

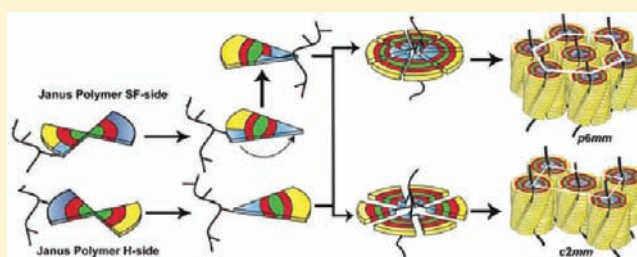
Self-Organizable Vesicular Columns Assembled from Polymers Dendronized with Semifluorinated Janus Dendrimers Act As Reverse Thermal Actuators

Virgil Percec,* Mohammad R. Imam, Mihai Peterca, and Pawaret Leowanawat

Roy & Diana Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323, United States

S Supporting Information

ABSTRACT: The synthesis and structural analysis of polymers dendronized with self-assembling Janus dendrimers containing one fluorinated and one hydrogenated dendrons are reported. Janus dendrimers were attached to the polymer backbone both from the hydrogenated and from the fluorinated parts of the Janus dendrimer. Structural analysis of these dendronized polymers and of their precursors by a combination of differential scanning calorimetry, X-ray diffraction experiments on powder and oriented fibers, and electron density maps have demonstrated that in both cases the dendronized polymer consists of a vesicular columnar structure containing fluorinated alkyl groups on its periphery. This vesicular columnar structure is generated by a mechanism that involves the intramolecular assembly of the Janus dendrimers into tapered dendrons followed by the intramolecular self-assembly of the resulting dendronized polymer in a vesicular column. By contrast with conventional polymers dendronized with self-assembling tapered dendrons this new class of dendronized polymers acts as thermal actuators that decrease the length of the supramolecular column when the temperature is increased and therefore, are called reverse thermal actuators. A mechanism for this reversed process was proposed.



INTRODUCTION

Traditional dendronized polymers are synthetic or natural linear backbones containing a dendritic group, which is most frequently a dendron, attached to each of their repeat units.¹ They are synthesized via covalent divergent,² convergent followed by covalent³ or supramolecular⁴ attachment to the backbone as well as by dendritic macromonomer,⁵ strategies. Recently, cyclic dendronized polymers^{1h,6} have been reported, and it is expected that even more complex topologies will emerge. The dendritic group attached to the backbone can be self-assembling⁷ or not.⁸ Self-assembling dendritic groups attached to polymer backbones generate dendronized polymers that self-organize in periodic⁹ and quasiperiodic^{9d} arrays. The analysis of these arrays by complementary methods, including small and wide-angle X-ray diffraction on powder and oriented fiber combined with electron density maps, electron diffraction combined with transmission electron microscopy (TEM), and atomic force and scanning force microscopy experiments, endow precise information on the 2- or 3-D structure of the dendronized polymer.⁹ In addition, monomers derived from self-assembling dendrons provide access to dendronized polymers with extremely narrow molecular weight distribution when polymerized by conventional methods in dilute solution^{9,10} and to extremely high molecular weight dendronized polymers when polymerized in self-assembled state.^{9a,10a-c} Various living polymerization methods have been^{5a,e,f,6,9f,11} and

continue to be investigated for the polymerization of a diversity of monomers containing dendrons. These methodologies lead to dendronized polymers with conjugated and nonconjugated backbones.^{5,11} Historical developments of this field and recent reviews are available.¹ Most of the research in this area involves dendrons that are attached to the polymer backbone from their apex.¹⁻¹² However, new architectural complexity was achieved when dendrons were attached to the polymer backbone from alternative positions than their apex or when other dendritic building blocks were used in the design of dendronized polymers.¹³ Here we report the synthesis and structural analysis of dendronized polymers obtained by the polymerization of self-assembling semifluorinated^{14a} Janus dendrimers.¹⁴ This new class of dendronized polymers produces self-organizable vesicular columns by an intramolecular self-assembly of the Janus dendrimer repeat units into supramolecular tapered dendrons followed by an intramolecular self-assembly of the resulting dendronized polymer. By contrast with self-organizable dendronized polymers containing conventional self-assembling tapered dendrons as side groups,^{5f} this new class of dendronized polymers acts as thermal actuators that decrease their length upon the increase of temperature. Therefore, these thermal actuators are called reverse thermal actuators.

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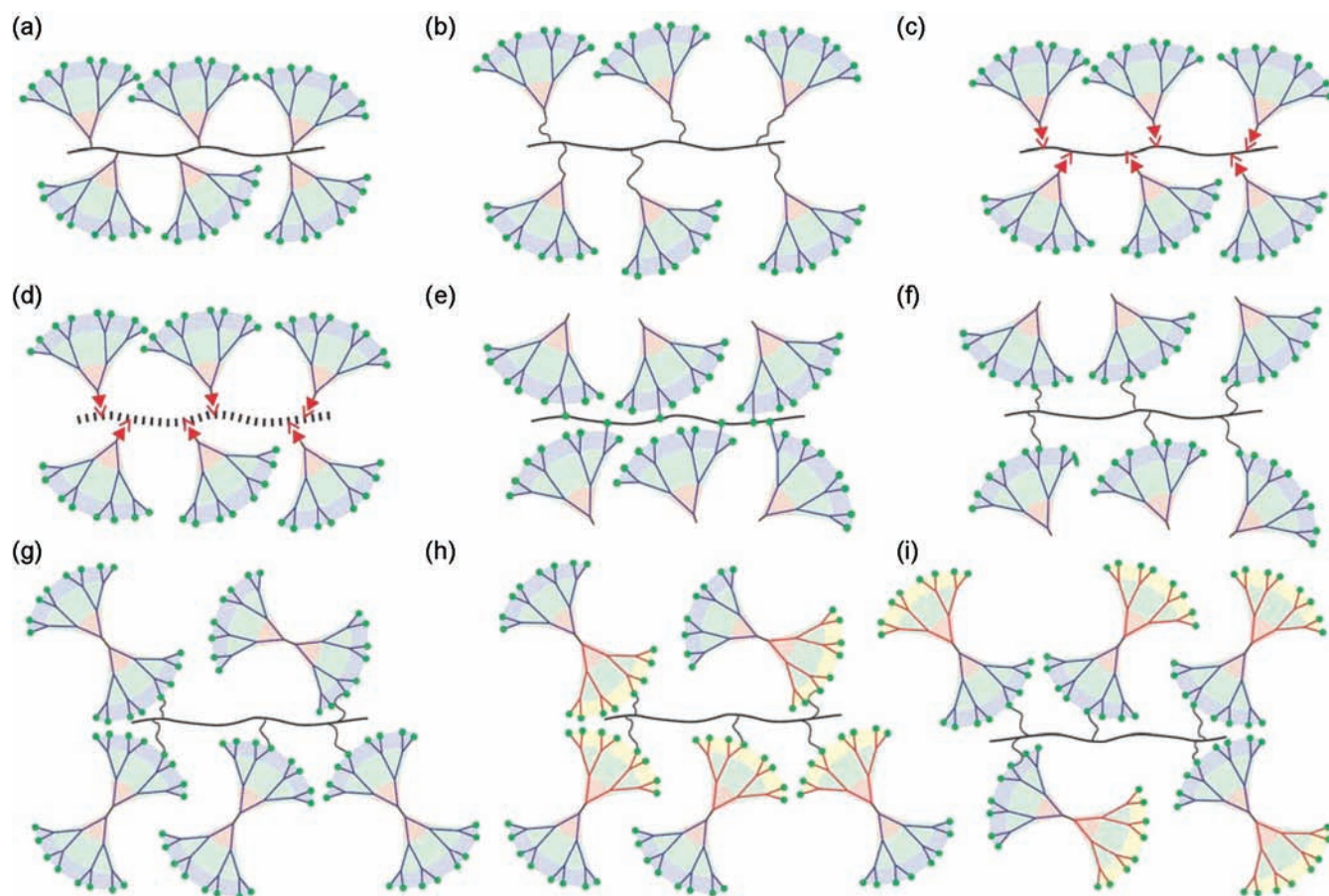


Figure 1. Topologies generated from linear covalent and supramolecular polymers dendronized with self-assembling dendrons, twin dendritic molecules, and Janus dendrimers.

RESULTS AND DISCUSSION

Topologies Generated from Polymers Dendronized with Self-Assembling Dendrons and Dendrimers.

The topologies investigated so far with linear polymers dendronized with self-assembling dendritic building blocks, including the one reported in this publication, are summarized in Figure 1. Early work started with self-assembling dendrons and with dendrons that do not self-assemble, being attached to the polymer backbone either via conventional chains,^{5,9a,10b} or by living^{5f,g,11} polymerizations of dendronized monomers. The divergent growth of a dendron from each repeat unit of a polymer,² the convergent attachment directly to the polymer backbone³ and the attachment to the backbone via a flexible spacer^{2c,15} are also part of the pioneering strategies (Figure 1a,b). Attachment of the dendrons to the backbone via supramolecular donor–acceptor,^{4a} ionic¹⁵ and other interactions followed (Figure 1c). The construction of supramolecular backbones via H-bonding,^{9c,16} donor–acceptor,^{4a} ionic, and other interactions¹⁵ provided additional methodologies (Figure 1d). The topologies outlined in Figure 1a–d were accomplished both with tapered and conical self-assembling dendrons.^{7,15} Subsequently, tapered self-assembling dendrons were attached directly or via a spacer from their periphery rather than from their apex (Figure 1e,f). Self-assembling twin dendritic molecules,^{13a,b} which are the simplest class of dendrimers, were also used to dendronize polymers (Figure 1g).

