulk polymer, they function as very effective nucleation agents during melt crystallization. This is presumably due to the ability of the "dangling" chains to more readily crystallize at higher temperatures, thereby providing nuclei for the crystallization of the bulk polymer chains as they are cooled further from the melt.

This approach is limited to polymers with melting temperatures, T_m, that are below that of the decomposition temperature (~300 °C) of polymer-CD-IC crystals. Because of the biodegradable/bioabsorbable and nontoxic natures of CDs, (n-s)-polymer-CD-ICs provide environmentally responsible nucleants for enhancing the melt crystallization of polymers and improving their properties.[6,7]

In addition, (n-s)-polymer-CD-ICs made with crystallizable guest polymers have also been demonstrated to exhibit shape-memory.[8,9] When heated between the polymer-CD-IC, they may be deformed into a new shape, which is retained following a rapid quench below T_m. When this newly shaped sample is heated above the T_m of the crystalline unincluded portions of the polymer, it reverts back to its original shape in response to the constraining CD-IC crystals.

Here, however, we are concerned with comparing the melt crystallization of neat bulk polymers and those chain portions of the same polymers that are constrained by and "dangle" from

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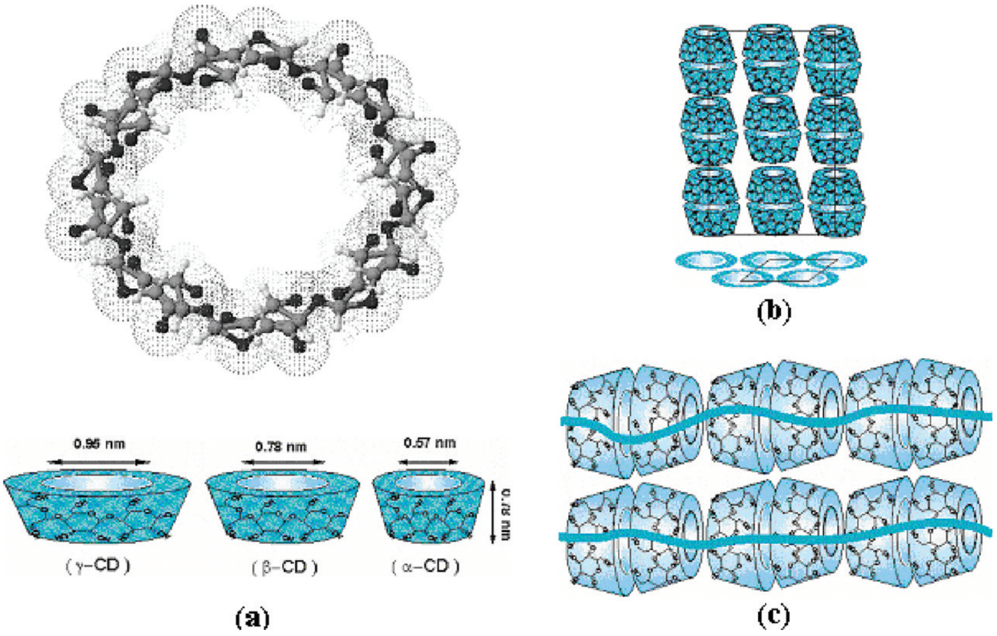

Figure 1. CD structures and cavity dimensions (a) and the channel crystal structure of polymer-CD-ICs (b) and (c).

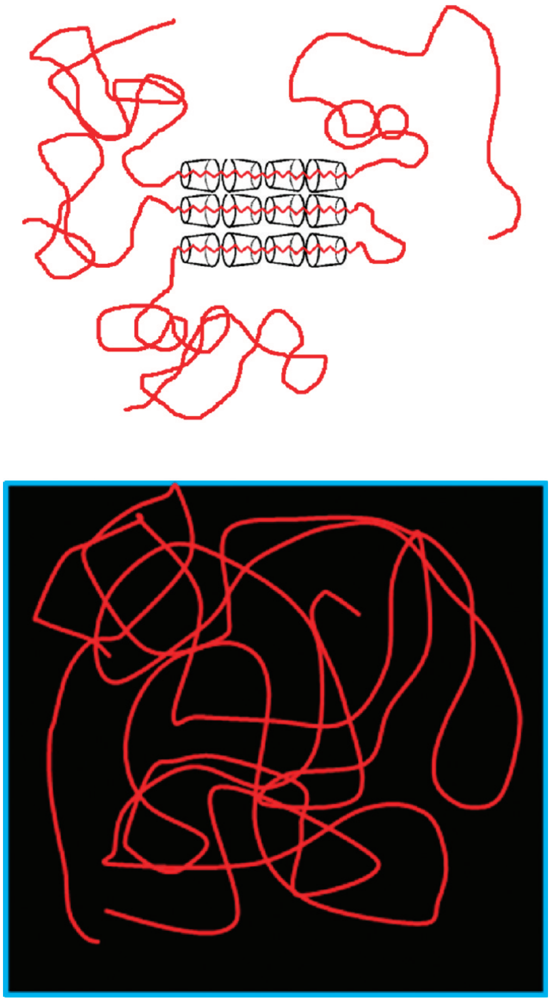

Figure 2. Schematic representations of a (n-s)-polymer-CD-IC (top) and a randomly coiling entangled polymer melt.

their (n-s)-CD-ICs (See Figure 2). For this purpose, we have employed nylon-6 (N-6), whose $T_m \sim 220$ °C, as both the bulk and (n-s)-CD-IC guest polymer. Anionically initiated, ring-opening polymerization of ε-caprolactam produced N-6 samples with different molecular weights (MW = M_w, with $M_w/M_n \sim 2$), ranging from 100000 to 600000 Da. When combined with commercial N-6 samples with MWs = 30000 and 60000 Da, this series of N-6 samples provides an opportunity to compare the effects of MW on the melt crystallization of "free" neat bulk and "dangling" constrained (n-s)-CD-IC N-6 chains.

Several different N-6/CD ratios were employed in the formation of (n-s)-N-6-CD-ICs to determine the effect of "dangling" chain length on their crystallizability. In addition, both α- and γ-CDs were selected as hosts, because single and pairs of side-by-side N-6 chains, respectively, are threaded through their ICs,[10] producing different constraints on the N-6 chains that "dangle" from them and which may effect their crystallization.

Experimental Section

Materials. N-6 samples with MW = 30000 and 60000 Da were commercial samples obtained from BASF. The N-6 samples with MW = 300000 and 600000 Da reported on here were prepared by the anionically initiated ring-opening polymerization of ε-caprolactam and were characterized with intrinsic viscosity and SEC/GPC measurements described previously.[11] ε-Caprolactam monomer and all solvents were obtained from Sigma-Aldrich and CDs were obtained from Cerestar.

