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Nanostructured Functional Block Copolymers for Electrooptic Devices

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ABSTRACT: Three dendron−linear diblock copolymers with a polyene-type nonlinear optical (NLO) chromophore incorporated in the dendron segment and polystyrene as the linear block were synthesized to investigate the effect of nanostructures on electrooptic (EO) properties. These block copolymers form nanostructures with a periodicity between 36 and 44 nm, which can be characterized using atomic force microscopy (AFM). High EO coefficients (r_{33}) up to 64 pm/V can be achieved in these materials that only have relatively low chromophore concentrations (the highest one is 18 wt %). The resulting poled copolymers also showed good temporal stability. More than 81% of the original r_{33} value can be retained after being isothermally heated at 85 °C for more than 500 h. On the contrary, the results from the guest−host systems (the chromophore was dispersed into polystyrene) only exhibited lower r_{33} values and very poor thermal stability (less than 30% of the original r_{33} values remained after 120 h at 85 °C). These results clearly demonstrate the advantages of using nanostructured block copolymers to improve both poling efficiency (a factor of ∼1.5) and temporal stability of EO materials.

1. Introduction

Block copolymers can form nanoscale phase separations (typically 5−50 nm) with cylindrical, lamellar, spherical, or bicontinuous morphologies depending on molecular weight and composition as well as the asymmetry and interaction between the repeating units comprising the blocks.[1] Along with the significant progress in synthesis and morphological studies of block copolymers, some recent research emphasis have been shifted to study the relationships between functional properties and nanostructure by incorporating suitable building blocks (especially those possess either electronic or optical properties) into block copolymers. There are several examples that show the influence of nanostructured block copolymers on fluorescence, conductivity, photoisomerization, and liquid crystalline property.[2] However, it is still quite challenging to create one-, two-, or three-dimensional confinement of the functional moieties with desirable nanostructures to effectively enhance their optical or electronic properties. Especially, there is almost no information concerning the use of nanostructured block copolymers to improve electrooptic (EO) properties. In order to explore this feasibility, we have prepared a series of dendron−linear block copolymers to study the influence of nanostructures on poling efficiency and thermal stability of these materials.

In the past decade, organic EO materials have been extensively investigated for potential applications in telecommunications and optoelectronic devices due to their intrinsic ultrafast response time and large bandwidth (in the terahertz regime).[3] In spite of this, the development of EO materials has been hindered because of the difficulties involved to achieve large EO coefficient (r_{33}) and good temporal stability simultaneously. A large number of highly active nonlinear optical (NLO) chromophores have been synthesized, and some of these exhibit large r_{33}'s (>100 pm/V) in poled guest−host polymers.[3p,4] The commonly used approaches to obtain good alignment stability are either employing high glass-transition temperature (T_g > 160 °C) guest−host polymers or using lattice hardening methods to lock the motion of the aligned chromophores.[3b,c,k−p] Nevertheless, there are several drawbacks in using these methods because strong intermolecular electrostatic interactions among dipolar chromophores and high-temperature aromatic polymers (e.g., polyimides and polyquinolines) facilitate the formation of aggregates. Poling with electric field at high temperatures also tends to decompose chromophores and result in poor EO properties. Moreover, the commonly used cross-linking conditions often cause isomerization or decomposition of chromophores. Therefore, it is imperative to develop novel methodologies that can be used to produce materials with high r_{33}'s and good thermal stability without encountering high-T_g polymers or cross-linking processes.

By tailoring the size, shape, and conformation of NLO chromophores and macromolecules, we have recently demonstrated significant progress in improving poling efficiency of EO materials.[5] To take this one step further, a series of dendron−linear diblock copolymers with NLO chromophores functionalized on the periphery of the dendron have been synthesized to explore the feasibility of using nanostructured block copolymers to improve poling efficiency and temporal stability simultaneously.

2. Results and Discussion

2.1. Design, Synthesis, and Characterization. The standard polyene-type chromophore (CLD) was chosen for EO study because of its proved molecular nonlinearity.[4c,6] Because of its chemical sensitivity, we have employed a postfunctionalization method[5c,7] to attach this chromophore onto a precursor block copolymer at the final stage without exposing it to vigorous polymerization conditions (Scheme 1 and Scheme 2).

To functionalize the chromophore with a carboxylic group (**4**, RCOOH) for covalent attachment, compounds **1**[6] and **2**[5b] were used as the starting materials. The synthesis was carried out using a microwave-assisted condensation reaction, with sodium ethoxide as catalyst, to afford **3** in 48% yield. Compound **3** was then reacted with succinic anhydride to afford **4** in 50% yield.

