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Formation of Organized Structures Through Variation in Molecular Architecture and Chemical Composition

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FORMATION OF ORGANIZED STRUCTURES THROUGH VARIATION IN MOLECULAR ARCHITECTURE AND CHEMICAL COMPOSITION

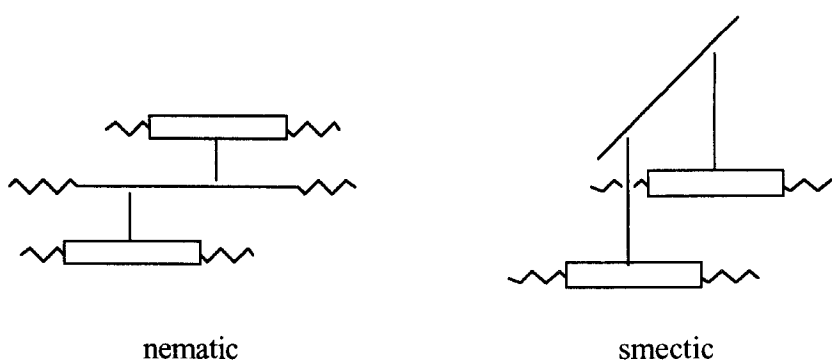
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ABSTRACT

Amphiphilic molecules were synthesized in order to force nematic liquid crystals to order into smectic mesophases, and to direct poly(ethylene oxide) to thread macrocrown ethers. The first concept is fairly well developed, with both hydrocarbon/fluorocarbon and hydrocarbon/oligo(dimethylsiloxane) analogs of 2,5-bis[(4'-*n*-alkoxybenzoyl)oxy]toluenes forming only smectic mesophases. In addition to the low molar mass model compounds, the corresponding side-chain liquid crystalline polynorbornenes with hydrocarbon/fluorocarbon substituents organize into smectic layers. Preliminary HPLC results also indicate that the second concept is viable; that poly(ethylene oxide) threads amphiphilic macrocrown ethers that are organized into lyotropic phases in solutions of toluene/H₂O or benzene/H₂O.

INTRODUCTION

The chemical anisotropy of amphiphilic molecules can be used to control both solution and solid-state behavior, and therefore enable the synthesis of compounds with unusual molecular architectures and phases. The first synthetic challenge to be addressed is that of smectic mesophase formation in side-chain