Methods. Formation of N-6-CD-ICs followed our previous work,[10,12] with the following example given for the stoichiometric 1:1 N-6-α-CD-IC. A total of 0.5 g of N-6 was dissolved in 15 mL of 90% formic acid at room temperature and 60 mL of 99% acetic acid was added to the solution. A total of 4.27 g of α-CD was dissolved in 21 mL of 99% dimethyl-sulfoxide. The dissolved α-CD was then added to the N-6 solution. Their combined solution was stirred and heated on a hot plate at 50 °C for 2 h, then cooled to room temperature, and continuously stirred for another 6 h. The precipitate was finally vacuum filtered and dried in a vacuum oven.

N-6 films containing (n-s)-N-6-CD-ICs and Talc as nucleants were produced by dissolution of N-6 in 90% formic acid, suspension of the nucleant by addition with stirring, and removal of the formic acid by evaporation.

Infrared spectral studies were conducted with a Nicolet 510P FTIR spectrometer in the range 4000−400 cm^{-1}, with a resolution of 2 cm^{-1}. Powdered N-6 and (n-s)-N-6-CD-IC

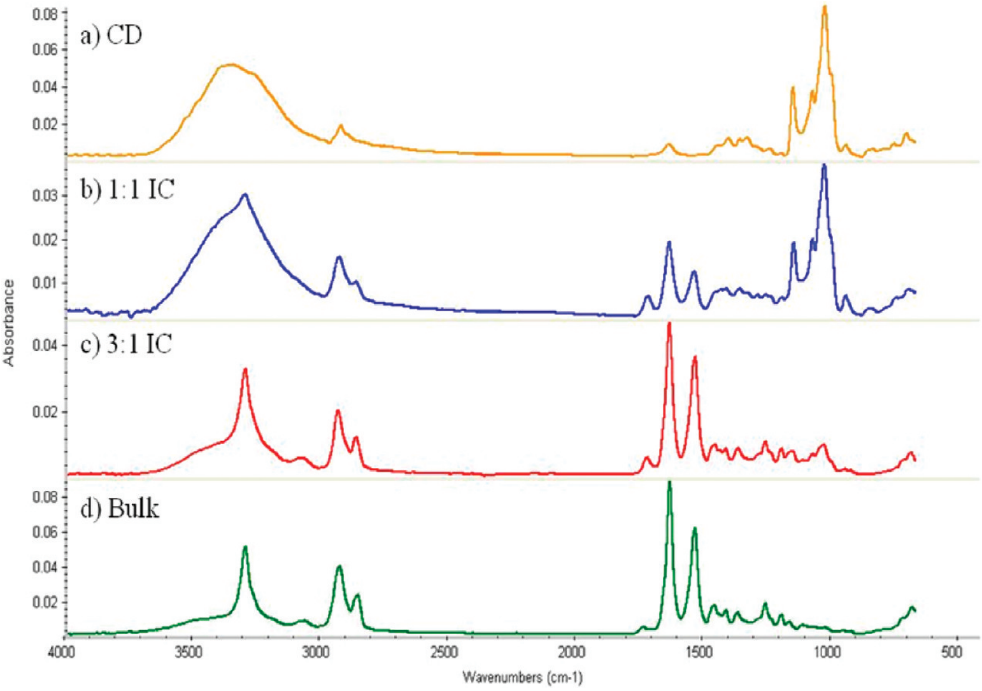

Figure 3. FTIR spectra for (a) α-CD, (d) 600000 g/mol N-6, and their (b) 1:1 stoichiometric and (c) 3:1 (n-s)-ICs.

samples were pressed into KBr pellets for the FTIR absorption measurements.

Differential scanning calorimetric (DSC) thermal scans were performed with a Perkin Elmer Diamond DSC-7 instrument. The measurements were run in the range 25−250 °C at heating and cooling rates of 10, 50, 100, 150, and 200 °C/min. Nitrogen was used as the purge gas.

Wide-angle X-ray diffraction (WAXD) of powdered samples were performed with a Siemens type-F X-ray diffractometer with a Ni-filtered Cu Kα radiation source ($\lambda = 1.54$ Å). The supplied voltage and current were 30 kV and 20 mA, respectively, and diffraction intensities were measured every 0.1° from $2\theta = 5$ to 30° at a rate of ($2\theta = 3°$)/minute.

Micrographs of melt crystallized N-6 films were obtained with a Nikon Eclipse 50i POL polarizing optical microscope. The images were captured on a CCID-IRIS/RGB color video camera made by Sony Corp.

Results and Discussion

FTIR. As is apparent in the FTIR spectra presented in Figure 3, both guest N-6 and host α-CD are present in the stoichiometric (1:1) and (n-s) (3:1) N-6-α-CD-ICs, with the latter sample containing an expectedly greater proportion of N-6 guest.

X-ray. As seen in Figure 4, the WAXD of the 3:1 (n-s)-N-6-α-CD-IC [(c)] evidences diffraction peaks attributable to both the columnar structure[12] of the host α-CD crystalline lattice [as in (b)] and those portions of the N-6 chains "dangling" from them that had crystallized [as in (d)]. In part (d) the diffractograms of as-received N-6 and the N-6 coalesced from its stoichiometric α-CD-IC, upon treatment with dilute HCl, show the presence of both α- and γ-polymorphs and predominantly the α-polymorph, respectively.[12] Comparison of (b), (c), and (d) suggests that the unincluded "dangling" N-6 chains in the 3:1 (n-s)-N-6-α-CD-IC are also crystallizing predominantly in the α-polymorph, with an antiparallel arrangement of neighboring chains. This observation would seem to suggest the possibility that (i) the N-6 chains in neighboring α-CD-IC channels are included in antiparallel directions, (ii) the N-6 chains "dangling" from the same α-CD-IC crystal are folding and reentering the same crystal in adjacent α-CD-IC channels, and (iii) the neighboring "dangling" N-6 chains are included in and contributed by different α-CD-IC crystals. Suggestion (iii) is supported by the shape-memory behavior exhibited by (n-s)-polymer-CD-ICs.[8,9]

DSC. In the 10 °C/min heating/cooling DSC scans shown in Figure 5, none and some of the N-6 chains in the stoichiometric 1:1 and 3:1 (n-s)-N-6-α-CD-ICs, respectively, are crystallizing. Thus, portions of the N-6 chains in the 3:1 N-6-α-CD-IC must not be included, but instead are "dangling" and able to crystallize. From Figure 6 we can see that upon identical cooling from the melt these "dangling" N-6 chains crystallize at a higher temperature than neat bulk N-6. In addition, from the selected DSC results presented in Table 1 it is observed that a higher fraction or proportion of the N-6 chains "dangling" from the 3:1 (n-s)-α-CD-IC crystals are able to crystallize compared to the N-6 chains in the neat melt. Qualitatively similar observations were made for the 6:1 N-6-γ-CD-IC and bulk samples with N-6 of MW = 600000.