Self-assembling twin dendritic molecules^{13a,b,16a} are the closest architectural motives resembling Janus dendrimers¹⁴

(Figure 1b,c). A major difference between twin dendritic molecules and Janus dendrimers is that Janus dendrimers can be attached to the polymer backbone via the two different dendrons forming the Janus dendrimer (compare panel g with panels h and i in Figure 1).

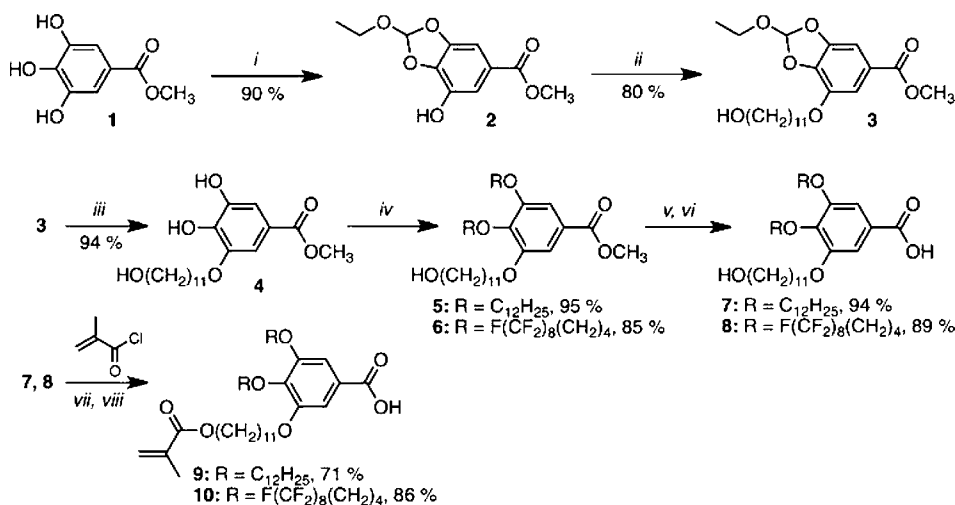
Synthesis of Self-Assembling Semifluorinated Janus-Dendrimers Containing Methacryloyl Groups.

Scheme 1 outlines the synthesis of hydrogenated, **9**, and fluorinated, **10**, first generation dendrons containing methacryloyl groups. Both **9** and **10** were prepared by the reaction of methyl gallate, **1**, with triethyl orthoformate in the presence of Amberlyst 15 in benzene at reflux to generate compound **2** containing two protected phenol groups in 90% yield.

Alkylation of **2** with $\text{HO}(\text{CH}_2)_{11}\text{Br}$ in DMF by using K_2CO_3 as base at 65 °C produced **3** in 80% yield after 4 h of reaction time. **3** was deprotected with HCl to yield 94% of **4**. Alkylation of **4** with 1-bromododecane in DMF at 70 °C for 4 h in the presence of K_2CO_3 produced **5** in 95% yield. Saponification of **5** with KOH in aqueous ethanol at reflux followed by acidification with HCl yielded **7** in 94% yield. **6** was obtained by the alkylation of **4** with 12-bromo-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptafluorododecane^{14a,17} in 90% yield. Esterification of **7** and **8** with methacryloyl chloride in CH_2Cl_2 in the presence of Et_3N followed by reflux with pyridine/ H_2O for 2 h cleaved the carboxylic acid anhydride intermediate to produce **9** in 71% and **10** in 86% yields.

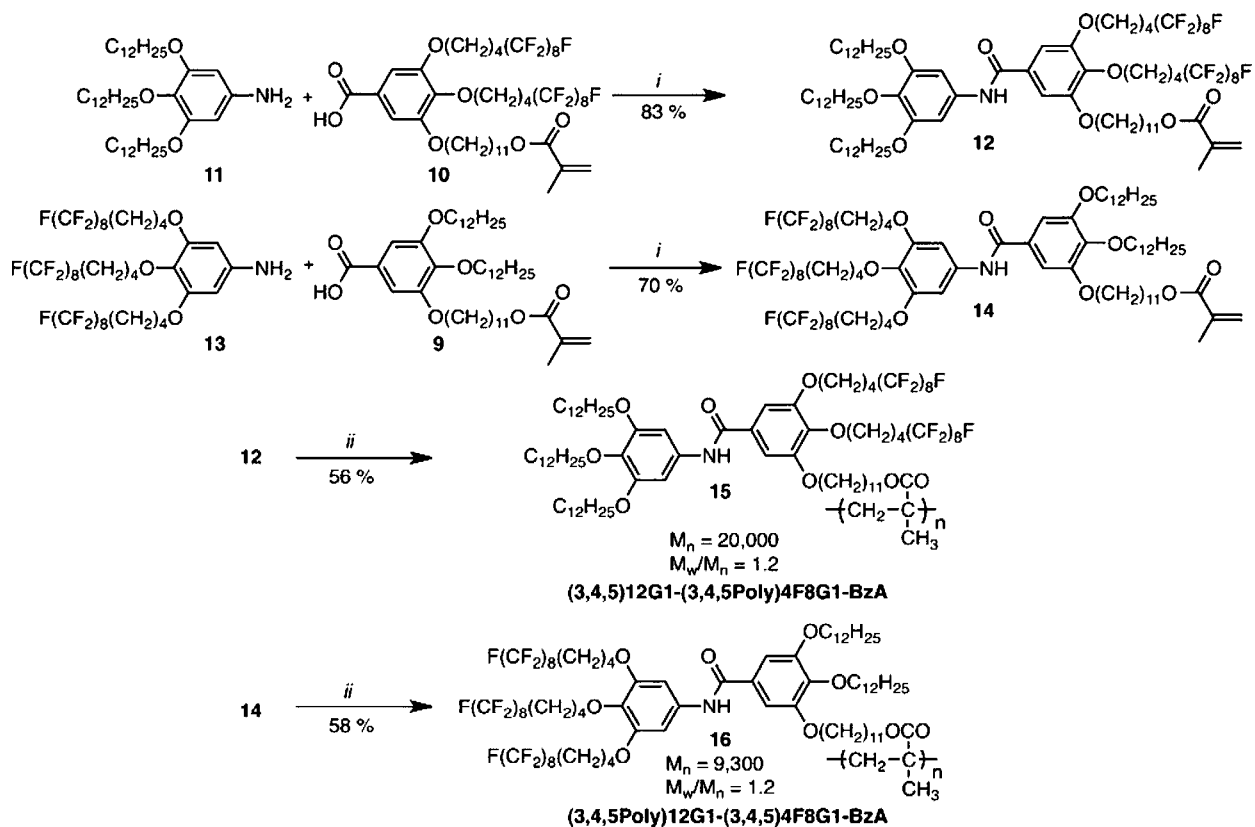
Scheme 2 outlines the final step in the synthesis of the Janus dendrimers containing the methacryloyl group.

Scheme 1. Synthesis of Hydrogenated and Fluorinated Dendrons Containing Methacryloyl Groups



Reagents and conditions: (i) (EtO)₃CH, Amberlyst 15, benzene, reflux, 18 h; (ii) HO(CH₂)₁₁Br, K₂CO₃, DMF, 65 °C, 4 h; (iii) HCl, MeOH, reflux, 12 h; (iv) R-Br, K₂CO₃, DMF, 65 °C, 1 h; (v) aq. KOH, EtOH, reflux, 2 h; (vi) HCl, 15 min; (vii) Et₃N, CH₂Cl₂, 6 h; (viii) pyridine-H₂O, reflux, 2 h.