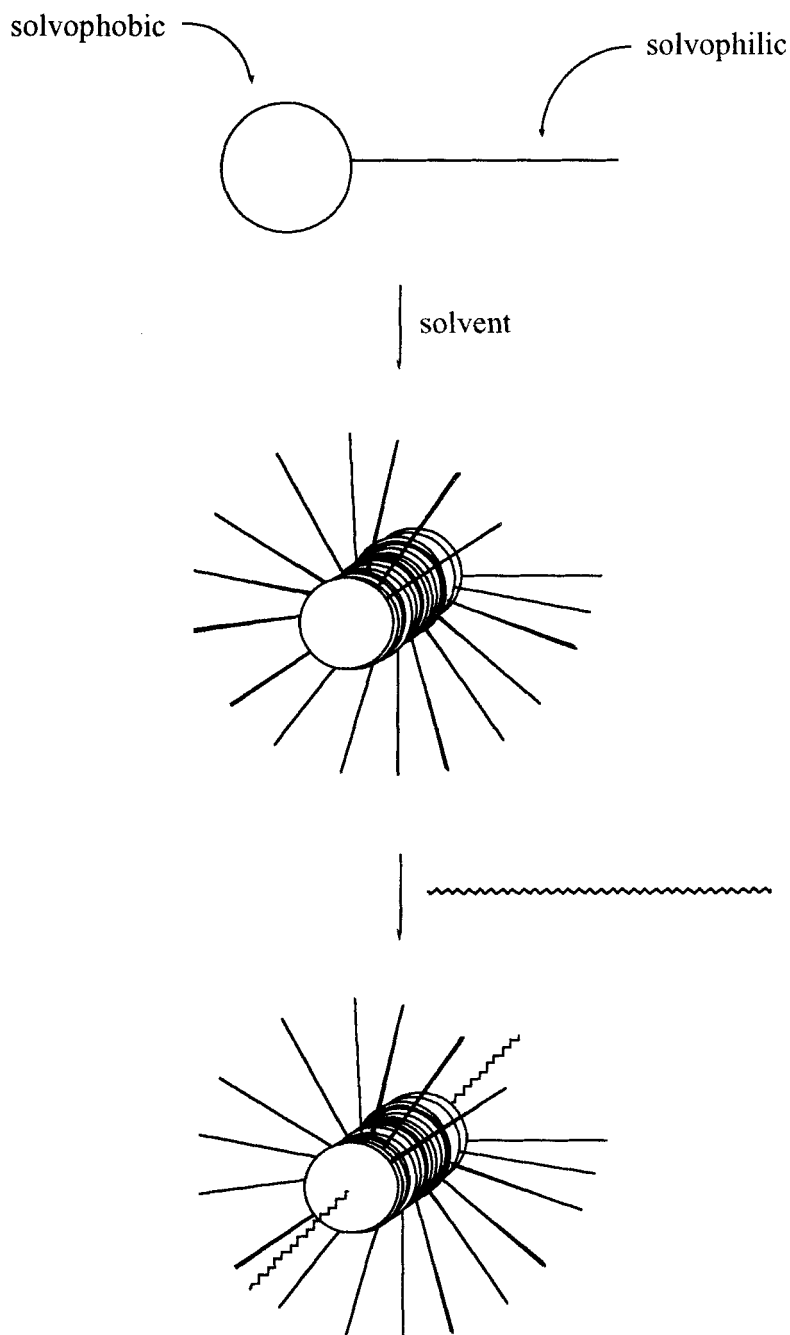


Scheme 1. Induction of smectic mesophases in SCLCPs with laterally attached mesogens by terminating their *n*-alkoxy substituents with immiscible segments.

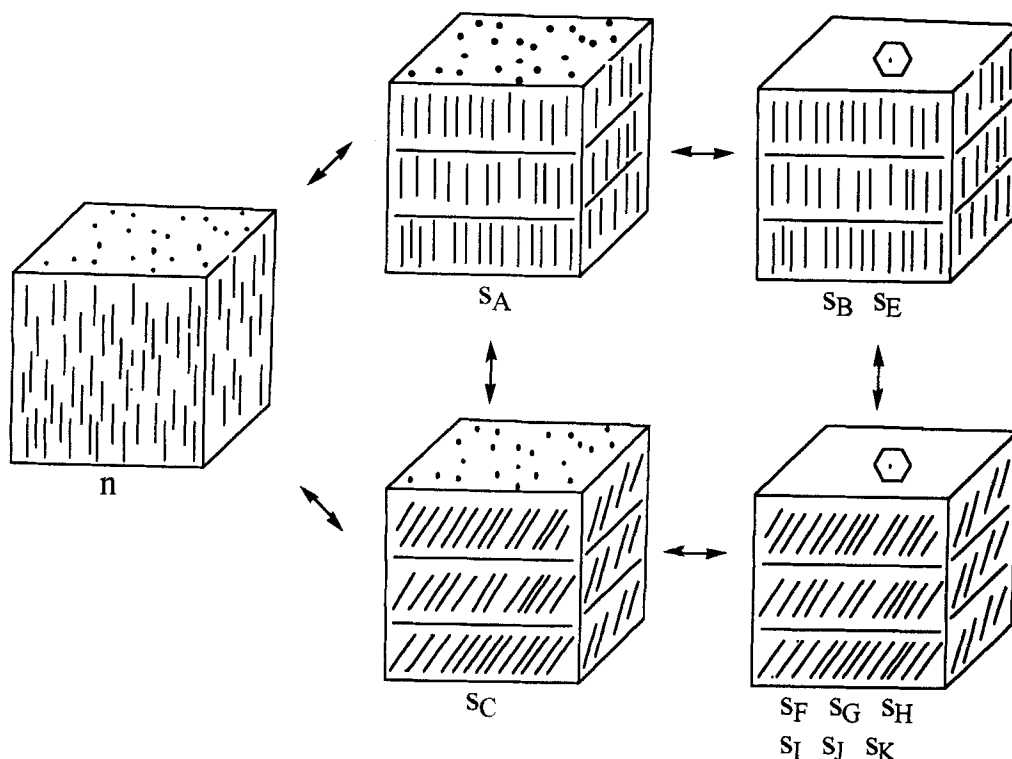
liquid crystalline polymers with laterally attached mesogens. We have chosen this architecture as the most challenging system possible for establishing chemical tools for transforming the mesophases exhibited by liquid crystalline molecules. Since it is commonly believed that the mesogens of this molecular architecture can only organize into nematic mesophases, we have used it to demonstrate that incorporation of immiscible components can be used to force nematogenic mesogens to organize into smectic layers according to Scheme 1. The second synthetic challenge addressed is that of polyrotaxanes in which both the cyclic and linear components are based on the same chemical structure. In order to induce high threading efficiencies in such systems lacking an enthalpic driving force, we have devised the statistical approach outlined in Scheme 2, which is based on the ability of amphiphiles to form lamellar and columnar micelles in solvents which selectively solvate one of its components. This communication briefly outlines the results of this work as presented in Sendai at the Japan-US Seminar on Macromolecular Architecture and Engineering.