For the N-6 chains "dangling" from nonstoichiometric N-6/α-CD = 3:1 and N-6/γ-CD = 6:1 ICs, X_C (dangling) > X_C (bulk), and {[X_C (dangling)]/[X_C (bulk)]} increases as the MW increases. For example, ΔH_c (3:1 α-CD-IC)/ΔH_c (bulk) = X_c (3:1 α-CD-IC)/X_c (bulk) = 1.3 (30k), 1.6 (60k), 2.1 (300k), and 2.4 (600k). As the MW of N-6 increases, the constraints on the "dangling" chains in 3:1 (n-s)-N-6-α-CD-ICs increasingly facilitate their crystallization in comparison to their neat melts, which, to the contrary, generally crystallize less readily as their MWs increase.

Our complete DSC data set is presented in Table 2, which also includes melting crystallinities (X_C) for their "dangling" chains in comparison to bulk N-6 and show increased T_Cs as well. Also, in agreement with the results reported for (n-s)-[poly(butylene succinate)] [PBS]-α-CD-ICs,[4,5] is the observation that the unincluded, uncovered N-6 chains in both 3:1 N-6-α-CD- and 6:1 N-6-γ-CD-ICs

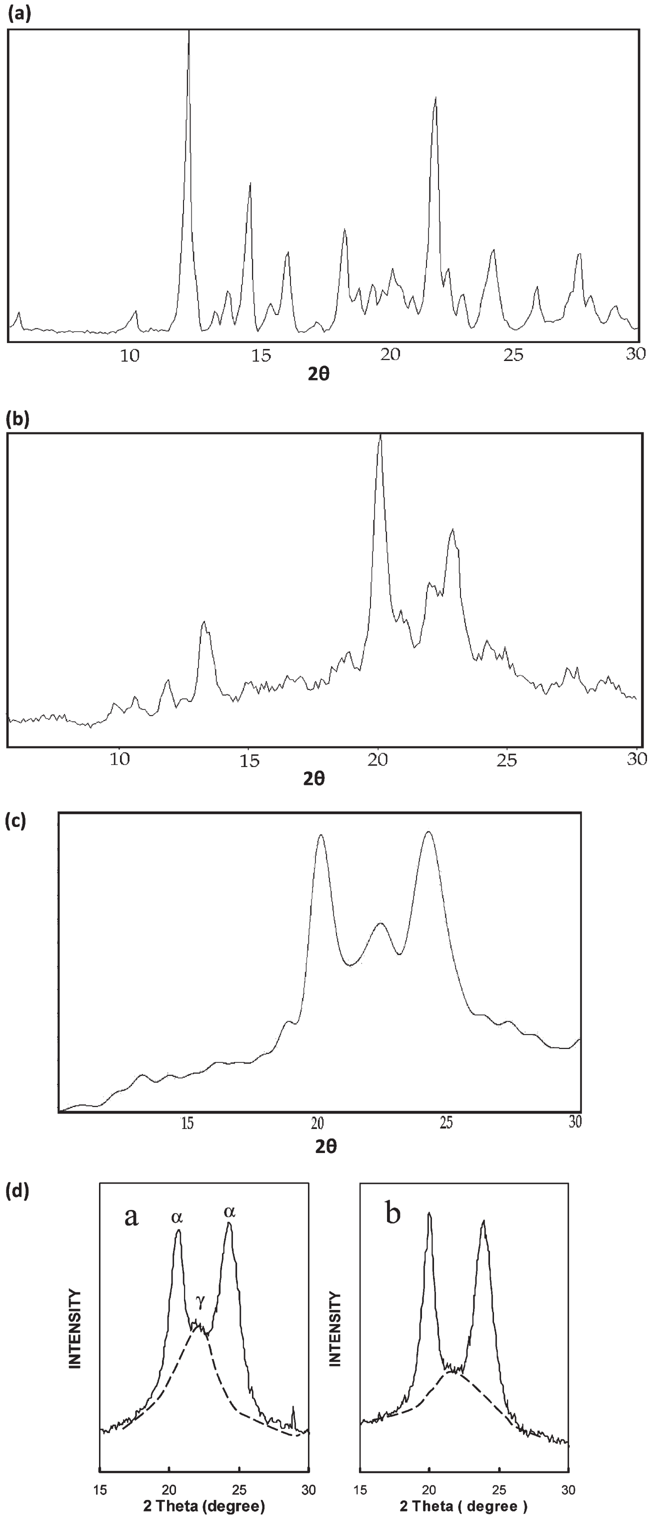

Figure 4. WAXD diffractograms for as-received cage α-CD (a), stoichiometric 1:1 N-6-α-CD-IC (b), 3:1 (n-s) N-6-α-CD-IC (c), and (d) as-received N-6 (left) and coalesced N-6 (right).

show X_Cs and T_Cs that are increased in comparison to the 2:1 N-6-α-CD- and 4:1 N-6-γ-CD-ICs. In fact, the N6 chains dangling from (n-s)-N6-α- and γ-CD-ICs with stoichiometries less than 3:1 and 6:1, respectively, crystallize less readily than bulk N-6 chains.

An alternative, and possibly more germane, measure of the crystallizability of bulk and "dangling" N-6 chains might be provided by comparing "dangling" N-6 chains of the same length (MW) as the bulk N-6. For example, the N-6 chains "dangling" from the 4:1 N-6(600000)-γ-CD-IC crystals should on average have a length characterized by MW = 300000, because the 2:1 N-6-γ-CD-IC is stoichiometric, with no unincluded "dangling" N-6 chain portions. Similarly, the 2:1 N-6(600000)-α-CD-IC should also have "dangling" chains of average MW = 300000. Bulk N-6(300000); 2:1 N-6 (600000)-α-CD-IC; and 4:1 N-6(600000)-γ-CD-IC show X_C, T_C = 0.23, 174; 0.15, 173; and 0.16, 162 °C, respectively, so the N-6 chains "dangling" from both (n-s-)-CD-ICs do not show enhanced crystallizability compared with bulk N-6 with MW = 300000. This observation holds for other like comparisons, except those between the chains "dangling" from 3:1 and 6:1 N-6-α- and γ-CD-ICs and bulk N-6 with the same MWs. However, as (N-6:CD) increases, the crystallinity [X_C (dangling)] increases, which is in opposition to observations reported[5] for (n-s)-PBS- and poly-(ε-caprolactone)-α-CD-ICs.

While ΔH_c [(n-s)-CD-IC]/ΔH_c (bulk) = X_c [(n-s)-CD-IC]/X_c (bulk) increases with N-6 MW for both 3:1 N-6-α-CD- and 6:1 N-6-γ-CD-ICs, their values of {T_c [(n-s)-CD-IC] − T_c (bulk)}s, which may be related to their comparative ease or rates of nonisothermal crystallization, do not. So, as the MW of N-6 increases, the levels of crystallnity achieved for the constrained "dangling" N-6 chains in (n-s)-N6-CD-ICs increase in comparison to their neat melts, while their rates of crystallization do not, even though they generally crystallize at temperatures higher than bulk N-6.