Scheme 2. Synthesis of Semifluorinated Janus Dendrimers Containing Methacryloyl Groups and of Their Corresponding Polymers

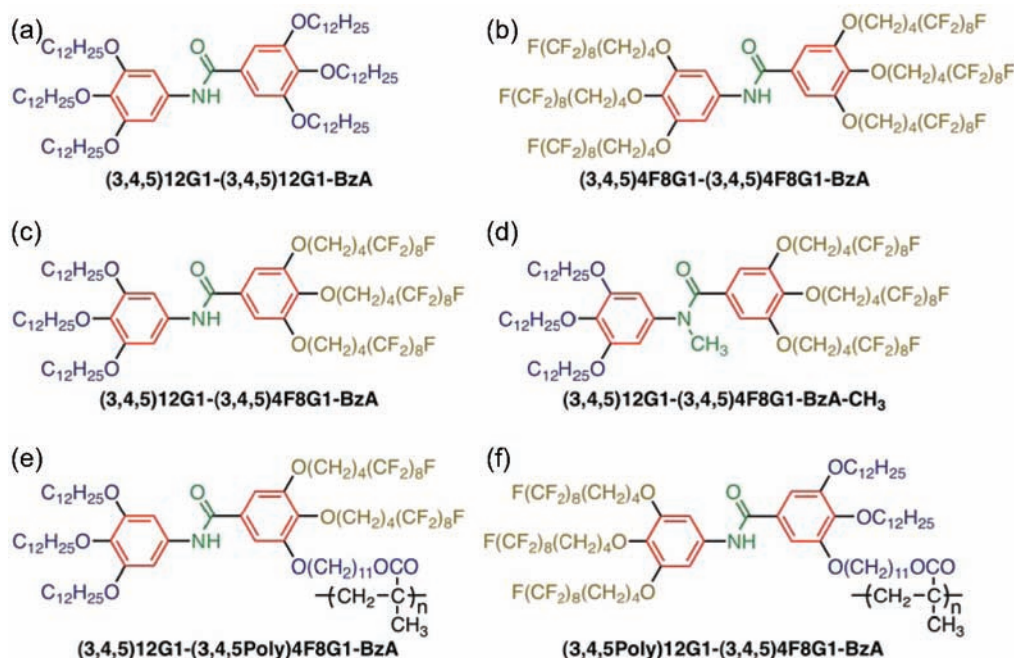


Reagents and conditions: (i) DCC, DPTS, α,α,α -trifluorotoluene, 50 °C, 4 h; (ii) AIBN, α,α,α -trifluorotoluene, 80 °C, 48 h.

11^{13a} was reacted with 10 in the presence of DCC/DPTS at 50 °C in α,α,α -trifluorotoluene for 4 h to yield 12 in 83% yield. Amidation of 13^{14a} with 9 under the same reaction conditions produced 14 in 70% yield. The corresponding dendronized polymers were obtained by radical polymerization of 12 and 14 with AIBN in α,α,α -trifluorotoluene at 80 °C

for 48 h to produce the isolated yields and the number average molecular masses relative to polystyrene standards (M_n) reported in Scheme 2. The absolute molecular weights of dendronized polymers are 3–6 times larger than those determined by gel permeation chromatography with polystyrene standards.^{10b} For structural

Scheme 3. Structures and Short Names of the Hydrogenated (a) and Fluorinated Twin Dendritic Molecules (b), of the Semifluorinated Janus Dendrimers (c and d), and of the Polymers Dendronized with Janus Dendrimers (e and f)



analysis experiments, lower molecular mass and soluble polymers that exhibit faster dynamics and can be characterized in solution and in solid state are desirable. Therefore, no experiments to synthesize higher molar mass polymers were required at this time.

Self-Assembly of Twin Dendritic Molecules, of Polymers Dendronized with Twin Dendritic Molecules and of Janus Dendrimers. Scheme 3 outlines the structures of all compounds studied. They follow the same color code as in their schematic representation from Figure 2. The left side of Figure 2 outlines the self-assembly of hydrogenated (blue) twin dendritic molecules and of polymers dendronized with twin dendritic molecules. Twin dendritic molecules self-assemble in a supramolecular column that self-organizes in a 2D columnar hexagonal phase.^{13a,b,16a} Polymers dendronized with twin dendritic molecules self-assemble in an architecture consisting of a polymer chain coated with a three-cylindrical bundle supramolecular dendrimer.^{13a} This polymer self-organizes in a thermotropic nematic liquid crystal phase.^{13a} Co-assembly of the polymer coated with a three-cylindrical bundle supramolecular dendrimer with twin dendritic molecules produces a novel 2D hexagonal column superlattice.^{13a} Fluorinated (yellow) twin dendritic molecules also self-assemble in a supramolecular column forming a hexagonal columnar 2D lattice.^{14a} Semifluorinated Janus dendrimers self-assemble in vesicular columns with diameter two times larger than that of the corresponding columns generated from fluorinated or hydrogenated twin dendritic molecules.^{14a} These vesicular columns self-organize in 2D hexagonal columnar lattices. During the self-assembly process the Janus dendrimer changes its conformation from Janus dendrimer to tapered dendron (right side of Figure 2).^{14a}

Structural and Retrostructural Analysis of Janus Dendrimers, of Polymers Dendronized with Janus Dendrimers, and of their Mixtures. The analysis of the

self-assembly and self-organization of the Janus dendrimers, of polymers dendronized with Janus dendrimers and of their mixtures was performed by a combination of differential scanning calorimetry, temperature dependent polarized microscopy, wide and small-angle X-ray diffraction experiments on powder and oriented fibers, and experimental density. Table 1 summarizes the X-ray diffraction data of the compounds investigated. The assignment of phases presented in Table 1 is based on small-angle powder diffraction data and on the analysis of the wide-angle X-ray diffraction patterns collected as a function of temperature from oriented fibers.

The XRD data presented in Figures 3–5 and in Table 1 demonstrate that the polymers dendronized with Janus dendrimers followed the pathways of self-assembly and self-organization of their Janus dendrimers that are their precursors. The relative intensity of the higher order X-ray powder diffraction peaks of the hexagonal (Φ_h) and centered rectangular (Φ_{r-c}) 2D columnar phases shown in Figure 3 are weak for all of the structures. Both Janus dendrimers and polymers dendronized with Janus dendrimers have similar powder diffraction intensity profiles and lattice dimensions (Figure 3 and Table 1). Furthermore, the XRD patterns of the oriented fibers collected in the low temperature orthorhombic crystalline phases (Φ_o^k) as well as in the high temperature Φ_h and Φ_{r-c} phases exhibit similar 4.9–5.3 Å stacking features in the wide angle region (Figure 4a,b).

Interestingly, all Janus dendrimers and polymers dendronized with Janus dendrimers exhibit at low temperature a Φ_o^k phase self-organized from supramolecular columns that are strongly correlated. Their column-to-column correlations are demonstrated by the wide-angle off-meridional features on the $2 \times (4.9-5.2) \text{ \AA } L = 1$ layer lines, marked in Figure 4a. These features together with the intense and sharp meridional maxima observed on the $4.9-5.2 \text{ \AA } L = 2$ layer lines (Figures 4a and 5)

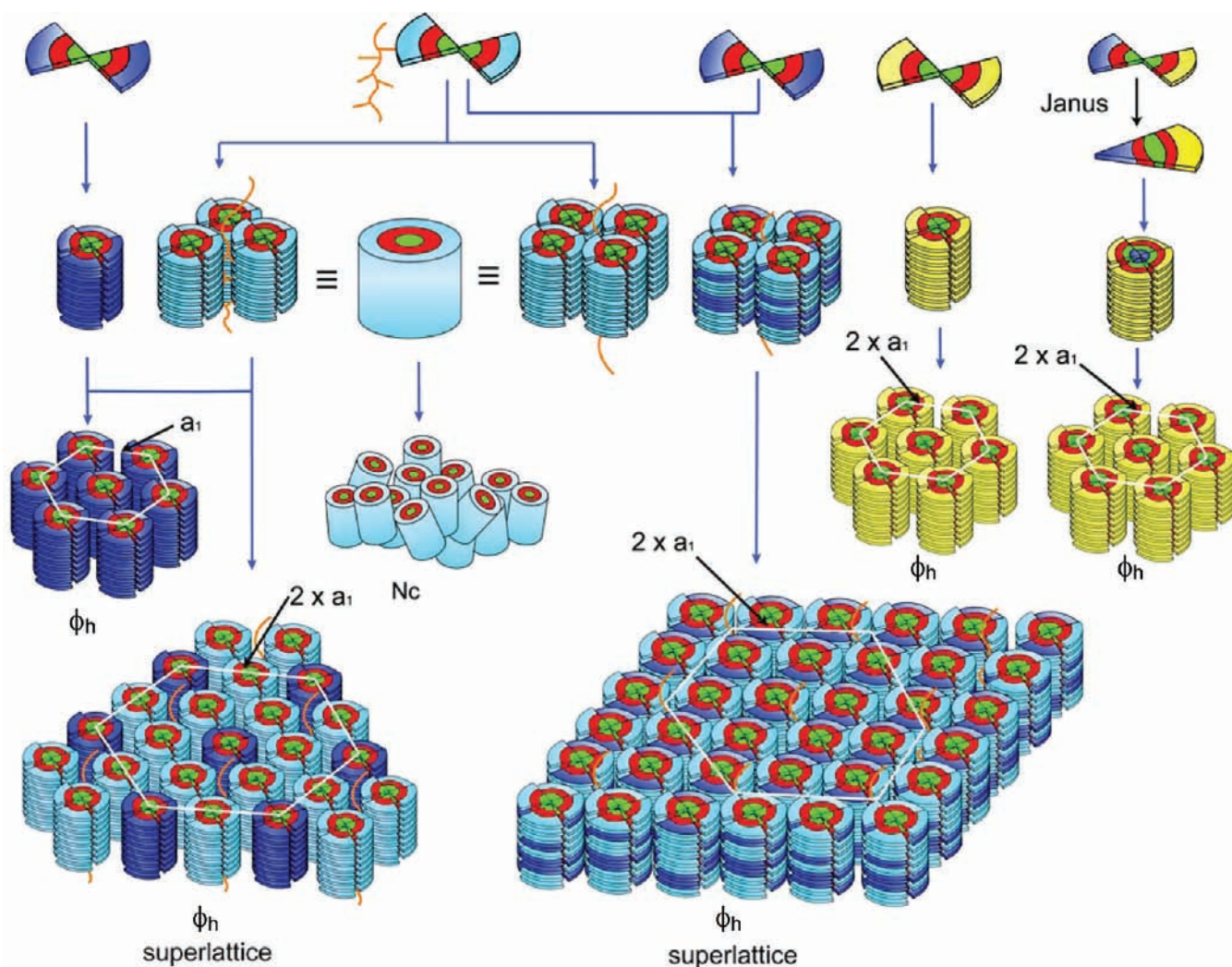


Figure 2. Self-assembly of hydrogenated twin dendritic molecules, of polymers dendronized with hydrogenated twin dendritic molecules, and their coassembly (all in blue). Self-assembly of fluorinated twin dendritic molecules (in yellow) and of semifluorinated Janus dendrimers (half in blue and half in yellow).