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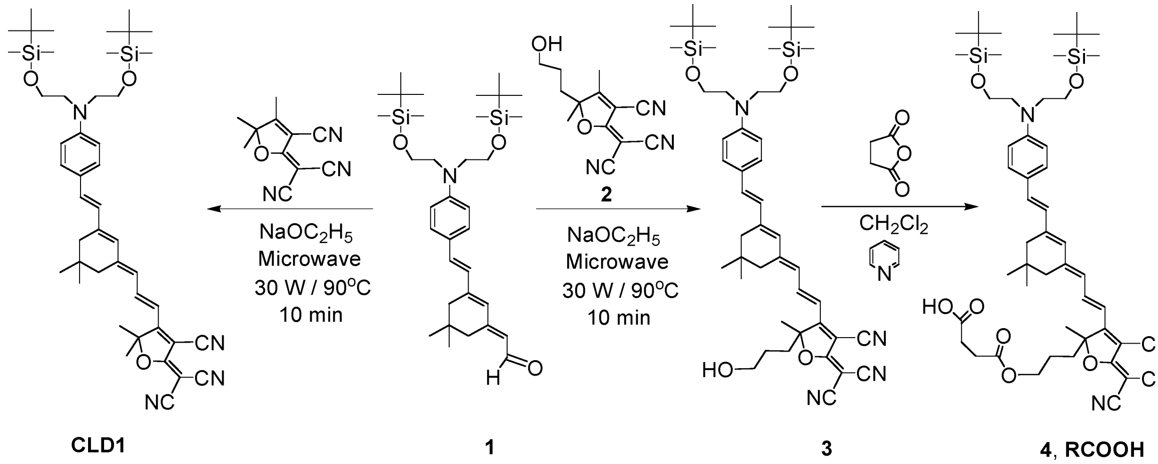
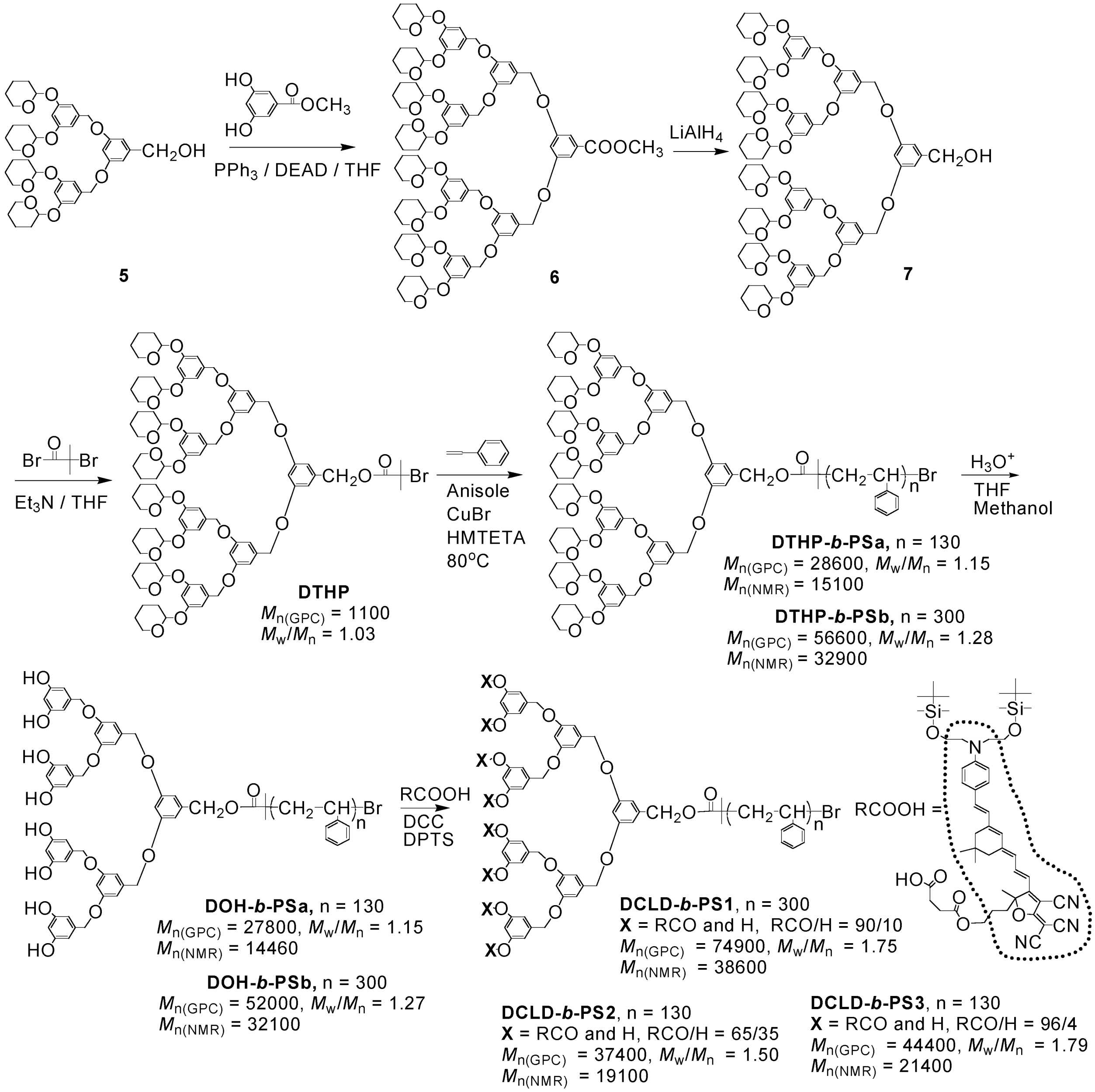
Scheme 1. Synthesis of the Carboxylic Group-Containing Chromophore 4 and CLD-1



Scheme 2. Synthesis of the Dendron−Linear Diblock Copolymer of DCLD-*b*-PS[a]



[a] The circled area in the RCOOH is the structure for the calculation of chromophore loading level.

In our polymer design, the dendron−linear diblock copolymer architecture was chosen because it possesses the combined properties of a dendritic macromolecule and processability and phase separation of a linear polymer.[8] The chromophore loading

Table 1. Physical Properties of the Synthesized Initiator and Its Related Polymers

	n^a	$M_{n(GPC)}{}^b$	$M_w/M_n{}^c$	$M_{n(NMR)}{}^d$	thermal properties^e	PS^f	DCLD^g	x^h (mol %)	η^i (%)
DTHP		1 100	1.03	1 694	$T_{g(DTHP)} \sim 123$ °C	0			
DTHP-*b*-PSa ^{j,k}	130	28 600	1.15	15 100	$T_{g(PS)} \sim 105$ °C	89			
DTHP-*b*-PSb ^{j,l}	300	56 600	1.28	32 900	$T_{g(PS)} \sim 106$ °C	95			
DOH-*b*-PSa	130	27 800	1.15	14 400	$T_{g(PS)} \sim 104$ °C, $T_{d(DOH)} \sim 152$ °C	93			
DOH-*b*-PSb	300	52 000	1.27	32 100	$T_{g(PS)} \sim 106$ °C, $T_{d(DOH)} \sim 150$ °C	97			
DCLD-*b*-PS1	300	74 900	1.75^m	38 600	$T_{g(PS)} \sim 106$ °C, $T_{g(DCLD)} \sim 119$ °C	81	19	90	10
DCLD-*b*-PS2	130	37 400	1.50^m	19 100	$T_{g(PS)} \sim 105$ °C, $T_{g(DCLD)} \sim 118$ °C	71	29	65	14
DCLD-*b*-PS3	130	44 400	1.79^m	21 400	$T_{g(PS)} \sim 105$ °C, $T_{g(DCLD)} \sim 119$ °C	63	37	96	18