Consider the constraints placed on N-6 chains "dangling" from (n-s)-N-6-α- CD-ICs, as they emerge from ~0.5 nm channels separated by ~1.4 nm, as indicated in Figure 7, to those experienced by the pair of closely adjacent N-6 chains in each ~1 nm γ-CD-IC channel, separated by ~1.7 nm. The distinctions observed between the behaviors of (n-s)-N-6-ICs made with α- and γ-CDs [lower T_Cs and ΔH_Cs for (n-s)-N-6 γ-CD-ICs] can at least in part be attributed to differences in the constraints imposed on the N-6 chains "dangling" from their CD-IC channels, which in fact are dense brushes that do not significantly "dangle", but are largely extended and parallel, and will be discussed further below.

The single and pairs of side-by-side N-6 chains that are included, respectively, in the α- and γ-CD-IC channels emerge from them with initial channel densities of ~4 and ~3 N-6 chains/nm^2 of channel, respectively, immediately above their crystalline CD-IC surfaces. However, with respect to the entire crystalline surface, or farther above the surface, the density of N-6 chains protruding above them is modestly greater for the (n-s)-N-6-γ-CD-ICs [0.8 (γ) vs 0.6 (α) N-6 chains/nm^2 of IC crystal surface].

Because we have observed the N-6 chains protruding from their 6:1 (n-s)-γ-CD-ICs to be only minimally more crystallizable (higher T_cs, but comparable ΔH_cs) than bulk N-6, and significantly less crystallizable than the N-6 chains protruding from their 3:1 (n-s)-α-CD-ICs, apparently the pairs of side-by-side N-6 chains emerging from each (n-s)-γ-CD-IC channel are less able to crystallize than the single N-6 chains emerging from each (n-s)-α-CD-IC channel. In and just above the surface of the (n-s)-γ-CD-IC crystals, the density of the emerging pair of N-6 chains is much greater (~3/nm^2 of γ-CD channel vs 1.4/nm^2 in the bulk crystal) than the N-6 chain density farther above the (n-s)-CD-IC crystal surfaces [0.6 (α)−0.8 (γ) chains/nm^2]. This may produce a strong association, such as hydrogen bonding, between the pair of side-by-side N-6 chains just emerging and may retard their interactions/crystallization with other such closely and strongly interacting pairs of N-6 chains emerging from nearby γ-CD-IC channels.

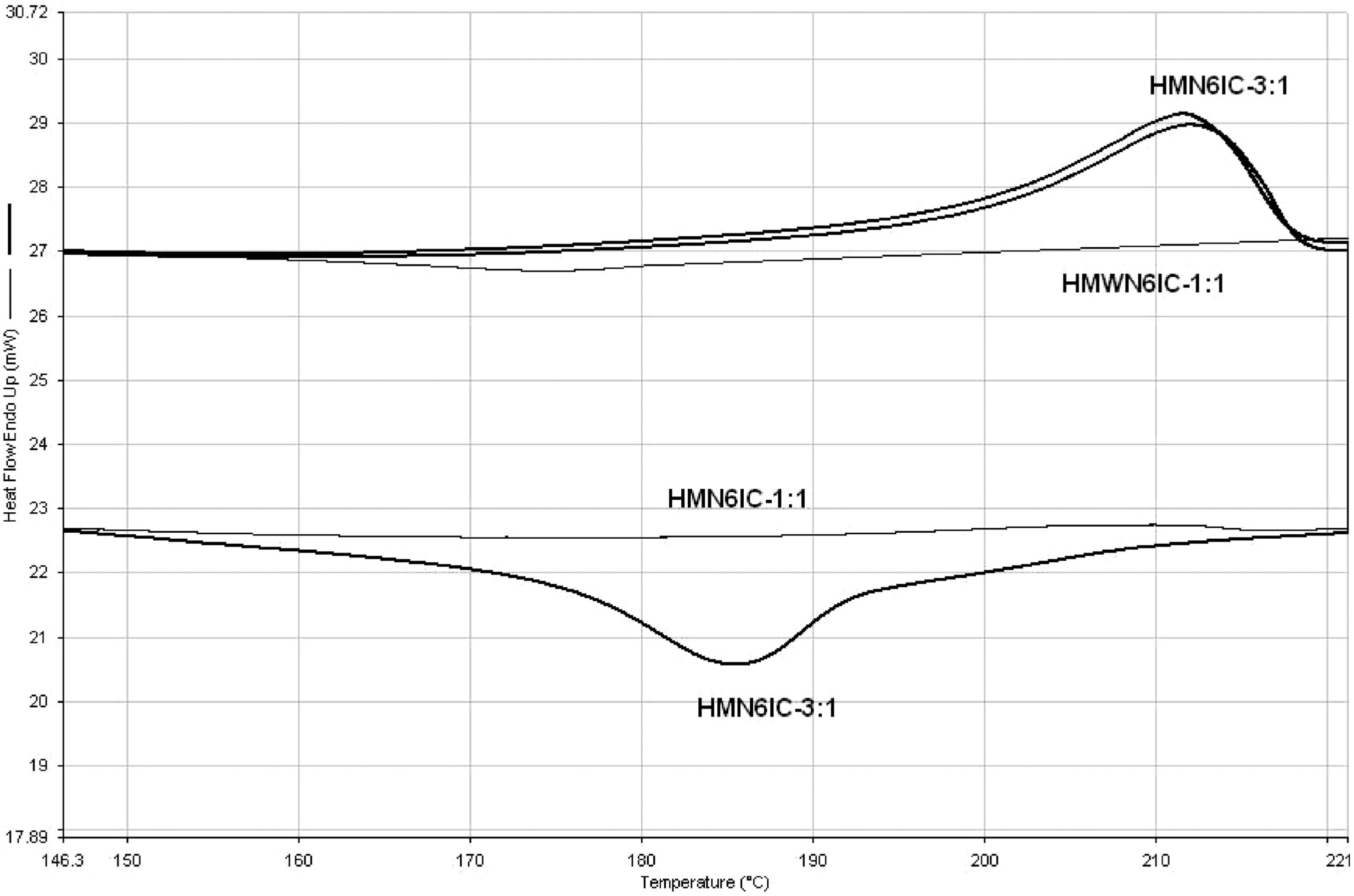

Figure 5. DSC heating and cooling scans (10 °C/min) for 1:1 and 3:1 (n-s)-N-6-α-CD-ICs (N-6 MW = 600000).