Induction of Smectic Mesophases using Immiscible Components

In spite of the maturity of the liquid crystals field [1], chemical concepts have not been developed for converting the type of mesophase(s) exhibited by a given chemical structure. We are therefore establishing chemical tools for transforming the mesophases exhibited by both low molar mass liquid crystals (LMMLCs) and side-chain liquid crystalline polymers (SCLCPs). As illustrated in Scheme 3, the most significant transformation will be from nematic to smectic



Scheme 2. Amiphilic approach for preparing homopolyrotaxanes.



Scheme 3. Relationships between liquid crystalline mesophases.

mesophases, and vice versa. Induction of smectic mesophases in SCLCPs with laterally attached mesogens is particularly challenging; it is commonly believed that attaching the mesogen laterally to a polymer backbone strongly favors formation of nematic mesophases [2], or even prevents ordering into smectic layers [3].

Almost all SCLCPs prepared to date with this architecture exhibit only nematic mesophases (eg. Table 1) [4]. However, most are based on 2,5-bis[(4'-*n*-alkoxybenzoyl)oxy]benzyl mesogens, which show little tendency to organize into layers. For example, 2,5-bis[(4'-*n*-alkoxybenzoyl)oxy]toluenes (Table 2) exhibit only nematic mesophases [5, 6]. However, Table 3 demonstrates that smectic layering can be induced in these model compounds by terminating the mesogen's *n*-alkoxy substituents with immiscible fluorocarbon segments [7]. Whereas the 2,5-bis[(4'-*n*-alkoxybenzoyl)oxy]toluenes form only nematic mesophases, the 2,5-bis{[4'-*n*-(perfluoroalkyl)alkoxybenzoyl]oxy}toluenes exhibit a s_C - s_A phase sequence. Although the temperature ranges of the s_A mesophases are relatively

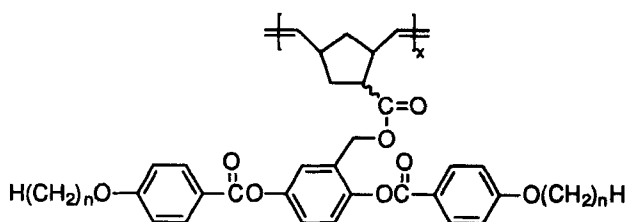


TABLE 1. Molecular Weight and Phase Transitions of Polynorbornenes with Laterally Attached 2,5-Bis[(4'-*N*-alkoxybenzoyl)oxy]benzyl Mesogens.^a

<i>n</i>	DP _n	M _n × 10 ⁻³	pdi	Phase Transitions ^b (°C)
1	100	53	1.16	g 97 n 163 i
2	32	18	1.19	g 92 n 172 i
3	44	26	1.24	g 83 n 140 i
4	23	14	1.17	g 73 n 138 i
5	45	29	1.18	g 60 n 123 i
6	66	44	1.24	g 56 n 126 i

^aNumber average degree of polymerization (DP_n), number average molecular weight (M_n), and polydispersity (pdi=M_w/M_n) determined by gel permeation chromatography (GPC) relative to polystyrene; from reference[4]. ^bObserved on heating; g = glass, n = nematic, i = isotropic.