[a] The degree of polymerization of the polystyrene block. [b] Number-average molecular weight determined by GPC with THF as eluent. [c] Polydispersity determined by GPC with THF as eluent. [d] Molecular weigh determined by ^{1}H NMR. [e] T_g (glass transition) and T_d (decomposition temperature) were determined by using DSC with a heating rate of +10 °C/min, the transitions were the on-site points, and the measured temperature range is from room temperature to 170 °C. [f] Weight fractions of the PS block based on the $M_{n(NMR)}$. [g] Weight fractions of the DCLD block based on the $M_{n(NMR)}$. [h] Grafting degree of the chromophore onto the DOH block. [i] Chromophore loading in weight fractions based on the $M_{n(NMR)}$. [j] The ATRP polymerizations were proceeded by using [HMTETA] and CuBr complex system. [Initiator]:[HMTETA]:[Cu(I)Br] = 1:1:1. Polymerization temperature is 80 °C. [k] Feed molar ratio of the monomer $[M]_0$ to initiator $[I]_0$ is 250. Polymerization time is 16 h. [l] Feed molar ratio of the monomer $[M]_0$ to initiator $[I]_0$ is 500. Polymerization time is 16 h. [m] After grafting the RCOOH onto the DOH-*b*-PS, the polydispersity becomes broader. One possibility of this observation is that some aggregates were formed in the THF solution due to the poor solubility of the DCLD segment in THF. Large aggregates with diameters of ~50−100 nm were observed under AFM (not shown) when the THF solution was cast onto silicon wafer.

Table 2. EO Performances and Morphologies of the Block Copolymers and Guest−Host Systems^a

			thermal stability at 85 °C		morphologies	
material systems	η^b (%)	r_{33} (pm/V)	$r_{33}/r_{33(0\,h)}$	aging time (h)	roughness^e (nm)	periodicity (nm)
DCLD-*b*-PS1	10	42	81	528	0.45	20,^{f} 44^g
DCLD-*b*-PS2	14	56	88	528	0.36	17,^{f} 36^g
DCLD-*b*-PS3	18	64	81	528	0.42	24,^{f} 40^g
guest−host 10%	10	30 (38^c, ~27^d) [6]	29	120	1.29	240−360^h
guest−host 14%	14	37 (47^c, ~34^d) [6]	8	120	1.22	60−240^i
guest−host 18%	18	42 (62^c, ~44^d) [6]	27	120	3.03	180−740^i

[a] All of the films were poled under a dc electric field of 125 V/μm and then measured at 1.3 μm. For block copolymers, the poling temperature is 120 °C. For the guest−host systems, the poling temperature is 90 °C. [b] Chromophore loading density in weight percent determined by using ^{1}H NMR. [c] Guest−host system using poly(methyl methacrylate) (PMMA) as the host. The film was measured at 1.06 μm. [d] Calculated value at 1.3 μm in PMMA. [e] Roughness determined as the root-mean-square of height deviations taken from the mean area plan. [f] Average diameters of the DCLD segment depending on the grafting degrees. [g] Periodicity of the block copolymer depending on the molecular weights. [h] The width of the CLD-1 domain. [i] The size of the CLD-1 domain.

level of these block copolymers can also be tuned by varying the generation of dendrons and length of the linear polystyrene (PS). The synthetic procedure used for making these block copolymers is shown in Scheme 2. A third generation dendron (DTHP) with eight tetrahydropyranyl (THP) protected hydroxyl groups as the hydroxyl precursors and a 2-bromoisobutyrate unit as the initiating moiety was prepared for block copolymerization. The DTHP was utilized as an initiator to polymerize styrene (S) through the atom transfer radical polymerization (ATRP) method[9] to yield a dendron−linear diblock copolymer of DTHP-*b*-PS. The THP groups were then deprotected under mild acidic condition to afford the hydroxyl-containing DOH-*b*-PS. Finally, the hydroxyl groups on the periphery of the dendron were condensed with the carboxylic acid-containing CLD-type chromophore (**4**, RCOOH) to afford the DCLD-*b*-PS through a well-established postesterification method.[5c,7] The DCLD-*b*-PS was purified through repetitive precipitations from chloroform into methanol, until no reactant (RCOOH) was detected from either thin-layer chromatography (TLC) or gel permeation chromatography (GPC).