suggest that every second layer within the supramolecular columns are in registry and that there are long-range helical correlations. One possible helical packing of the Janus dendrimers within the supramolecular columns consistent with the observed wide-angle diffraction features of the oriented fibers in the Φ_h^k phases shown in Figures 4a and SF1 is a criss-cross one demonstrated previously from single crystal X-ray experiments performed on twin dendritic molecules.^{16a} Therefore, the helix parameter φ , that corresponds to the angle of rotation around the column axis of adjacent column strata, is $360^\circ/(2\mu)$ where μ is the number of Janus dendrimers forming the supramolecular layer of the column (Table 2). The helix parameter φ varies between $\sim 30^\circ$ for (3,4,5)12G1-(3,4,5)Poly)4F8G1-BzA to $\sim 36^\circ$ for (3,4,5)Poly)12G1-(3,4,5)4F8G1-BzA. The helix parameter corresponding to the translation of the layer along the column axis varies in the narrow range of 4.9–5.2 Å, as shown in Figures 4a and 5a,b (t values listed in Table 2). The criss-cross type of helical packing of the supramolecular columns self-organized in the Φ_h^k phases was most probably facilitated by the formation of the intermolecular H-bonding interactions. This mechanism is indirectly supported by the observation that the structure lacking the potential of forming H-bonding due to the methylation of its –CONH– group,

(3,4,5)12G1-(3,4,5)4F8G1-BzA-CH₃, which self-organizes in a simple orthorhombic columnar phase, Φ_{s-o}^k , exhibits wide-angle off-meridional features only on the 6.3 Å $L = 1$ (Figure 6a).

The absence of secondary layers of wide-angle off-meridional features in the XRD fiber pattern, shown in Figure 6a, suggests that the supramolecular columns self-assembled from (3,4,5)12G1-(3,4,5)4F8G1-BzA-CH₃ are not forming the helical criss-cross packing observed in the Janus dendrimers and polymers dendronized with Janus dendrimers that are capable of forming H-bonding along the long axis of their column.

Figure 5 presents the meridional plots of the wide-angle region of the XRD fiber patterns shown in Figure 4. In the high temperature range of the Φ_h and Φ_{r-c} phases the degree of order within the supramolecular columns spans through about 5–7 column strata, as estimated from the width of their wide-angle meridional maxima (Figure 5c,d). Interestingly, in the low temperature range of the Φ_o^k phase the dendronized polymer (3,4,5)Poly)12G1-(3,4,5)4F8G1-BzA exhibits a degree of long-range order of $\xi \approx 35$ layers comparable with that of the Janus dendrimer ($\xi \approx 48$ layers, Figure 5b). This is expected considering that the Janus dendrimer is attached to the polymer backbone through an alkyl group spacer containing 11 methylenic units. On the other hand, in the case of the dendronized

Table 1. XRD Data Collected from the Janus Dendrimers, Polymers Dendronized with Janus Dendrimers, and their Mixtures

compound	T (°C)	phase ^a	a, b, c (Å)	d ₁₀ , d ₁₁ , d ₂₀ , d ₂₁ , d ₃₀ (Å)	
				d ₂₀ , d ₄₀ , d ₀₂ , d ₅₀ , d ₁₂ , d ₀₃ , d ₄₀ (Å)	d ₅₀ , d ₄₂ , d ₆₀ (Å)
(3,4,5)12G1-(3,4,5Poly)4F8G1-BzA	130	Φ _h	56.3	48.9, -, 24.3, 18.3, 16.2	
	25	Φ _o ^k	97.5, 51.8, 10.4	49.0, 24.4, -, 22.9, -, 17.8, 16.3	
(3,4,5Poly)12G1-(3,4,5)4F8G1-BzA	100	Φ _{r-c}	103.3, 49.5	51.9, 25.9, 24.8, -, 19.1, -, 17.2	
	25	Φ _o ^k	99.8, 47.6, 9.8	49.9, 24.9, -, -, -, 17.2, 16.7	
(3,4,5Poly)12G1-(3,4,5)4F8G1-BzA + (3,4,5)12G1-(3,4,5)4F8G1-BzA (80/20 molar ratio)	120	Φ _{r-c}	103.3, 49.7	51.9, 25.9, 24.9, -, 19.1, -, 17.2	
	25	Φ _o ^k	98.8, 47.3, 9.8	49.6, 24.8, -, -, -, 17.1, 16.5	
(3,4,5Poly)12G1-(3,4,5)4F8G1-BzA + (3,4,5)12G1-(3,4,5)4F8G1-BzA (70/30 molar ratio)	140	Φ _{r-c}	101.0, 49.6	50.7, 25.3, 24.8	
	25	Φ _o ^k	97.6, 46.3, 9.8	49.0, 24.4, -, -, -, 16.8, 16.3	
(3,4,5Poly)12G1-(3,4,5)4F8G1-BzA + (3,4,5)12G1-(3,4,5)4F8G1-BzA (50/50 molar ratio)	140	Φ _h	58.8	50.9, -, 25.5, 19.3, 17.0	
	30	Φ _o ^k	97.6, 46.8, 9.8	49.0, 24.4, -, -, -, 16.9, 16.3	
(3,4,5Poly)12G1-(3,4,5)4F8G1-BzA + (3,4,5)12G1-(3,4,5)4F8G1-BzA (30/70 molar ratio)	140	Φ _h	58.9	51.0, -, 25.5, 19.3, 17.0	
	25	Φ _o ^k	95.0, 46.6, 9.8	47.5, 23.8, 23.3, -, -, 16.7, 15.8	
	98	Φ _{r-c}	96.2, 47.8	48.1, 24.1, 24.0, 21.4, -, 16.9, 16.0	
(3,4,5)12G1-(3,4,5Poly)4F8G1-BzA + (3,4,5)12G1-(3,4,5)4F8G1-BzA (50/50 molar ratio)	140	Φ _h	56.9	49.4, -, 24.6, 18.6, 16.4	
	30	Φ _o ^k	95.8, 46.8, 9.8	47.9, 23.9, -, 21.1, -, 16.8, 15.9	
(3,4,5)12G1-(3,4,5)4F8G1-BzA-CH ₃	60	Φ _{s-o} ^k	63.0, 52.2, 6.3	31.5, 26.1, 24.1, 17.5, 15.8	

^aPhase notations: Φ_h, columnar hexagonal 2D phase; Φ_o^k, columnar orthorhombic crystalline; Φ_{r-c}, centered rectangular columnar 2D phase; and Φ_{s-o}^k, columnar simple orthorhombic crystalline phase.

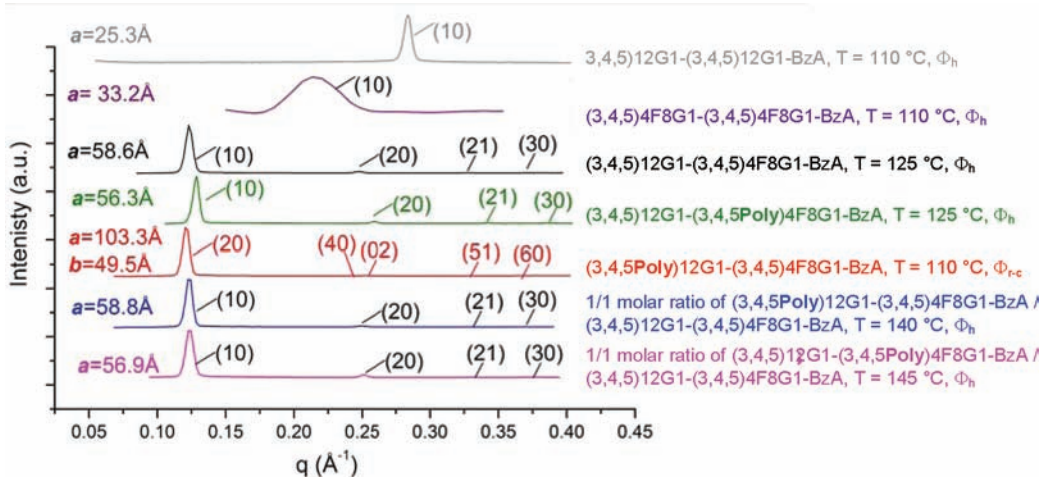


Figure 3. Small-angle powder X-ray diffraction data collected at the indicated temperatures from twin dendritic molecules, Janus dendrimers, polymers dendronized with Janus dendrimers, and of their 1/1 molar mixtures. All structures are detailed in Scheme 3.

polymer of (3,4,5)12G1-(3,4,5Poly)4F8G1-BzA, the degree of order is about 4 times lower ($\xi \approx 9$ layers, Figure 5b). Therefore, for this dendronized polymer the alkyl spacer connecting the polymer to the Janus dendrimer is embedded in the fluorinated region, and, therefore, is subjected to additional steric constraints that limit the degree of order and the correlation length within the supramolecular column.