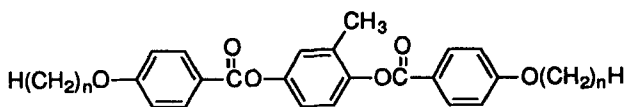


TABLE 2. Thermotropic Behavior of 1,4-Bis[(4'-*n*-alkoxybenzoyl)oxy]toluenes.^a

<i>n</i>	Phase Transitions ^b (°C)
1	k 166 n 252 i
2	k 187 n 248 i
3	k 138 n 209 i
4	k 115 n 206 i
5	k 90 n 178 i
6	k 88 n 173 i
7	k 86 n 161 i
8	k 40 n 157 i

^a *n* = 1-6 from ref. [5]; *n* = 7,8 from ref. [6].

^bObserved on heating; k = crystalline, n = nematic, i = isotropic.

TABLE 3. Thermal transitions and thermodynamic parameters of 1,4-bis[(4'-*n*-alkoxybenzoyl)oxy]toluenes derivatives.^a

n	m	Phase Transitions (°C)		
4	6	k 110	s _C 205	s _A 214 i
5	6	k 101	s _C 197	s _A 208 i
6	6	k 102	s _C 200	s _A 204 i
8	6	k 104	s _C 190	s _A 193 i
4	7	k 124	s _C 215	s _A 222 i
5	7	k 119	s _C 208	s _A 216 i
6	7	k 130	s _C 206	s _A 212 i
8	7	k 120	s _C 199	s _A 200 i
4	8	k 132	s _C 218	s _A 226 i
5	8	k 122	s _C 214	s _A 221 i
6	8	k 130	s _C 211	s _A 217 i
8	8	k 124	s _C 201	s _A 205 i
4	1	k 52	[s _C 42] i	
5	1	k 63	s _C 70 i	
6	1	k 58	s _C 74 i	
8	1	k 44	s _C 88 i	
4	2	k 28	[s _C 24] i	
5	2	k 66	[s _C 54] i	
6	2		s _C 48 i	
8	2		s _C 71 i	

^a Observed on heating; k = crystalline, s_C = smectic C, s_A = smectic A, i = isotropic.

narrow, that of the s_C mesophases are quite broad. In general, the transition temperatures decrease with increasing hydrocarbon length and increase with increasing fluorocarbon length. In addition, the temperature range of the s_A mesophase studies confirm both the s_C and s_A mesophases, and demonstrate that the tilt angle

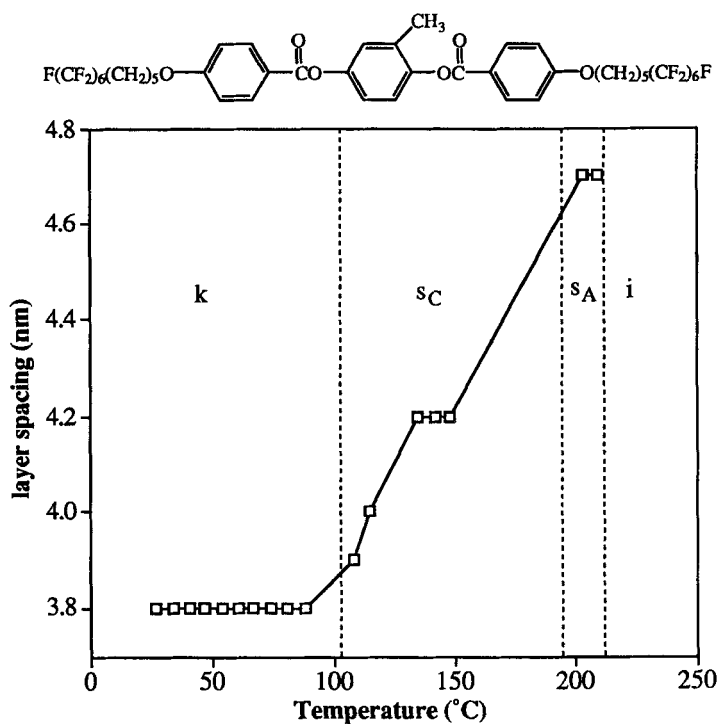


Figure 1. SAXS layer spacing of 2,5-bis[(4'-*n*-((perfluoropentyl)hexyloxy)benzoyloxy)toluene as a function of temperature.

of the s_C mesophase decreases with increasing temperature, until the molecular axes are orthogonal to the layer planes at the s_C - s_A transition (Figure 1).