By controlling the degree of PS polymerization (*n*, Scheme 2) and grafting of chromophore onto the dendron part (RCO/H, Scheme 2 and Table 1), the chromophore concentrations can be determined as 10, 14, and 18 wt % by ^{1}H NMR (Table 1). The weight fractions of the dendron segments containing the CLD chromophore (DCLD) are calculated to be 19, 29, and 37 wt % when compared to the weight of the whole block copolymers. Thermal analysis of DCLD-*b*-PS using DSC showed two distinct endothermic transitions at ~105 and ~118 °C, corresponding to the T_gs of the PS and the DCLD segments, respectively. These two thermal transitions were also observed through the stationary shear-modulated force microscopy (SM-FM) technique in thin film state.[10]

2.2. EO Properties of the Block Copolymers and Their Counterpart Guest−Host Systems. In order to determine the EO coefficient, the solutions of block copolymers in cyclopentanone (11 wt %) were spin-coated as thin film (~1.5 μm) onto indium tin oxide-coated glass substrates. After baked at 85 °C overnight under vacuum to remove residual solvent, gold electrodes with a diameter of 4 mm and a thickness of 100 nm were sputtered onto the exposed surface. The in-situ generated second harmonic signals were also used to monitor the poling dynamics as a function of ramping temperature in order to find the optimal poling conditions for the polymers. The optimal poling temperature for these block copolymers is ~120 °C. For poling, the films were preheated at the poling temperatures for 30 min, then poled under nitrogen with a dc electric field of 125 V/μm for 25 min, and then slowly cooled down to room temperature under the electric field. The poled films (measured by using the thin film reflection technique at 1.3 μm)[11] showed large EO coefficients with the highest value (64 pm/V) for the polymer with 18 wt % chromophore loading (Table 2). This number is higher than the reported values using this chromophore in a guest−host polymer with a similar loading level.

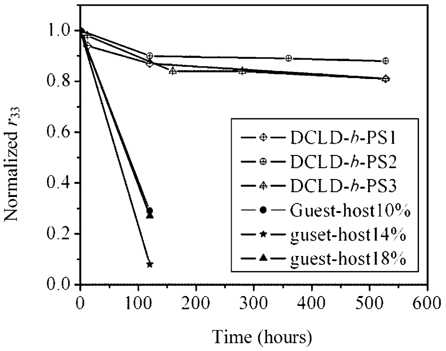


Figure 1. Temporal stability of the poled DCLD-*b*-PS and guest−host systems at 85 °C under nitrogen. The normalized r_{33} was plotted as a function of baking time.

More importantly, higher than 81% of the original r_{33} values could be retained after the films were isothermal heated at 85 °C for >500 h (Figure 1 and Table 2).

For comparison, the widely used guest−host system was also investigated. The guest−host polymers with a similar chromophore (CLD-1,[6] structure is given in Scheme 1) doped at 10, 14, and 18 wt % in polystyrene ($M_n = 15\,800$, $M_w/M_n = 1.05$, from Aldrich) were studied. The best r_{33} value obtained from these poled guest−host polymers under the same electric filed was only 42 pm/V (Table 2).[12] The resulting poled film also possesses much worse temporal stability with only <30% of its original r_{33} value retained after isothermal heated at 85 °C for 120 h. These results clearly show that the poling efficiency and thermal stability of EO polymers could be simultaneously enhanced in these novel block copolymers.

2.3. Possible Mechanism of the Enhancement of the EO Coefficient and Stability Using the Block Copolymers. The significantly different EO properties between the dendron−coil block copolymers and the model guest−host system might be attributed to their morphologies. To confirm this point, the surface of the films prepared similarly to those used for EO characterization but without the gold electrode were examined by atomic force microscopy (AFM). The phase images of block copolymers and their guest−host counterpart systems are shown in Figure 2. For the block copolymers, smooth surfaces with roughness of 0.36−0.45 nm (Table 2) were observed. The DCLD phase forms microphase-separated domains having an average diameter of ∼17−24 nm, increasing with the increase of chromophore grafting degrees. These DCLD phases are evenly dispersed in the PS matrix with an average periodicity of 36−44 nm, depending on the molecular weights, whereas the surface of the guest−host system was much rougher, exhibiting roughness of 1.22−3.03 nm, due to the incompatibility between the CLD-1 chromophore and the PS host. Heterogeneous phase separation with large and irregular CLD-1 domain of ∼60−740 nm was also observed.

For a given EO polymer, the r_{33} value is determined by how well the dipoles of the chromophores can be aligned by poling. In the guest−host system, chromophores tend to form large size aggregates due to incompatibility between chromophores and polymer host and the strong dipole/dipole electrostatic interactions between chromophores. As a result, these large chromophore aggregates are very difficult to align under the poling field. In the case of block copolymers, the chromophores also form aggregates but with much smaller domains (17−24 nm). Normally, poling of these aggregated chromophores should be also quite difficult, but the nanostructures and thermal characteristics of the block copolymers surmount the above problem, resulting in higher poling efficiency than the guest−host systems. For block copolymers, the poling temperature (120 °C) is higher than the T_g of polystyrene (105 °C) and is quite close to that of the DCLD phase (∼118 °C). At this poling temperature, the PS phase is softened around the nanosized DCLD domain, providing a smaller chromophore rotational hindrance under the poling electric field. As a result, the alignment of chromophore's dipole is easier and more efficient, resulting in higher r_{33} values.

The high temporal stability of the poled block copolymer is also quite surprising considering its relatively low T_g. For the poled DCLD-*b*-PS, an r_{33} greater than 81% of the original value was retained after being isothermally heated at 85 °C for >500 h. This was achieved without using any high-T_g polymer or cross-linking reaction. Thermal stability of this polymer even outperforms a cross-linked system reported earlier (∼80% of its original r_{33} value was retained after aging at 70 °C for 250 h) using the analogous CLD-type chromophore.[5c] Since the annealing temperature (85 °C) is lower than both the T_g*s* of DCLD and PS, the PS glassy matrix acts as a stiff wall around the nanosized DCLD domain. This nanoconfinement effect is very similar to that of the network formation in a cross-linked system that hinders the rotation of the aligned chromophores and results in better alignment stability.

3. Conclusion

We have designed and synthesized several NLO dendron−linear diblock copolymers that form nanostructures with periodicity between 36 and 44 nm. The resulting diblock copolymers showed much improved poling efficiency (∼1.5-fold higher than the guest−host systems) and temporal stability through the nanostructures formation (more than 81% of the original r_{33} values were retained after isothermally heated at 85 °C for >500 h compared to only less than 30% of that retained after 120 h in the guest−host systems). These results show the significant influence of nanostructures on EO properties and the potential of using supramolecular block copolymers for photonics. Further investigation is in progress for getting much larger EO coefficient with more efficient NLO chromophores.