Reconstruction of the Electron Density Distributions.

The similarity of the X-ray powder diffraction intensity profiles of the Janus dendrimers and of the polymers dendronized with Janus dendrimers (Figure 3) and of their wide angle XRD fiber patterns (Figure 4b), all collected in the high temperature 2D phases, demonstrated that the internal organization of their supramolecular columns is similar. Based on this observation, the relative electron density maps shown in Figure 7, reconstructed from the powder XRD data shown in Figure 3, suggest

that the fluorinated chains are forming the periphery of the supramolecular columns of the high temperature columnar hexagonal phases regardless of the place of the Janus dendrimer from which it is attached to the polymer backbone.

The relative electron density histograms constructed from the corresponding distributions shown in Figure 7 are presented in Figure 8. The histograms exhibit two maxima: one in the low electron density region that corresponds mainly to the aliphatic region "continuum" and a second one in the high electron density region that corresponds to the aromatic and fluorinated region of the supramolecular columns. These maxima are in agreement with the expected aliphatic–aromatic–fluorinated microphase segregation within the supramolecular assemblies. The relative variation of the histogram profiles, which is proportional to the number of electrons within the hydrogenated and fluorinated chains (Figure 8) support the

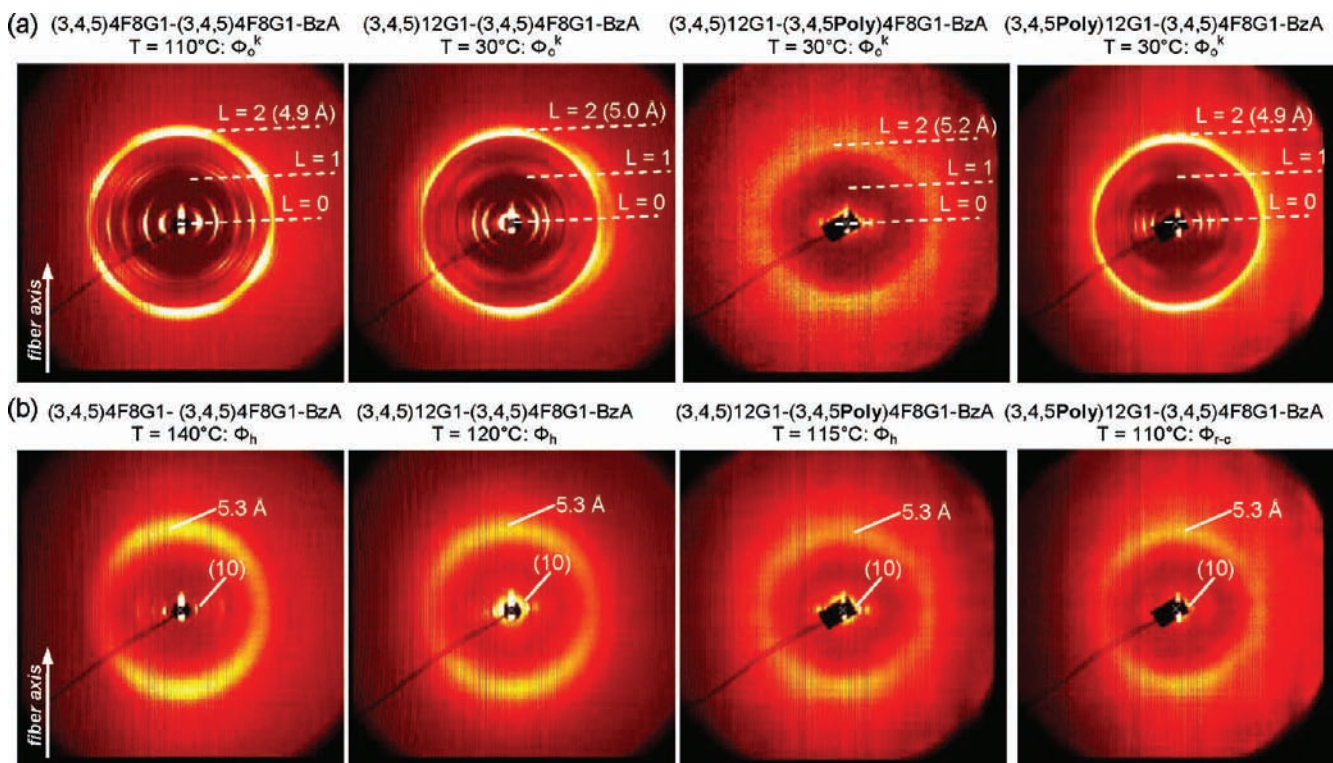


Figure 4. Wide-angle X-ray patterns collected from oriented fibers of Janus dendrimers and polymers dendronized with Janus dendrimers at the indicated temperatures. The name of the compound, the fiber axis, their phases and diffraction features are indicated.

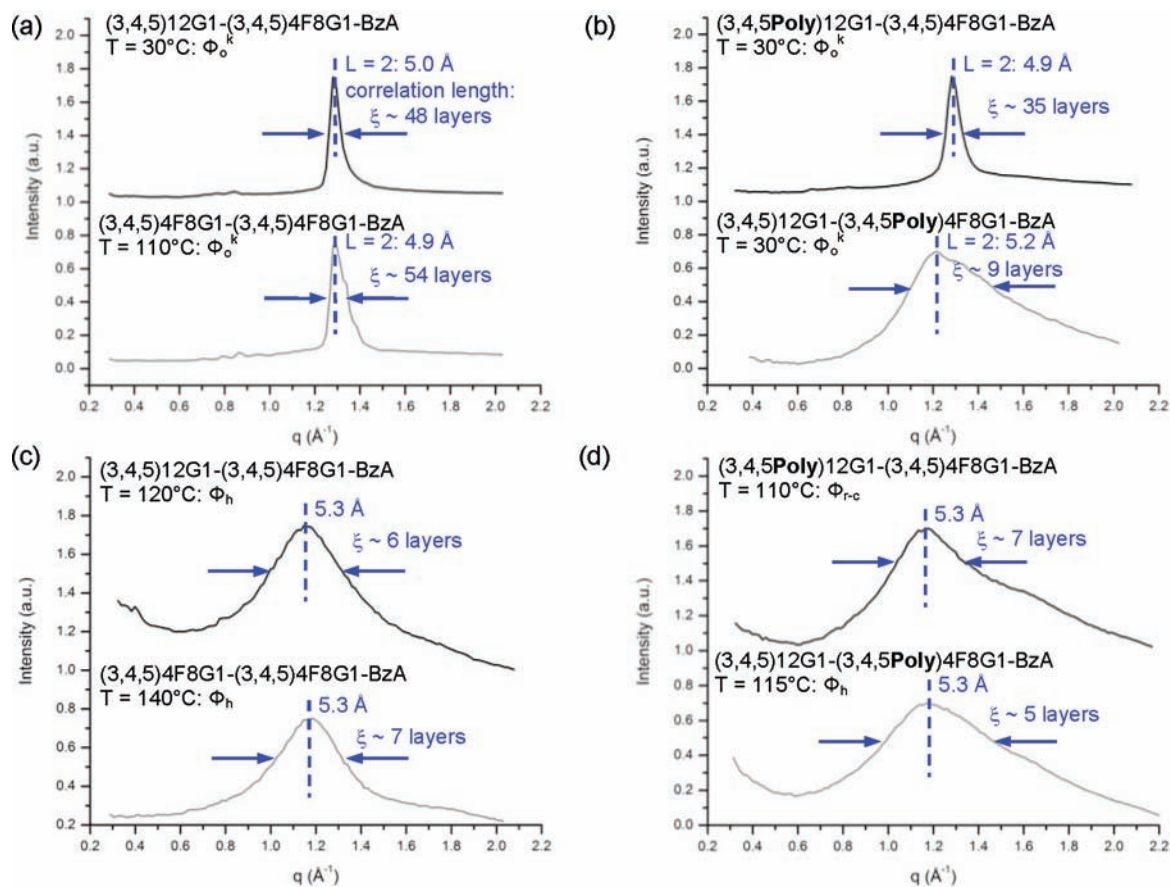


Figure 5. Meridional plots of the wide-angle X-ray fiber patterns shown in Figure 4. The short name of the compounds, the temperature, their phase, their meridional maxima features, and their average correlation length ξ are indicated. All structures are detailed in Scheme 3.