Table 3 also demonstrates that terminating the *n*-alkoxy substituents with immiscible oligo(dimethylsiloxane) segments is very effective at inducing smectic layering in LMMLCs. That is, the 2,5-bis{[4'-*n*-(oligodimethylsiloxane)alkoxybenzoyloxy]toluene} exhibit s_C mesophases. This induction of smectic layering is in spite of the fact that oligo(dimethylsiloxane)s are not nearly as incompatible with hydrocarbons as fluorocarbons are. For example, the enthalpy of mixing of an equimolar mixture of hexane and perfluorohexane is 2.175 kJ/mol, whereas only 0.135 kJ/mol of energy is required for hexane to mix with 1,1,1,3,3,5,5,7,7,7-decamethyltetrasiloxane [8]. Oligo(dimethylsiloxane)s are also very flexible. For example, poly(dimethylsiloxane) (PDMS) is primarily amorphous with a glass transition at -125°C , although it does exhibit a crystalline melting at -40°C [9]. Therefore, the transition temperatures of the 2,5-bis{[4'-*n*-(oligodimethylsiloxane)-

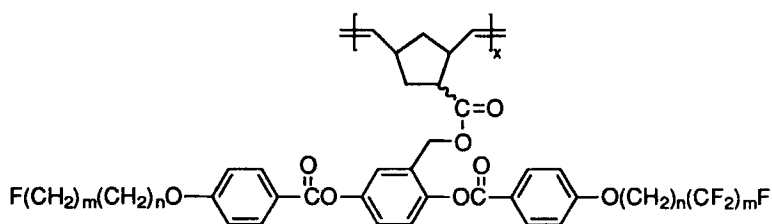


TABLE 4. Thermal Transitions and Thermodynamic Parameters of Poly{5-[[[2',5'-bis(4"-*n*-((perfluoroalkyl)alkoxy)benzoyl)oxy]benzyl]oxy]carbonyl]-bicyclo[2.2.1]hept-2-ene}_s.^a

n	m	Phase Transitions (°C)		
4	6	g 106	s _C 227	s _A 234 i
5	6	g 96	s _C 228 ^b	s _A 231 i
6	6	g 90	s _C 216 ^b	s _A 223 i
8	6	g 77	s _C 213 ^b	s _A 216 i
4	7	g 90	s _C 242	s _A 251 i
5	7	g 96	s _C 239 ^b	s _A 248 i
6	7	g 93	s _C 230 ^b	s _A 236 i
8	7	g 97	s _C 228 ^b	s _A 232 i
4	8	g 93	s _C 251 ^b	s _A 264 i
5	8	g 93	s _C 258 ^b	s _A 262 i
6	8	g 98	s _C 250 ^b	s _A 261 i
8	8	g 98	s _C 231 ^b	s _A 234 i

^a Observed on heating; g = glass, s_C = smectic C, s_A = smectic A, i = isotropic.

^b Transition detected only by polarized optical microscopy.

alkoxybenzoyl]oxy}toluenes increase with increasing hydrocarbon length and decrease with increasing (oligodimethylsiloxane) length.

Comparison of the data in Tables 1 and 4 demonstrates that terminating the *n*-alkoxy substituents with immiscible fluorocarbon segments is also very effective at inducing smectic layering in polynorbornenes with laterally attached mesogens. The s_C mesophase is confirmed by preliminary X-ray scattering of the *n*=5 SCLCPs at room temperature, in which the s_C alignment is frozen in the glassy state. As shown by the diffractograms in Figure 2, the *m*=6, *m*=7 and *m*=8 polymers have sharp reflections at 43.1, 45.8 and 48.9 Å, respectively, which correspond to tilt angles of 31.2, 30.8 and 29.0° relative to the layer normal. The