4. Experimental Section

4.1. General Information. ^{1}H NMR spectra were measured using a Bruker 300 instrument spectrometer operating at 300 MHz with TMS internal standard as a reference for chemical shifts. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) and high-resolution mass spectrometry (HRMS) were performed by the UW Bio Mass Spectrometry Lab. The purity of low molecular weight compounds was determined by a combination of thin-layer chromatography (TLC) on silica gel plates (Whatman) with fluorescence indicator, high-pressure liquid chromatography (HPLC) using a Varian PrepStar SD-1 high-pressure liquid chromatograph, and/or elemental analysis. Molecular weights of polymers were determined using a Waters-1515 gel permeation chromatography (GPC) coupled with UV and RI detectors, in reference of polystyrene standards with THF as the eluent. Purity of the polymers was determined using GPC and ^{1}H NMR spectra. Thermal transitions were measured on a TA Instruments differential scanning calorimeter (DSC) 2010 with a heating and cooling rates of 10 °C/min. An atomic force microscope (NanoScope III, Digital Instrument) equipped with an integrated silicon tip/cantilever with resonance frequency ∼240 kHz in height and phase image models were utilized for observation of morphologies. The AFM topographies showed no evidence of tip-induced modification during successive scans.

4.2. Electrooptic Characterization. A thin-film reflection technique[11] was used to measure the electrooptical coefficient. Block copolymers and guest−host blends were spun-cast into ∼1.5 μm

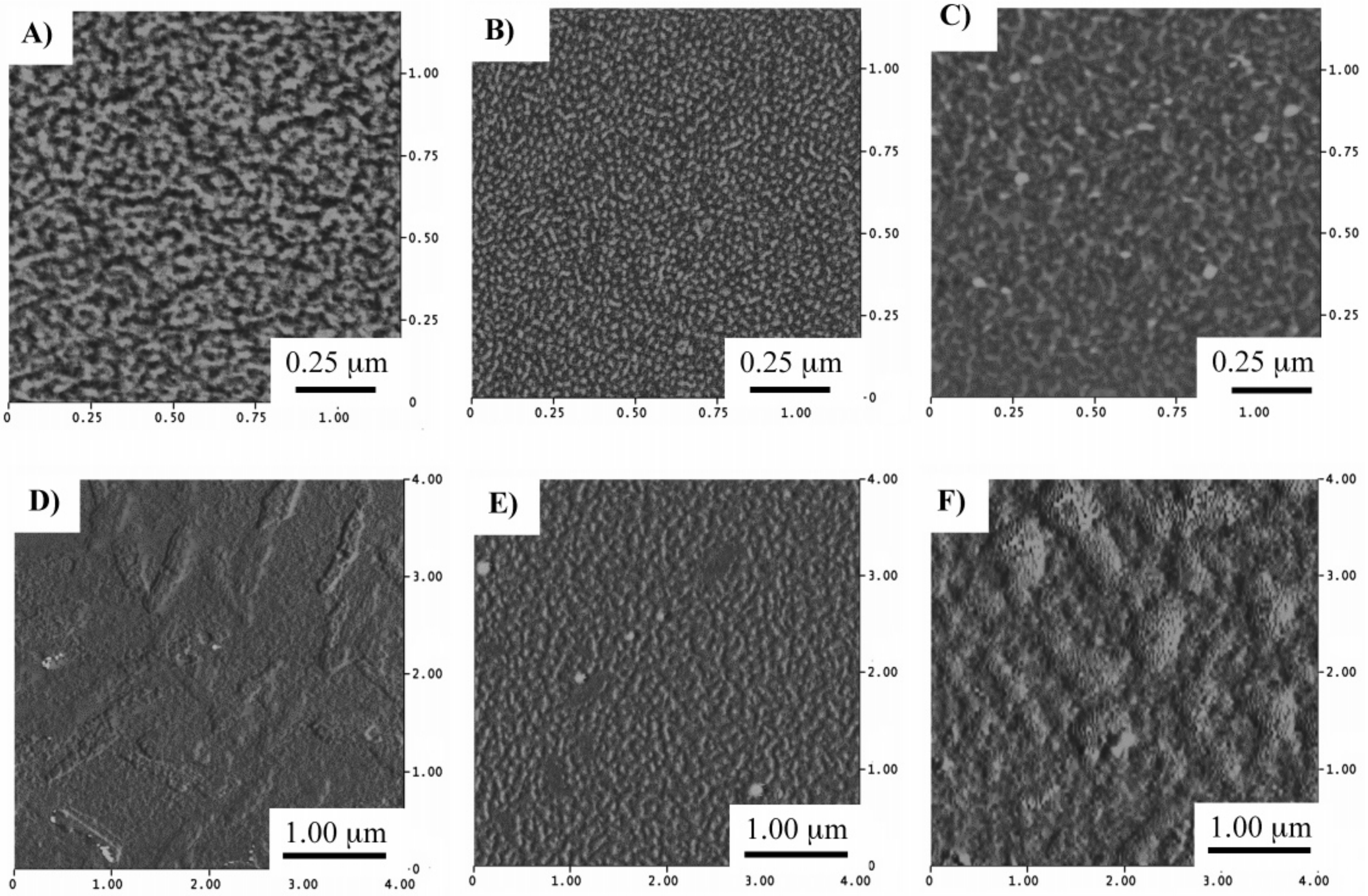


Figure 2. AFM phase images of the DCLD-*b*-PS1 (A), DCLD-*b*-PS2 (B), DCLD-*b*-PS3 (C), guest−host 10 wt % (D), guest−host 14 wt % (E), and guest−host 18 wt % (F). The brighter areas in the phase images are attributed to the DCLD (A, B, and C) or CLD-1 (D, E, and F) phase due to the concern of their higher glass transition temperature or melting point. Note the scale bar between the block copolymer and guest−host system is different.

films from cyclopentanone (11 wt %) on indium tin oxide-coated glass substrates at a spin-coating rate of 800 rpm for 40 s. After the films cured at 85 °C overnight under vacuum to remove residual solvent, gold electrodes with a diameter of 4 mm and a thickness of 100 nm were sputtered onto the exposed surfaces. In-situ generated second harmonic signals were also used to monitor the poling dynamics as a function of ramping temperature in order to find the optimized poling conditions for the polymers. For block copolymers, the optimal poling temperature is 120 °C. For the guest−host systems, the poling temperature is 90 °C. For poling, the films were preheated at the optimized poling temperatures for 30 min, then poled under nitrogen with a dc electric field of 125 V/μm for 25 min, and finally cooled down to room temperature under the electric field.