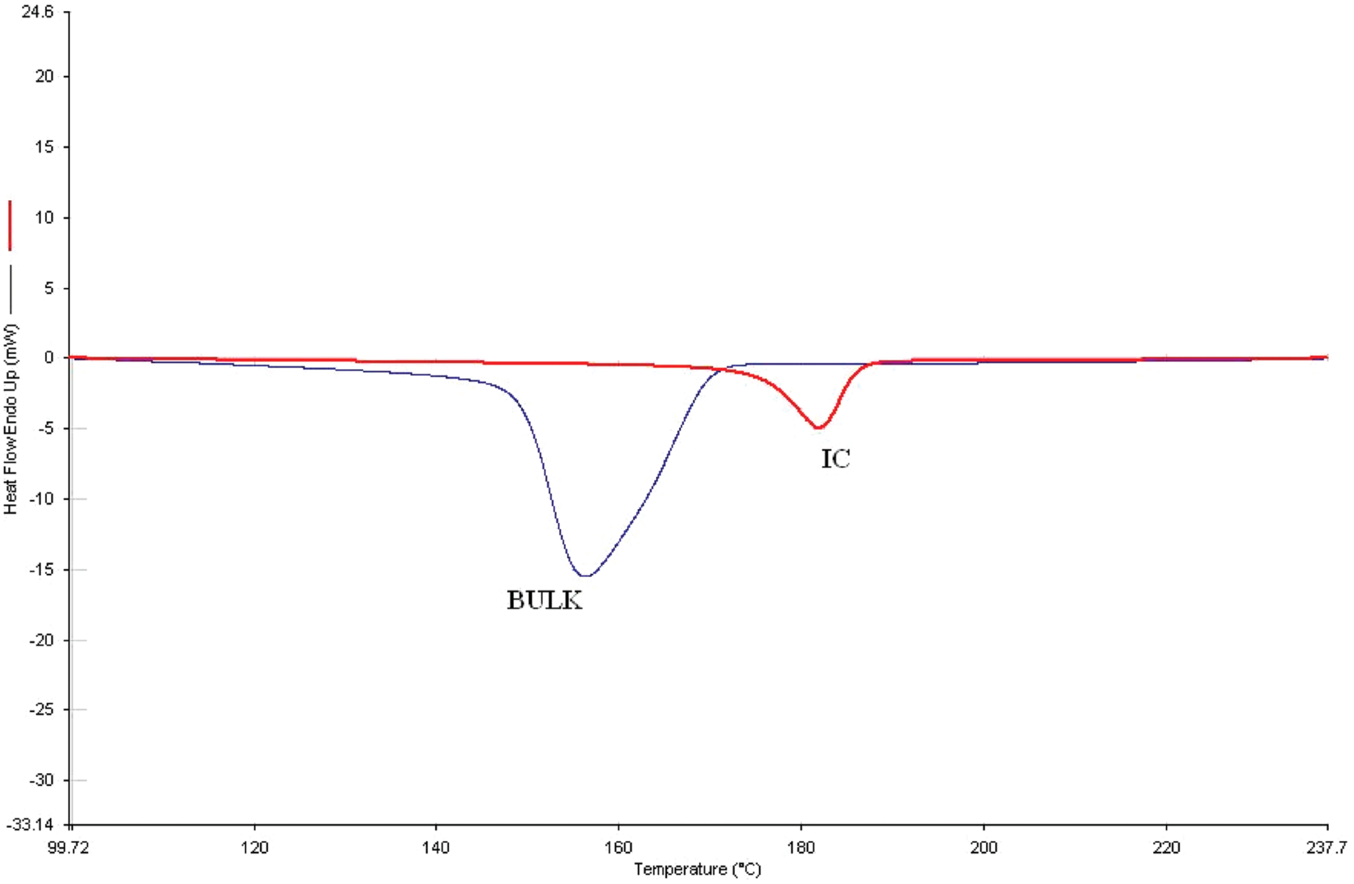

Figure 6. DSC cooling scans from the melts of 600000 g/mol bulk N-6 and its 3:1 (n-s)-N-6-α-CD-IC.

Table 1. Enthalpies or Heats of Crystallization (ΔH_c, J/g) and Degrees of Crystallinity, X_c, Observed upon Cooling Selected Neat N-6 and 3:1 α and 6:1 γ (n-s)-N-6-CD-ICs from the Melt

	←	ΔH_c, J/g	→
N-6 (MW) g/mol	bulk	[(n-s) 3:1 α-CD-ICs] (total)	[(n-s) 6:1 γ-CD-ICs] ("dangling" N-6)[a]
30000	−53 (0.40)[b]	−12	−70 (0.44)[b]
60000	−56 (0.42)	−15	−89 (0.58)
300000	−43 (0.32)	−15, −6[c]	−89, −26[c] (0.58, 0.17[c])
600000	−46 (0.35)	−19,-12	−112, −52 (0.71, 0.32)

[a] Only ∼17 and 23 wt % of 3:1 α and 6:1 γ (n-s)-N-6-CD-ICs are contributed by the 2/3 portions of N-6 chains that are not threaded and included, but are "dangling" and can crystallize. ΔH_c (J/g, "dangling" N-6) = [ΔH_c (J/g, total IC sample)]/(0.17 and 0.23) for 3:1 α and 6:1 γ (n-s)-N-6-CD-ICs, respectively. [b] Degree of crystallinity, X_c, based on $X_c = \Delta H_c/\Delta H^\circ_m$, with $\Delta H^\circ_m = 160$ J/g for 100% crystalline N-6.[13,14] [c] 6:1 (n-s)-N-6-γ-CD-ICs.

Table 2. DSC Data for Neat and (n-s)-CD-IC N-6 Samples[a]

samples	T_m	T_c	ΔH_c	X_c
30000	221.6	173	55	35
2:1 N6-α-CD-IC	213	176	7 (41)[b]	26
3:1 N6-α-CD-IC	214	180	12 (71)	44
60000	222	175	58	37
2:1 N6-α-CD-IC	217	174	8 (47)	30
3:1 N6-α-CD-IC	219	178	15 (88)	56
300000	222	174	43	28
2:1 N6-α-CD-IC	214	173.8	7 (41)	26
3:1 N6-α-CD-IC	220	178.2	16(94)	59
4:1 N6-γ-CD-IC	214.5	168.4	7 (28)	18
5:1 N6-γ-CD-IC	214.5	166.4	9 (37)	23
6:1 N6-γ-CD-IC	212	171.6	12 (52)	32
600000	223	174	45	29
2:1 N6-α-CD-IC	216	173.3	5 (29)	18
3:1 N6-α-CD-IC	222	182	19 (111)	70
4:1 N6-γ-CD-IC	216	162	7 (30)	19
5:1 N6-γ-CD-IC	214	171	8 (33)	20
6:1 N6-γ-CD-IC	215	174	15 (35)	41