Table 2. Structural and Retrostructural Analysis of the Janus Dendrimers, of Polymers Dendronized with Janus Dendrimers, and of Their Mixtures

compound	T ($^{\circ}\text{C}$)	phase ^a	a, b (\AA)	γ (deg) ^a	t (\AA) ^a	A (\AA^2) ^a	M_{wt}	μ^a
(3,4,5)12G1-(3,4,5Poly)4F8G1-BzA	130	Φ_{h}	56.3	60.0	5.3	5490.1	1984	6.9
	25	$\Phi_{\text{o}}^{\text{k}}$	97.5, 51.8	62.0	5.2	5050.5	1984	6.3
(3,4,5Poly)12G1-(3,4,5)4F8G1-BzA	100	$\Phi_{\text{r-c}}$	103.3, 49.5	64.4	5.3	5113.4	2290	5.6
	25	$\Phi_{\text{o}}^{\text{k}}$	99.8, 47.6	64.5	4.9	4750.5	2290	4.8
(3,4,5Poly)12G1-(3,4,5)4F8G1-BzA + (3,4,5)12G1-(3,4,5)4F8G1-BzA (80/20 molar ratio)	120	$\Phi_{\text{r-c}}$	103.3, 49.7	64.3	5.3	5134.0	2276	5.7
	25	$\Phi_{\text{o}}^{\text{k}}$	98.8, 47.3	64.4	5.0	4673.2	2276	4.9
(3,4,5Poly)12G1-(3,4,5)4F8G1-BzA + (3,4,5)12G1-(3,4,5)4F8G1-BzA (70/30 molar ratio)	140	$\Phi_{\text{r-c}}$	101.0, 49.6	63.8	5.3	5009.6	2269	5.5
	25	$\Phi_{\text{o}}^{\text{k}}$	97.6, 46.3	64.6	5.0	4518.9	2269	4.7
(3,4,5Poly)12G1-(3,4,5)4F8G1-BzA + (3,4,5)12G1-(3,4,5)4F8G1-BzA (50/50 molar ratio)	140	Φ_{h}	58.8	60.0	5.3	5988.5	2255	6.7
	30	$\Phi_{\text{o}}^{\text{k}}$	97.6, 46.8	64.3	5.0	4567.7	2255	4.8
(3,4,5Poly)12G1-(3,4,5)4F8G1-BzA + (3,4,5)12G1-(3,4,5)4F8G1-BzA (30/70 molar ratio)	140	Φ_{h}	58.9	60.0	5.3	6008.8	2241	6.7
	25	$\Phi_{\text{o}}^{\text{k}}$	95.0, 46.6	63.9	5.0	4427.0	2241	4.7
	98	$\Phi_{\text{r-c}}$	96.2, 47.8	63.6	5.0	4598.4	2241	4.8
(3,4,5)12G1-(3,4,5Poly)4F8G1-BzA + (3,4,5)12G1-(3,4,5)4F8G1-BzA (50/50 molar ratio)	140	Φ_{h}	56.9	60.0	5.3	5607.7	2137	6.6
	30	$\Phi_{\text{o}}^{\text{k}}$	95.8, 46.8	63.9	5.2	4483.4	2137	5.2

^aPhase and symbol notations: Φ_{h} , columnar hexagonal 2D phase; $\Phi_{\text{o}}^{\text{k}}$, columnar orthorhombic crystalline; and $\Phi_{\text{r-c}}$, centered rectangular columnar 2D phase; $\gamma = \arctan(a/b)$, a unit cell parameter corresponding to the angle between a and $a + b$ directions; t , the thickness of the column stratum obtained from the X-ray pattern of the oriented fiber; A , area of the unit cell where $A = a \times b$ (for $\Phi_{\text{o}}^{\text{k}}$ and $\Phi_{\text{r-c}}$) and $A = a \times a\sqrt{3}$ for Φ_{h} ; μ , is the number of Janus dendrimers forming a column stratum of thickness t . The calculations of all parameters were performed as reported in previous publications.⁷

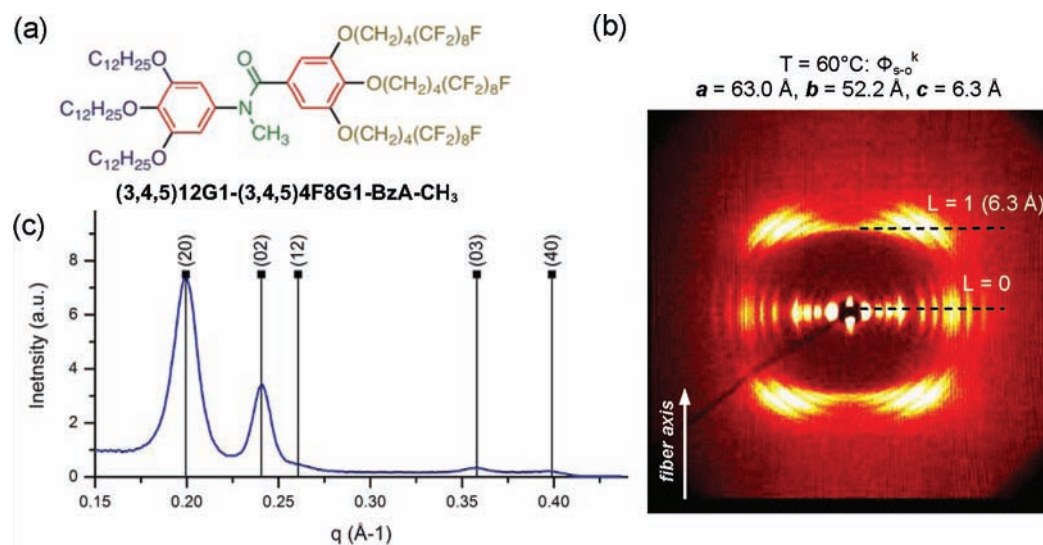


Figure 6. Structure of the (3,4,5)12G1-(3,4,5)4F8G1-BzA-CH₃ Janus dendrimer (a). The wide-angle X-ray pattern collected from the oriented fiber of this Janus dendrimer at the indicated temperature (b) and the corresponding small angle powder XRD data (c).

proposed phases of the powder diffraction amplitudes presented in Figure 7. Therefore, the relative electron density distributions shown in Figure 7 suggest that upon self-assembly all Janus dendrimers and polymers dendronized with Janus dendrimers form supramolecular columns with a fluorinated periphery, regardless if the polymeric backbone is attached to the hydrogenated or fluorinated region of the Janus dendrimer.

This result is also supported by the observation that the fluorinated chains have a decreased conformational freedom in comparison with the hydrogenated ones. Therefore, the more flexible alkyl spacer connecting the polymer backbone to the Janus dendrimer was expected to form the core region of the

supramolecular columns since such confinement requires an increased statistical distribution of its gauche conformers.

Reversed Thermal Nanoactuators Generated from Polymers Dendronized with Janus Dendrimers. First order transitions between columnar phases of conventional dendronized polymers (Figure 1a,b) accompanied by changes of the diameter of the supramolecular columns have been demonstrated to generate nanomechanical functions.^{5f} Oriented fibers produced from these dendronized polymers extend their length with up to 42% when the temperature is increased from 20 to 110 $^{\circ}\text{C}$.^{5f} This change is associated with a novel helix-helix transition. For example, libraries of dendronized

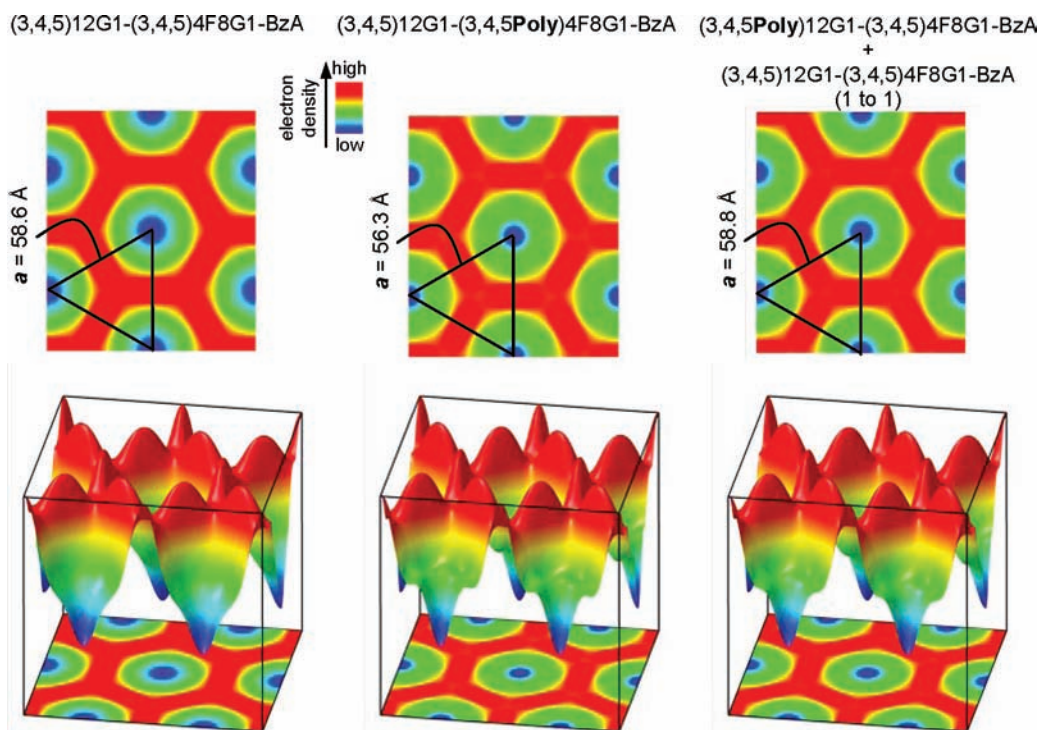


Figure 7. Reconstructed relative electron density maps of the Janus dendrimers, polymers dendronized with Janus dendrimers and of their 1/1 molar mixtures self-assembled in the columnar hexagonal phases from Table 2. The phases of the powder diffraction amplitudes used in the reconstruction: (10)⁻, (20)⁺, (21)⁻, and (30)⁻.