4.3. Chemicals. Methyl 3,5-dihydroxybenzoate, 3,4-dihydro-2*H*-pyran, triphenylphosphine, lithium aluminum hydride, 2-bromoisobutyryl bromide, diethyl azodicarboxylate (DEAD), triethylamine, 1,3-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridium 4-toluenesulfonate (DPTS), 4-(dimethylamino)pyridine (DMAP), 1,1,4,7,10,10-hexamethyltriethylenetetraamine (HMTETA), and anisole were purchased from Aldrich and used without purification. CuBr (Aldrich) was washed with acetic acid and ether and then dried under vacuum. Styrene was purified by distillation under vacuum with CaH_2 as dehydrating reagent. Tetrahydrofuran (THF) was distilled from sodium/benzophenone under nitrogen. Methylene chloride (CH_2Cl_2) was distilled with CaH_2 as a dehydrating reagent. Compounds **1**[6], **2**[5b], and **5**[13] were prepared according to the published procedures.

4.4. Synthesis of the Chromophore and Block Copolymers. *4.4.1. 3-Cyano-2-dicyanomethylidene-4-{trans,trans,trans-[3-(2-(p-N,N-bis(2-tert-butyldimethylsiloxyethyl)aminophenyl)vinyl)cyclohex-2-enylidene]-1-propenyl}-5-(3-hydroxypropyl)-5-methyl 2,5-dihydrofuran (**3**).* A mixture of **1** (400 mg, 0.69 mmol), **2** (332 mg, 1.37 mmol), and $NaOC_2H_5$ (20 mg, 0.35 mmol) in 2 mL of ethanol was irradiated under microwave[14] (30 W) at 90 °C for 16 min. The resulting mixture was then purified through flash chromatography on silica gel with hexane/ethyl acetate (10:1 by volume) as eluent to afford 230 mg of **3** in 48% yield. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.02$ (t, 1H), 7.46 (d, 2H), 6.81 (m, 4H), 6.38 (s, 1H), 6.34 (d, 1H), 6.26 (d, 1H), 3.77 (m, 6H), 3.57 (m, 4H), 2.42 (d, 4H), 2.05 (m, 2H), 1.69 (m, 5H), 1.05 (s, 6H), 0.88 (s, 18H), 0.02 (s, 12H). Purity (HPLC): 99+%; mp 215−218 °C. HRMS: calcd 809.4857 ($M + H^+$); found 809.4834.

*4.4.2. 3-Cyano-2-dicyanomethylidene-4-{trans,trans,trans-[3-(2-(p-N,N-bis(2-tert-butyldimethylsiloxyethyl)aminophenyl)vinyl)cyclohex-2-enylidene]-1-propenyl}-5-(3-[(3-carboxy)propionyloxy]])propyl)-5-methyl-2,5-dihydrofuran (**4**).* A mixture of compound **3** (230 mg, 0.28 mmol), succinic anhydride (30 mg, 0.3 mmol), DMAP (30 mg), and pyridine (0.1 mL) in 10 mL of anhydrous methylene chloride was stirred at room temperature overnight. The mixture was then washed successively with 5% aqueous $NaHCO_3$ and brine. After drying the organic phase over $NaSO_4$, the solvent was removed under reduced pressure. The residue was purified by silica column chromatography with methylene chloride/ethyl acetate (3:1 by volume) as eluent to afford 128 mg of **4** in 50% yield. Purity (HPLC): 99+%. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.04$ (t, 1H), 7.36 (t, 2H), 6.81 (m, 4H), 6.38 (s, 1H), 6.34 (d, 1H), 6.26 (d, 1H), 4.21 (t, 2H), 3.82 (m, 4H), 3.57 (m, 4H), 2.65 (m, 4H), 2.42 (d, 4H), 2.05 (m, 2H), 1.69 (m, 5H), 1.25 (t, 3H), 1.06 (t, 3H), 0.88 (s, 18H), 0.02 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = -5.20$, 18.43, 22.74, 25.71, 25.82, 26.06, 28.54, 28.67, 29.02, 29.07, 31.65, 35.97, 39.65, 40.05, 53.66, 54.67, 60.51, 63.66, 98.82, 98.99, 112.01, 124.43, 125.89, 127.99, 129.24, 129.73, 134.82, 149.18, 149.83, 156.42, 171.87, 172.25, 176.86. HRMS: calcd 909.5018 ($M + H^+$); found 909.5004. Anal. Calcd for $C_{51}H_{72}N_4O_7Si_2$: C, 67.36; H, 7.98; N, 6.16. Found: C, 67.02; H, 7.86; N, 6.35.