[a] The stoichiometric 1:1 N6-α-CD- and 2:1 N6-γ-CD-ICs show no N-6 crystallization, as expected, and the 3:1 (n-s)-N6-γ-CD-IC also does not show a significant crystallization peak. (n-s)-N6-γCD-ICs could not be formed with 30000 and 60000 g/mol N-6 samples. [b] Values are for the "dangling" chains only. X_c is calculated with $\Delta H_{100\%c}$ for N-6 = 160 J/g.[13,14]

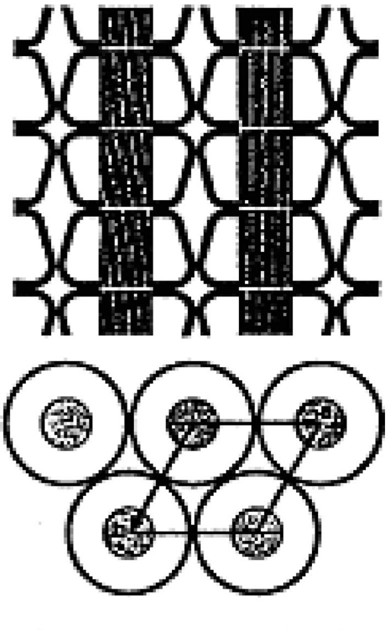

Figure 7. Channel structure α-CD-IC: 0.6 (α-CD), 0.8 (γ-CD) N-6 chains/nm^2 of CD-IC crystal surface. Protruding N-6 chains form dense polymer brushes (for comparison, in the α-form N-6 crystal there are 1.4 N-6 chains/nm^2).

Another way to express this suggestion is by comparison of two chain "one-dimensional N-6 nano-crystals" with multichain "three-dimensional N-6 micro-crystals", with the former resulting from pairs of side-by-side N-6 chains included and initially emerging from the γ-CD-IC channels. If this suggestion is viable, then as the lengths (MWs) of the chains protruding from N-6-(n-s)-γ-CD-ICs are reduced, the constraint opposing crystallization produced by the pairs of N-6 chains emerging from the γ-CD-IC channels should increase making their crystallization more difficult, which receives some support from the DSC results presented in Tables 1 and 2.

When (n-s)-N-6-CD-ICs are added in small amounts, they are observed to be effective nucleating agents for enhancing the melt crystallization of bulk N-6. As can be seen in Figure 8, the N-6 sample with 2 wt % 3:1 (n-s)-N-6-α-CD-IC crystallizes at a higher temperature and over a narrow temperature range than neat bulk N-6. From Figures 6 and 8, it is apparent that, upon cooling, molten N-6 chains protruding from the 3:1 (n-s)-N-6-α-CD-ICs, and, though not shown, the 6:1 (n-s)- γ-CD-ICs crystallize at a higher T_C before the bulk N-6 chains. When an (n-s)-N-6-CD-IC is added to bulk N-6 in small amounts it causes the bulk N-6 chains to crystallize sooner at a higher T_C, as reported previously.[2−9]

Preliminary Conclusions

Generally, as the length of N-6 chains or their MW increases, their melt-crystallization temperatures T_C decrease/increase and the levels of crystallinity X_C decrease/increase for bulk and (n-s)-CD-IC samples, respectively. In the case of neat molten polymers, the increased entanglement between higher MW chains and the structural defects they produce are usually cited[14] as the reasons that they may crystallize more slowly and not as completely as lower MW samples. Because the opposite behavior is observed here for the "dangling" yet constrained chains in (n-s)-N-6-CD-ICs, their degree of entanglement, if any, is apparently unimportant to their ability to crystallize.

Because their relative center-of mass diffusion is limited by the constraining CD-IC crystals from which they emanate, entanglement and unentanglement of the dangling chains, if they occur at all, would be significantly retarded in comparison to that in unconstrained neat N-6 samples. Though not presented here, DSC observations of (n-s)-N-6-CD-ICs, such as those presented in Figures 5, 6, and 8, remain unchanged upon subsequent repeated heating/cooling scans, which suggests the absence of CD dethreading.

The major factor contributing to the enhanced melt crystallizability observed for the protruding N-6 chains (higher T_Cs and larger ΔH_Cs ∝ X_Cs), which can increase with an increase in MW, is likely due to the concomitant increase in their extension and orientation with respect to the CD-IC crystal surfaces. This may at first seem discordant with the well-known behavior of most polymer brushes whose chains lose orientation perpendicular to and extension from their surfaces as their MW increases and which initiates a brush-to-mushroom transition. However, it must be remembered that polymer brushes are generally formed with noncrystallizable polymers and at much lower surface