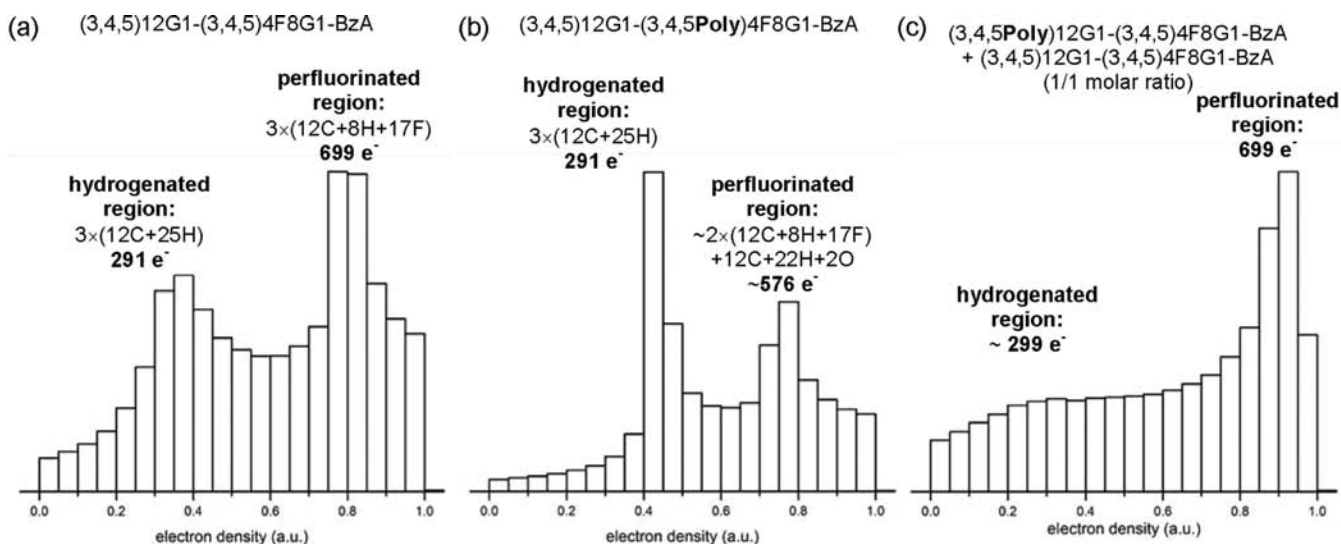


Figure 8. Histograms of the electron density distributions shown in Figure 7 and their correspondence with the number of electrons within the hydrogenated and fluorinated regions, respectively, calculated from the chemical structures of the Janus dendrimers and of the polymers dendronized with Janus dendrimers.

helical polyphenylacetylenes have been used to fabricate molecular actuators capable of displacing 250 times their weight.^{5f} The mechanism of the nanomechanical function was attributed to a decrease of the diameter and an increase of the length of the supramolecular columns upon the increase of temperature. This change is mediated by the unwinding of the helical conformation or the polymer backbone, that is confined to its cylindrical dendritic coat, as the temperature increases. The decrease of the diameter of the dendronized polymer corresponds to a reduction of the number of dendrons forming

the supramolecular column stratum from $\mu = 5$ at low temperature, to $\mu = 4$ at high temperature.^{5f} By contrast, for the polymers dendronized with Janus dendrimers the number of Janus dendrimers that form the column stratum increases at higher temperatures (Table 2). Therefore, the expectation was that all oriented fibers prepared from Janus dendrimers and polymers dendronized with Janus dendrimers should exhibit a thermally induced nanomechanical function that is the “reversed” of that generated from polymers dendronized with self-assembling tapered dendrons attached to the backbone

from their apex (Figure 1a,b). In other words, the polymers dendronized with Janus dendrimers must be capable of displacing large weights upon the decrease of temperature and therefore, will provide additional molecular motives needed to fabricate complex nanomachines.

Figure 9 demonstrates that indeed oriented samples prepared from polymers dendronized with Janus dendrimers exhibit an

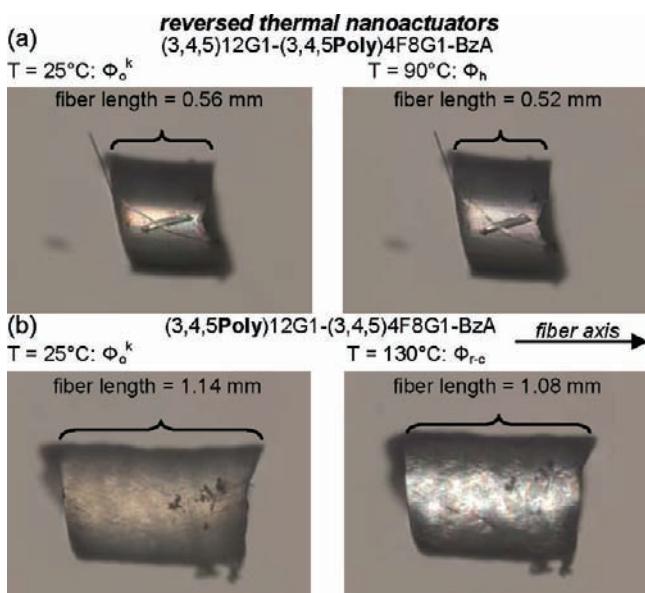


Figure 9. Unusual contraction along the fiber axis upon the increase of temperature of the polymers dendronized with Janus dendrimers (a and b). In both dendronized polymers the contraction is associated with the transition from a crystalline columnar orthorhombic phase to a 2D columnar phase that is accompanied by an unusual increase of the column diameter.

unusual thermal contraction along the fiber axis upon the increase of temperature, as expected from the decrease of μ (Table 2). Within the error of the calculation, the contraction along the fiber axis, which coincides with the axis of the supramolecular columns, observed for polymers dendronized with Janus dendrimers correlates with the increase of the diameter of the supramolecular columns calculated from the XRD data. For example, the macroscopic scale contraction of the (3,4,5)12G1-(3,4,5Poly)4F8G1-BzA is 0.52 mm/0.56 mm \approx 0.928 \pm 0.015 (Figure 9a).

The microscopic scale data, extracted from the XRD results reported in Tables 1 and 2, demonstrated that the contraction is expected to be proportional with the inverse of the unit cell area: $(5490.1 \text{ \AA}^2)^{-1}/(5050.5 \text{ \AA}^2)^{-1} \approx 0.919$. This calculation was based on the assumption that the density of the compound does not change upon the increase of temperature. Similarly, the thermal contraction calculated from the macroscopic and microscopic scale data of (3,4,5Poly)12G1-(3,4,5)4F8G1-BzA are 1.08 mm/1.14 mm \approx 0.947 \pm 0.015 and $(5113.4 \text{ \AA}^2)^{-1}/(4750.5 \text{ \AA}^2)^{-1} \approx 0.929$, respectively. Interestingly, the thermal contraction upon the increase of temperature was observed at the transition from the ordered rectangular phase to either the hexagonal or to the rectangular 2D liquid crystalline phases. These results suggest that the change of the lattice symmetry, from “triangular” for columnar hexagonal and “rectangular” for the columnar orthorhombic phases, is most probably not correlated with the unusual thermal induced contraction upon

heating and that the additional column-to-column correlations of the ordered phases might play an important role in facilitating this change. Such column-to-column correlations were not present in the previously reported dendronized polymers containing self-assembling dendrons attached from their apex on each repeat unit of their backbone.^{5f} These conventional dendronized polymers exhibit the opposite function of chain expansion upon heating.^{5f} In contrast with the polymers dendronized with Janus dendrimers, the Janus dendrimers and their mixtures with the polymer dendronized with Janus dendrimers exhibit a slight expansion along the axis of the supramolecular column upon the increase of temperature (Figure 10a,b).

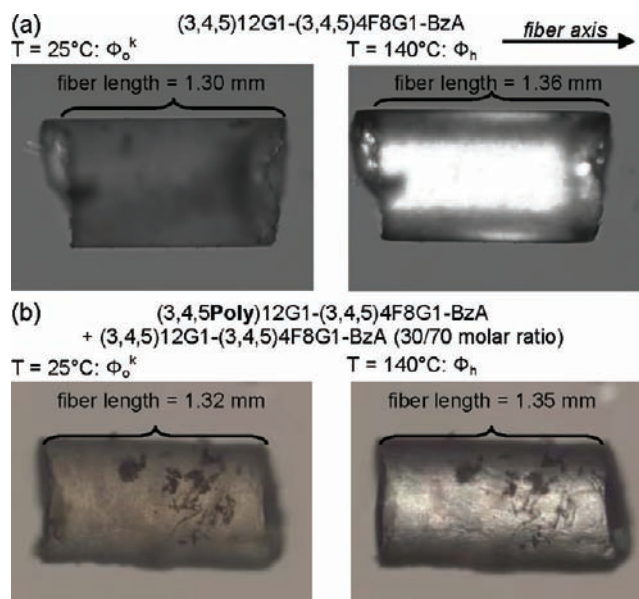


Figure 10. Slight expansion along the fiber axis prepared by extrusion from Janus dendrimer (a) and from its mixture with the polymer dendronized with Janus dendrimers (b).