*4.4.3. Methyl 3,5-Bis{3,5-bis[3,5-(bis(tetrahydropyranoxy)benzyloxy]benzyloxy}benzoate (**6**).* To a cooled solution (0−5 °C) of 6.6 g (9.2 mmol) of compound **5**, 0.70 g of methyl 3,5-dihydroxybenzoate (4.2 mmol), and 2.4 g of triphenylphosphine (12.5 mmol) in 50 mL of anhydrous THF was slowly added DEAD (40 wt % in toluene, 4 mL, ∼10 mmol). The mixture was allowed to warm to room temperature overnight. After the THF was removed under reduced pressure, the residue was purified by column chromatography with hexane/ethyl acetate (4:1 by volume) as eluent to yield a white solid (5.9 g) in 89% yield. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.48-2.10$ (m, 48H), 3.41−3.60 (m, 8H), 3.84−3.98 (s and m, 11H), 4.95 (s, 12 H), 5.41 (m, 8H), 6.50−6.80 (m, 21H). MALDI-TOF MS calcd 1572.7: found 1595.8 (M + Na).

*4.4.4. 3,5-Bis{3,5-bis[3,5-(bis(tetrahydropyranoxy)benzyloxy]benzyloxy}benzyl Alcohol (**7**).* Compound **6** (5.2 g, 3.3 mmol) in 50 mL of THF was slowly added into a suspension of $LiAlH_4$ (1.0 g, 30 mmol) in 100 mL of THF. The mixture was stirred at room temperature for 3 h. Then 10 mL of H_2O was added very carefully into the mixture. The precipitated solid was removed by filtration, and the THF solution was evaporated under reduced pressure. The residue was then passed through a silica gel column with hexane/ethyl acetate (4:1 by volume) to get a white solid of **7** (4.7 g) in 90% yield. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.48-2.10$ (m, 48H), 3.41−3.60 (m, 8H), 3.84−3.98 (m, 8H), 4.60 (d, 2H), 4.95 (s, 12 H), 5.41 (m, 8H), 6.50−6.80 (m, 21H). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 18.95$, 27.47, 33.90, 63.16, 67.40, 69.72, 94.93, 96.58, 104.90, 106.48, 108.86, 138.83, 139.09, 158.54, 158.45, 160.15, 160.21. MALDI-TOF MS calcd 1544.7: found 1568.0 (M + Na), 1584.0 (M + K).

4.4.5. 3,5-Bis{3,5-bis[3,5-(bis(tetrahydropyranoxy)benzyloxy)-benzyloxy]benzyl 2-Bromo-2-methylpropionate (DTHP). To a cooled solution (0−5 °C) of 2.0 g of compound **9** (1.29 mmol) and triethylamine (5 mL) in 50 mL of THF was slowly added 2-bromoisobutylryl bromide (2.0 g, 8.7 mmol). The reaction mixture was stirred at room temperature for 16 h. Pure product as a white solid was obtained after column chromatography with methylene chloride/ethyl acetate (10:1 by volume) as eluent. Yield: 1.9 g (87%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.53-1.65$ (m, 24H, CH_2, pyrane), 1.80−1.90 (m, 16H, CH_2, pyrane), 1.96 (s, 6H, CH_3), 1.90−2.02 (m, 8H, CH_2, pyrane), 3.57 (m, 8H, CH_2O, pyrane), 3.87 (m, 8H, CH_2O, pyrane), 4.92 (d, 12H, CH_2O, benzyloxy), 5.10 (s, 2H, CH_2OCO, ester), 5.37 (m, 8H, OCHO, pyrane), 6.50−6.80 (m, 21H, phenyl). $M_{n(GPC)} = 1100$, $M_w/M_n = 1.03$. T_g: ∼123 °C. Purity (HPLC): 99+%. ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 18.79$, 25.28, 30.41, 30.85, 55.87, 62.08, 67.40, 70.11, 96.36, 96.52, 104.86, 106.49, 108.83, 138.93, 139.12, 158.32, 158.38, 160.13, 160.22, 171.47. MS: calcd 1692.7; MALDI-TOF MS: 1715.6 (M + Na), 1731.6 (M + K). Anal. Calcd for $C_{93}H_{113}BrO_{24}$: C, 65.91; H, 6.72. Found: C, 65.51; H, 6.74.

4.4.6. DTHP-b-PSa. 272.8 mg (0.16 mmol) of initiator DTHP and 23 mg of CuBr (0.16 mmol) were added into a Schlenk tube and then vacuumed for 10 min. Under a nitrogen atmosphere, a solution of 50 μL (0.16 mmol) of HMTETA and 4 g of styrene (40 mmol) in 4 mL of anisole was added into the Schlenk tube. The mixture was degassed three times and then filled with argon. After stirring at ambient temperature for 30 min, the Schlenk tube was immersed into an oil bath at 90 °C for 16 h. After being cooled down to room temperature, the mixture was passed through an Al_2O_3 column to remove the copper and then precipitated into excess amount of methanol resulting in the DTHP-*b*-PSa (1.50 g) as a white solid (yield 36%). $M_{n(GPC)} = 28\,600$, $M_w/M_n = 1.15$, $M_{n(NMR)} = 15\,100$. Degree of polymerization (DP) of PS is 130. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.28-2.30$ (m, 438H, CH, CH_2), 3.57 (m, 8H, CH_2O, pyrane), 3.87 (m, 8H, CH_2O, pyrane), 4.9−5.0 (m, 14H, CH_2O, benzyloxy), 5.41 (m, 8H, OCHO, pyrane), 6.30 − 6.90 (m, 280H, phenyl), 6.9−7.24 (m, 390H, phenyl). T_g: ∼105 °C. The T_g of the dendron phase was not detected possibly due to the low weight fraction of the dendron phase in this block copolymer.

4.4.7. DTHP-b-PSb. The block copolymer was prepared similarly as DTHP-*b*-PSa. $M_{n(GPC)} = 56\,600$, $M_w/M_n = 1.28$, $M_{n(NMR)} = 32\,900$. Degree of polymerization (DP) of PS is 300. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.28-2.30$ (m, 948H, CH, CH_2), 3.57 (m, 8H, CH_2O, pyrane), 3.87 (m, 8H, CH_2O, pyrane), 4.9−5.0 (m, 14H, CH_2O, benzyloxy), 5.41 (m, 8H, OCHO, pyrane), 6.30−6.90 (m, 620H, phenyl), 6.9−7.24 (m, 900H, phenyl). T_g: ∼106 °C.