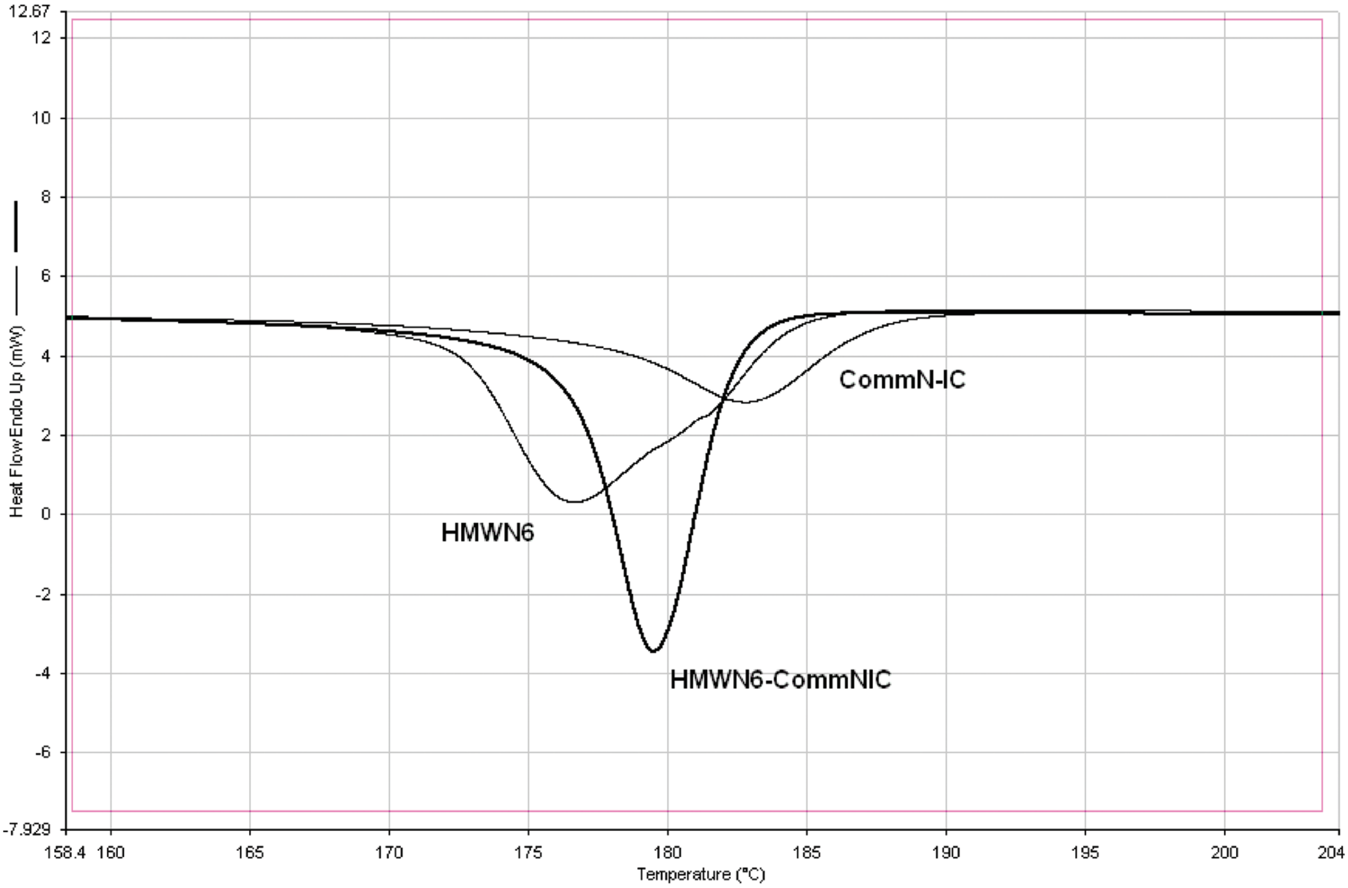

Figure 8. Nonisothermal crystallization of N-6, 3:1 (n-s)-N-6-α-CD-IC, and N-6 with 2 wt % 3:1 (n-s)-N-6-α-CD-IC . In each case, N-6 with MW = 60000 was employed.

densities than the 0.6−0.8 N-6 chains/nm^2 emanating from the (n-s)-N-6-CD-IC crystal surfaces.

At higher brush densities, for example, chain densities similar to those expected for (n-s)-polymer-α-CD-ICs (see Figures 2 and 7), it has been observed[15,16] that even the chains in noncrystallizing brushes are highly extended and, thus, highly aligned, perpendicular to the surfaces of their attachment, and increasingly so as MW increases. This may explain the observed enhancement of their crystallizabilty, both kinetically and thermodynamically, with increased MW of the protruding N-6 chains, especially for the 3:1 α- and 6:1 γ-CD-ICs (see Tables 1 and 2). No matter whether the protruding N-6 chains begin crystallizing near the CD-IC crystalline surfaces or farther removed and nearer to their "free" chains ends,[16] both would favor the enhancement of their crystallization as their MWs increase. This also suggests that the possibility for entanglement, if it were important to the crystallization of the N-6 chains protruding from the surfaces of (n-s)-N-6-CD-IC crystals, is also reduced as MW increases.

It was noted above that the surface densities of N-6 chains emerging from the crystal surfaces of (n-s)-N-6-α-CD-ICs and the α crystalline polymorph of neat N-6 are ~0.6 and 1.4 chains/nm^2, respectively. What then might be the consequence of the increase in chain density that accompanies the crystallization of N-6 chains protruding from their (n-s)-N-6-α-CD-IC crystals? This likely means that near the (n-s)-N-6-α-CD-IC crystalline surface the N-6 chain segments may not be able to crystallize at all.[16] The proportionate effect produced by the disparity in N-6 chain densities between the (n-s)-N-6-α-CD-ICs and α-form bulk crystals would be expected to diminish with increasing N-6 MW, consistent with the enhanced crystallizabilities observed here for the higher MW protruding N-6 chains.

While we have also observed high MW N-6 chains protruding from the crystalline surfaces of 6:1 (n-s)-N-6-γ-CD-ICs to crystallize more easily than bulk N-6s, though only modestly so, they crystallize much less readily than N-6 chains protruding from the crystalline surfaces of 3:1 (n-s)-N-6-α-CD-ICs. In (n-s)-N-6-γ-CD-ICs pairs of side-by-side N-6 chains emerge from each ~1 nm diameter γ-CD channel, while only a single N-6 chain emerges from each ~0.5 nm diameter α-CD channel. While the surface density of N-6 chains is higher in (n-s)-N-6-γ-CD-ICs than in (n-s)-N-6-α-CD-ICs, it is still below that in bulk N-6 crystals. Why then do the N-6 chains protruding from their (n-s)-γ-CD-ICs crystallize less readily than those protruding from their (n-s)-N-6-α-CD-ICs? This might be due to the strong association between the individual pairs of N-6 chains emerging from the channels just above and near to surfaces of the (n-s)-N-6-γ-CD-IC crystals.

We have seen that the portions of N-6 chains that are unincluded and protrude from their (n-s)-N-6-CD-ICs crystallize more readily (faster at higher temperatures, over a narrow temperature range, and to greater extents) than bulk N-6 chains. However, the melting temperatures, T_m, of their resulting crystals are very similar. $T_m = \Delta H_m/\Delta S_m$, is the ratio of the enthalpy to the entropy of melting, and apparently this ratio is very similar for N-6 chains in bulk and those constrained by and protruding from (n-s)-CD-IC crystals. This despite the expectation that, in the melt, N-6 chains protruding from the surfaces of their (n-s)-CD-ICs likely constitute a high density brush with largely extended chains, which are expected to possess less conformational entropy than an unconstrained neat N-6 melt. Because the ΔS_m of polymers is generally dominated by the difference in the intramolecular conformational entropies, ΔS_{conf}, of their randomly coiling molten and highly extended and conformationally