In these structures, the macroscopic scale expansion is in contradiction with the microscopic scale changes established from the analysis of the XRD data. For example, the (3,4,5Poly)-12G1-(3,4,5)4F8G1-BzA + (3,4,5)12G1-(3,4,5)4F8G1-BzA 30/70 molar mixture was expected to exhibit a contraction of $(6008.8 \text{ \AA}^2)^{-1}/(4427.0 \text{ \AA}^2)^{-1} \approx 0.736$ (Tables 1 and 2). There are at least two possibilities that can account for this difference. First, it is possible that the density of the compounds might decrease upon the increase of temperature. Second, it is possible that the degree of the column-to-column interdigitation changes as a function of temperature.

The results presented in Figures 9 and 10 suggest that the unusual thermal induced contraction upon heating and expansion upon cooling of the oriented fibers observed only in the case of polymers dendronized with Janus dendrimers was induced by the additional dendrimer–dendrimer connectivity that interconnects the polymer backbones from different columns. One possible mechanism that explains the increase of the column diameter upon the increase of temperature is the gradual reduction of column-to-column interdigitation. At low temperatures, the fluorinated chains are stiff and therefore, their rigidity favors a larger degree of column-to-column correlation via the interdigitation of mostly all-trans fluorinated alkyl chains. Wide angle fiber XRD data collected in the low temperature Φ_0^k phases shown in Figure 4a demonstrated the

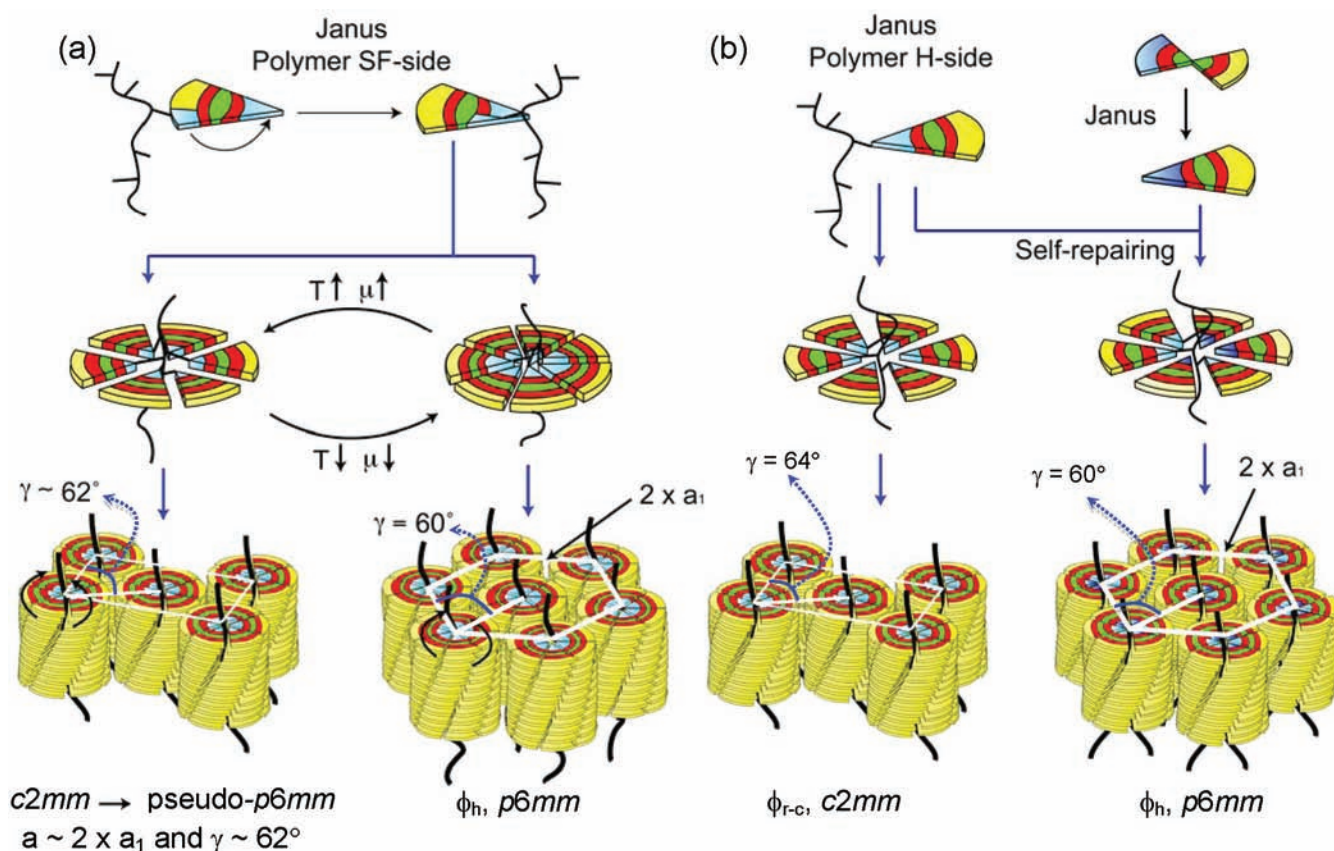


Figure 11. Thermally induced changes of the supramolecular columns self-assembled from polymers dendronized with Janus dendrimers (a) and the self-repairing of the polymers dendronized with Janus dendrimers by mixing with Janus dendrimers (b). Notations: a_1 = lattice dimension for assemblies generated from twin dendritic molecules (see Figure 2); a = lattice dimension for assemblies generated from Janus dendrimers (see Figure 2).

presence of long-range column-to-column correlations and a reduced conformational freedom of the fluorinated chains (Figure 5a,b). In the Φ_h and Φ_{r-c} phases, the presence of diffuse and broad wide-angle features observed in the fiber XRD patterns suggest that there are no significant long-range column-to-column correlations (Figure 6b). This indicates that the degree of column-to-column interdigitation is significantly reduced due to the increased conformational freedom of the fluorinated chains (Figure 5c,d). Therefore, the transition from strongly coupled and interdigitated columns forming the columnar orthorhombic crystalline phase, to uncoupled and less interdigitated columns forming the high temperature 2D liquid crystalline phase can explain the unexpected increase of the column diameter. For example, the cross-section of the supramolecular columns self-assembled from the (3,4,5Poly)12G1-(3,4,5)4F8G1-BzA + (3,4,5)12G1-(3,4,5)4F8G1-BzA 30/70 molar mixture increases with more than 36% from 4427.0 Å²/2 to 6008.8 Å²/2 upon the increase of temperature (Table 2). This variation is attributed to the suggested mechanism involving a certain degree of column-to-column interdigitation that, in addition, does not require any other thermal induced change, including the change in the density of the compound.

Figure 11a summarizes the thermal induced changes of the vesicular supramolecular columns generating the contraction along the column axis upon the increase of temperature and also illustrates the criss-cross helical packing in the Φ_h^k phase. The self-repairing process observed in the high temperature phase of the polymer dendronized with Janus dendrimers by

mixing with Janus dendrimer with molar ratios larger than 50:50 (Table 1) is illustrated in Figure 11b.

CONCLUSIONS

The synthesis and structural analysis of polymers dendronized with Janus dendrimers containing one fluorinated and one hydrogenated dendron are reported. The Janus dendrimers were attached to the polymer backbone both from the hydrogenated and from the fluorinated parts of the Janus dendrimer. Structural analysis of the polymers dendronized with Janus dendrimers, of their model Janus dendrimers,^{14a} and of the corresponding hydrogenated and fluorinated twin dendritic molecules^{14a} demonstrated the assembly of these dendronized polymers into vesicular columns. The surface of these vesicular columns contains fluorinated alkyl groups regardless of whether the Janus dendrimer is attached to the backbone from its hydrogenated or fluorinated parts. The diameter of these vesicular columns is two times larger than that of the corresponding supramolecular columns assembled from the hydrogenated or fluorinated twin dendritic molecules. These vesicular columnar structures are generated by a mechanism that involves an intramolecular self-assembly of the Janus dendritic side groups into tapered dendrons followed by the intramolecular self-assembly of the resulting dendronized polymer in a vesicular column. By contrast with conventional polymers dendronized with self-assembling tapered dendrons this new class of dendronized polymers acts as actuators that decrease the length of the supramolecular column when the temperature

is increased and, therefore, are called reverse thermal actuators. A mechanism for this reverse process was advanced. This new class of reverse nanoactuators are complementary to the previously reported direct nanoactuators^{5f} and to many other examples of molecular architectures capable of undergoing directional motion¹⁸ that are expected to provide access to complexity currently unavailable in synthetic nanomachines.

■ ASSOCIATED CONTENT

● Supporting Information

Experimental procedures with complete spectral and structural analysis and complete reference 14b. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

percec@sas.upenn.edu

Notes

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