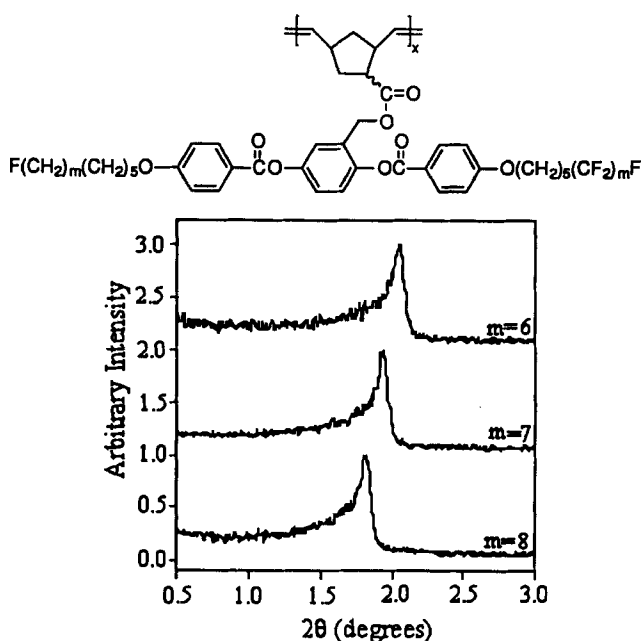


Figure 2. Small angle X-ray scattering curves of poly{5-[[[2',5'-bis[(4''-*n*-(perfluoroalkyl)pentyl)oxy]benzoyloxy]benzyl]oxy]carbonyl]bicyclo[2.2.1]hept-2-ene}s ($n=5$) recorded in the glassy state at room temperature.

influence of the fluorocarbon segments is so strong that the polymer backbone appears to have little effect; the transition temperatures are similar to those of the corresponding model compounds, with only the melting peak replaced by a glass transition. This confirms that SCLCPs with laterally attached mesogens can form smectic mesophases.

An Amphiphilic Approach for the Synthesis of Homopolyrotaxanes of Poly-(Ethylene Oxide)

A polyrotaxane is composed of multiple cyclic molecules threaded with a linear polymer. Polyrotaxanes and rotaxanes are typically synthesized with high threading efficiencies when the cycle and chain form specific [10] interactions driven by enthalpy, or hydrophobic [11] interactions driven by both enthalpy and entropy. Homopolyrotaxanes, in which the rings are based on the same chemical repeat unit as the chain, lack an enthalpic driving force ($\Delta H \sim 0$) for threading. In order to induce high threading efficiencies in systems composed of ethylene oxide ($-\text{CH}_2\text{CH}_2\text{O}-$)