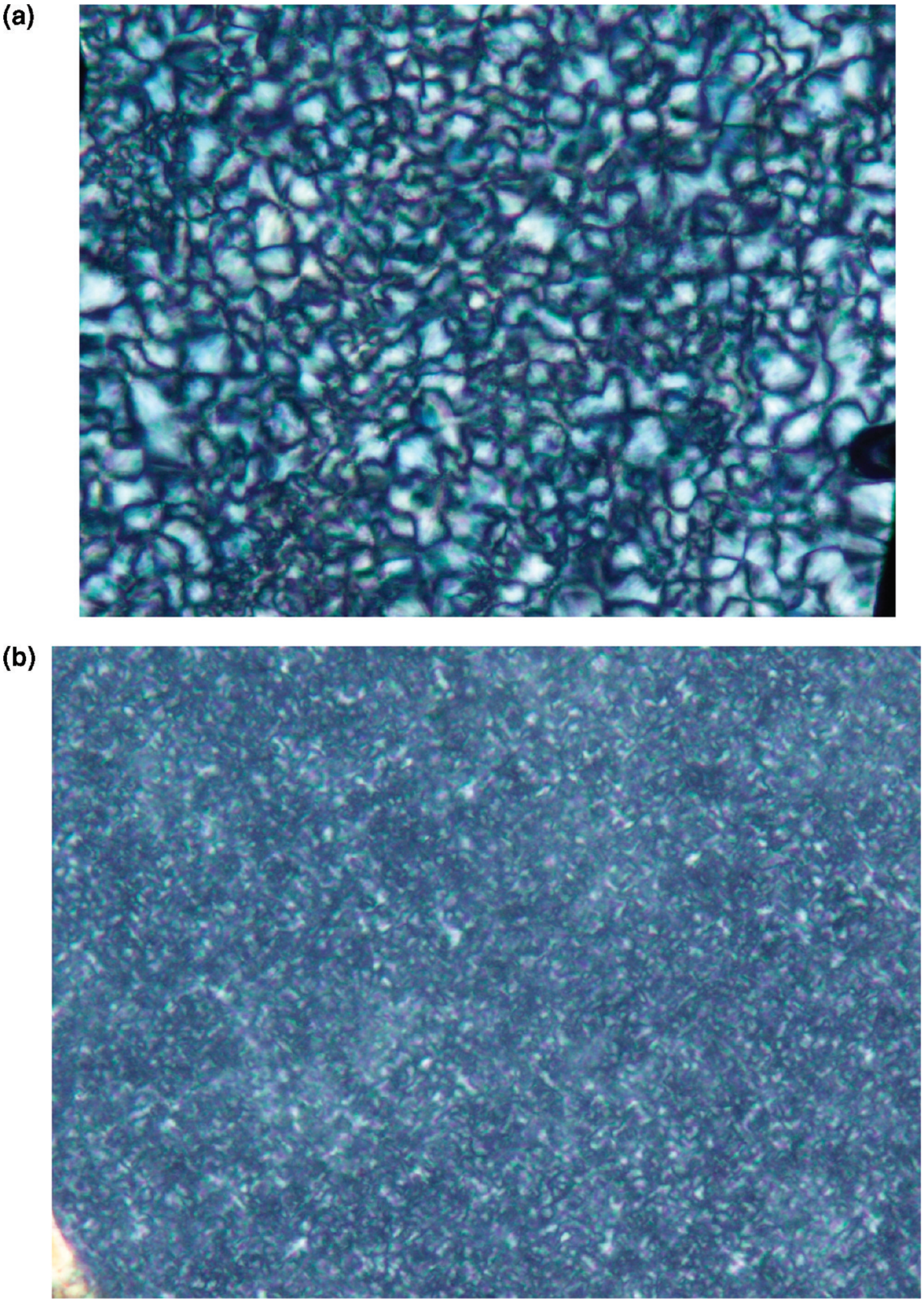

Figure 9. (a) Polarized micrograph of high molecular weight N-6 (MW = 600000) film crystallized from the melt. (b) Polarized micrograph of high molecular weight N-6 (MW = 600000) film with 2 wt % 3:1 (n-s)-N-6(MW = 600000)-α-CD-IC crystallized from the melt.

restricted crystalline chains,[17] we would expect the melting of the crystals formed by the N-6 chains protruding from their (n-s)-CD-ICs to have smaller ΔS_ms and, therefore, higher T_ms than neat N-6 crystals.

Apparently the melting of N-6 chains protruding from their (n-s)-CD-ICs is accompanied by ΔH_ms that are similarly reduced, because they show T_ms close to neat N-6 samples. This may be a result of the greater extension and orientation of chains expected in their dense brush-like arrangement in the melt, which likely increases the interactions between molten N-6 chains, in comparison to neat N-6 melts, and would serve to lower the difference in enthalpies (ΔH_m) between crystalline and molten N-6 chains protruding from the surfaces of their (n-s)-CD-IC crystals .

As can be seen in Figure 9, the addition of small amounts of (n-s)-N-6-α-CD-ICs to neat bulk N-6s results in melt-crystallized, semicrystalline morphologies that are both more uniform and finer in scale than those in neat N-6s. In a subsequent paper we will present DSC observations that show both the crystallization temperatures and levels of crystallinity achieved from the nonisothermal crystallization of N-6 samples containing (n-s)-N-6-α-CD-ICs as potential nucleants are higher than for the neat N-6 samples. Thus, (n-s)-N-6-α-CD-ICs appear to be very effective N-6 nucleants, providing a nontoxic alternative to commonly used nucleants, such as talc, mica, or clays. Physical properties, such as mechanical strengths and densities of films and fibers produced from (n-s)-N-6-CD-IC nucleated N-6 samples obtained by solution-casting and melt mixing, will also be measured and compared there to those made with neat N-6. This should provide us a measure of how their contrasting morphologies, as seen in Figure 9, effect their physical behaviors.

Summary

Noncovalently bonded crystalline inclusion compounds (ICs) have been formed by threading the host cyclic starches, cyclodextrins (CDs), onto guest nylon-6 (N-6) chains. When excess N-6 is employed, nonstoichiometric (n-s)-N-6-CD-ICs with partially uncovered and protruding N-6 chains result. The constrained crystallization of the N-6 chains protruding from (n-s)-N-6-CD-ICs has been compared to the crystallization of bulk N-6 samples, as functions of N-6 molecular weights, lengths of uncovered N-6 chains (N-6/CD stoichiometry), and the CD host used. In the IC channels formed with host α- and γ-CDs containing six and eight glucose units, respectively, single and pairs of side-by-side N-6 chains are threaded and included. In α-CD-ICs, the ~0.5 nm channels produced by stacked α-CDs are separated by ~1.4 nm, while in γ-CD-ICs the ~1 nm channels are ~1.7 nm apart, with each stacked γ-CD channel including two N-6 chains. N-6 chains in the bulk and in the dense (n-s)-N-6-CD-IC brushes, with protruding chain densities of ~0.6−0.8 N-6 chains/nm^2, show distinctly different kinetic and thermodynamic crystallization behaviors. The protruding and constrained chains in the dense (n-s)-N-6-α-CD-IC brushes crystallize faster and to a significantly greater extent than those in bulk N-6 melts, and this behavioral distinction is enhanced as the molecular weights/lengths of N-6 chains are increased.

The N-6 chains dangling from the surfaces of (n-s)-N-6-γ-CD-ICs do not, however, show the same degree of enhanced crystallizability, although they too show an increased degree of crystallinity as their MW increases. The unincluded N-6 chains protruding from the surfaces of the γ-CD-ICs also constitute high density brushes whose chains are highly extended and aligned perpendicular to the surfaces of their attachment and increasingly so as their MW increases. However, strong interactions between the pairs of N-6 chains emerging from each γ-CD-IC channel may reduce the ability of the resulting N-6 dense brush to crystallize.

When added at low concentrations, the nontoxic, biodegradable/bioabsorbable (n-s)-N-6-CD-ICs serve as effective nucleating agents for the melt crystallization of bulk N-6.

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