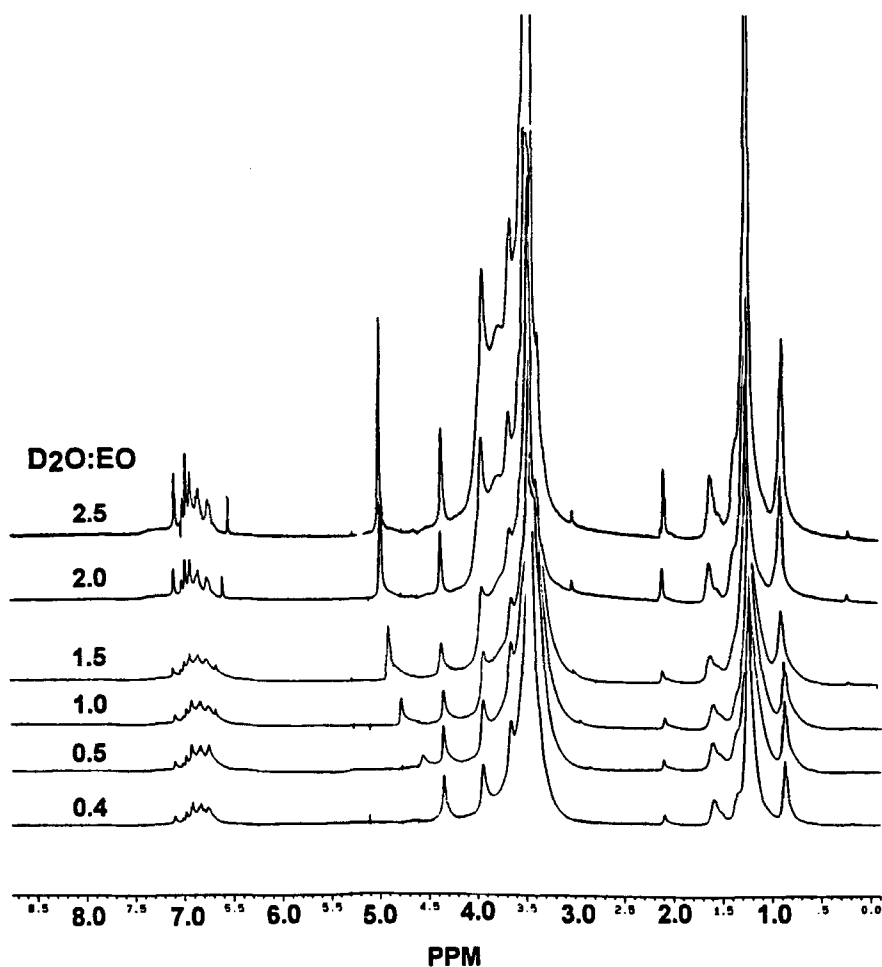


Figure 3. ^1H -NMR spectra of 70 wt% toluene- d_8 /30 wt% (D_2O /MC-12) as a function of the amount of D_2O added per ethylene oxide repeat unit.

repeat units, we have devised a new statistical approach based on the ability of amphiphiles to aggregate and form organized solutions in solvents which selectively solvate one of its components. That is, if the macrocrown ether is substituted with a hydrophobic alkyl tail, it should aggregate into reversed micelles in hydrocarbon solvents due to selective solvation of the hydrocarbon segment. When hydrophilic poly(ethylene oxide), which is normally not soluble in hydrocarbon solvents, is then added to the organized solution, it will also be forced into the interior of the micelle where it should thread (many of) the crown ethers (Scheme 2).

TABLE 5. Detection by Light Scattering of the Critical Concentration of H₂O for Micelle Formation of 0.35 mM MC-12 in Toluene.

[H ₂ O]/[MC-12]	[H ₂ O]/[EO]	Normalized Average Voltage		
		48° detector	90° detector	132° detector
0	0	0.1649	0.0573	0.0451
12.3	0.73	0.1853	0.0589	0.0472
61.5	3.6	0.2050	0.0704	0.0575
123	7.3	0.9496	0.4939	0.3810
615	36	0.9465	1.6874	1.0121

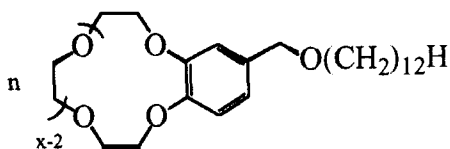
We have synthesized a 44-membered macrocrown ether by reacting the dimesylate of PEG-600 with 3,4-dihydroxybenzaldehyde under pseudo-high dilution conditions using excess K₂CO₃ as base, and therefore multiple potassium template ions [12]. Following reduction of the aldehyde, the hydrocarbon segment is introduced by reacting the benzyl alcohol with bromododecane to produce amphiphilic MC-12.

MC-12 is insoluble in hydrocarbon solvents such as hexane and heptane, but does aggregate in benzene and toluene if small amounts of water are added. Micellar aggregation is evident when the transparent solutions of MC-12 in toluene-d₈ become turbid upon addition of D₂O. This is accompanied by a continuous downfield shift and broadening of the ¹H-NMR resonances of the ethylene oxide units at approximately 3.5 ppm (Figure 3). A water pool also appears at 4.7-5 ppm once aggregation occurs. Light scattering can also be used to detect the critical concentration of water for micelle formation. For example, Table 5 shows that micelle formation occurs in a 0.35 mM solution (15 ml) of MC-12 in toluene when approximately 7.3 equivalents of water per ethylene oxide unit are added.

X-ray diffraction and polarized optical microscopy demonstrate that the 70 wt% toluene/30 wt% (H₂O/MC-12) containing approximately 5 eq H₂O forms a lamellar phases. The ordered nature of these phases is also demonstrated by the ¹³C-NMR T₁ spin-lattice relaxation times determined by the inversion recovery method. As demonstrated by the shorter relaxation times of the aliphatic protons in the turbid solution compared to the isotropic solution (Table 6), the turbid solution containing 4 eq D₂O/EO is more ordered than the homogeneous solution. In contrast, the relaxation times of the ethylene oxide carbons increase upon going from the isotropic to the anisotropic solution; this is apparently because the ethylene

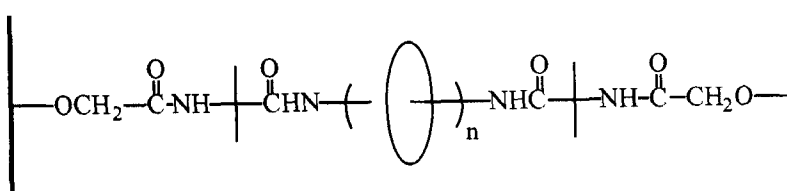
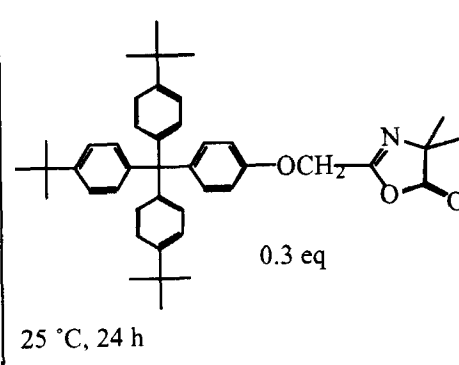
TABLE 6. 90 MHz ^{13}C -NMR T_1 Spin-Lattice Relaxation Times of Isotropic and Anisotropic Solutions of 70 wt% Toluene-d₈ /30 wt% ($\text{D}_2\text{O}/\text{MC-12}$).

	$T_{1\text{C}}$ (ms)	
	[D_2O] / [EO]	
	0 (isotropic)	4 (anisotropic)
Aromatic (av)	150 - 200	
- OCH_2CH_2 - (av)	200	400
Aliphatic $-\text{CH}_2-$ @ 21 ppm	800	450



toluene, H_2O
25 °C, 20 min

0.1 $\text{H}_2\text{N}-\text{PEG}3350-\text{NH}_2$
25 °C, 24 h



Scheme 4. Preliminary route for the synthesis of a poly(ethylene oxide) polyrotaxane using the amphiphilic approach.

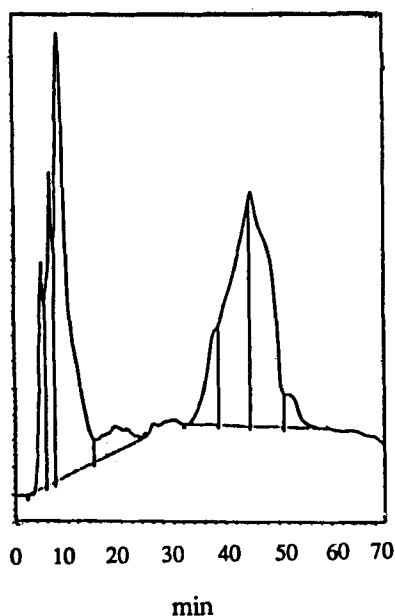


Figure 4. Reverse phase HPLC (C_{18} -derivatized column) of polyrotaxane in 30% H_2O in methanol.

oxide units are now in a pool of water, which is a better solvent for such structures than toluene is.

Threading experiments must be performed with polyethylene glycol derivatives that can be endcapped with blocking groups to prevent dethreading. Water-soluble PEG derivatives destroy the micelles. However, many water-insoluble PEG derivatives, including H_2N -PEG3350- NH_2 , with higher molecular weight and/or hydrophobic endgroups are solubilized inside the hydrophilic core of the reverse micelles. {2-*p*-[Tris(*p*-*t*butylphenyl)methyl]phenoxy}methyl-4,4-dimethylazalactone is an ideal endcapping group for this thread because the azalactone both reacts rapidly with amines [13] and tolerates the water used to induce micelle formation in these systems. Reverse phase HPLC of the preliminary threading experiment outlined in Scheme 4 demonstrates that polyrotaxane forms. As shown in Figure 4, there is a high molecular weight fraction eluting at approximately 45 minutes in addition to MC-12, which elutes at 10 minutes; unreacted thread was removed.

CONCLUSIONS

Compounds which normally form only nematic mesophases can be forced to order into smectic layers by incorporating segments which are immiscible with the basic hydrocarbon chemical structure. Smectic layering is induced in low molar mass liquid crystals by terminating the *n*-alkoxy substituents with either fluorocarbon or oligo(dimethylsiloxane) segments, and in side-chain liquid crystalline polymers using fluorocarbon segments.

Amphiphilic MC-12 aggregates and forms organized solutions in benzene and toluene when small amounts of water are added. The aggregates are destroyed by water soluble PEG derivatives, whereas water insoluble H₂N-PEG3350-NH₂ goes to the interior of the micelles where it threads some of the rings.

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