4.4.8. DOH-b-PSa. 320 mg of DTHP-*b*-PSa was dissolved into 20 mL of THF and 2 mL of methanol, and then 2 mL of 2 N HCl aqueous solution was added into the solution. The reaction mixture was stirred at room temperature for 2 days. After the solvent was removed under reduced pressure, the residue was washed with methanol. The solid was redissolved into 2 mL of methylene chloride and reprecipitated into excess amount methanol to afford the hydroxyl-containing polymer DOH-*b*-PSa (300 mg) in 93% yield. $M_{n(GPC)} = 27\,800$, $M_w/M_n = 1.15$, $M_{n(NMR)} = 14\,400$. ^{1}H NMR (300 MHz, CD_3COCD_3): $\delta = 1.28-2.30$ (m, 390H, CH, CH_2), 4.9−5.1 (m, 14H, CH_2O, benzyloxy), 6.30−6.90 (m, 280H, phenyl), 6.9−7.24 (m, 390H, phenyl), 8,25, 8.48, and 8.66 (s, 8H, OH). T_g: ~104 °C (PS phase). T_d: ~152 °C (DOH phase).

4.4.9. DOH-b-PSb. The block copolymer was prepared similarly as DOH-*b*-PSa. $M_{n(GPC)} = 52\,000$, $M_w/M_n = 1.27$, $M_{n(NMR)} = 32\,100$. ^{1}H NMR (300 MHz, CD_3COCD_3): $\delta = 1.28-2.30$ (m, 900H, CH, CH_2), 4.9−5.1 (m, 14H, CH_2O, benzyloxy), 6.30−6.90 (m, 620H, phenyl), 6.9−7.24 (m, 900H, phenyl), 8,25, 8.48, and 8.66 (s, 8H, OH). T_g: ~106 °C (PS phase). T_d: ~150 °C (DOH phase).

4.4.10. DCLD-b-PS2. A mixture of DOH-*b*-PSa (80 mg, ~0.044 mmol of HO−), CLD chromophre **4** (RCOOH, 50 mg, 0.055 mmol), DCC (100 mg, 0.49 mmol), and DPTS (20 mg, 0.07 mmol) in 20 mL of anhydrous CH_2Cl_2 was stirred at room temperature for 24 h. After removing the solvent, the residue was washed with hot methanol three times. The obtained polymer was redissolved into 3 mL of CH_2Cl_2 and reprecipitated into 100 mL of methanol twice to obtain 100 mg of pure polymer with a yield of 83%. $M_{n(GPC)} = 37\,400$, $M_w/M_n = 1.50$, $M_{n(NMR)} = 19\,100$. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.05$ (m, CH_3), 0.90 (m, CH_3), 1.05−2.20 (m, CH_2, CH), 2.94 and 2.95 (m, CH_2), 3.5, 3.8, and 4.1 (m, CH_2), 4.9−5.1 (m, CH_2O), 6.3−8.2 (m, phenyl and conjugated double bond). T_g: ~105 °C (PS phase) and ~118 °C (DCLD phase). According to the ratio of integration at 4.9−5.1 ppm (14H of benzyloxy groups from dendron part) to that at 0.05 ppm (2 × $(CH_3)_2Si$ from chromophore (RCOO) part), the grafting degree of the chromophore can be calculated to be 65%, resulting in a total molecular weight of 19 100. The weight fraction of the dendron with chromophores can be calculated as 29 wt % using $(941 + 893 \times 8 \times 0.65 + 1 \times 8 \times 0.35)/19100 = 29\%$, where 941 is the dendron with eight hydroxyl groups before the reaction, 893 is the molecular weight of the chromophore (RCO), 1 is the molecular weight of H, 0.65 is the grafting degree of the chromophores, and 0.35 is the remained fraction of −OH groups. The chromophore loading level was then calculated to be 14 wt % using $(515 \times 8 \times 0.65)/19100 = 14\%$, where 515 is the molecular weight of the chromophore used for loading calculation in the polymer.

4.4.11. DCLD-b-PS1. A mixture of DOH-*b*-PSb (280 mg, ~0.070 mmol of HO−), CLD chromophre **4** (RCOOH, 98 mg, 0.108 mmol), DCC (100 mg, 0.49 mmol), and DPTS (20 mg, 0.07 mmol) in 10 mL of anhydrous CH_2Cl_2 was stirred at room temperature for 24 h. After removing the solvent, the residue was washed with hot methanol three times. The obtained polymer was redissolved into 3 mL of CH_2Cl_2 and reprecipitated into 100 mL of methanol twice to obtain 195 mg of pure polymer with a yield of 57%. $M_{n(GPC)} = 74\,900$, $M_w/M_n = 1.75$, $M_{n(NMR)} = 38\,600$. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.05$ (m, CH_3), 0.90 (m, CH_3), 1.05−2.20 (m, CH_2, CH), 2.94 and 2.95 (m, CH_2), 3.5, 3.8, and 4.1 (m, CH_2), 4.9−5.1 (m, CH_2O), 6.3−8.2 (m, phenyl and conjugated double bond). The weight fraction of the dendron with chromophores can be calculated as 19 wt %, and the chromophore loading level was then calculated to be 10 wt %. T_g: ~106 °C (PS phase) and ~119 °C (DCLD phase).

4.4.12. DCLD-b-PS3. A mixture of DOH-*b*-PS (160 mg, ~0.088 mmol of HO−), CLD chromophre **4** (RCOOH, 100 mg, 0.106 mmol), DCC (200 mg, 0.98 mmol), and 20 mg of DPTS (0.07 mmol) in 20 mL of anhydrous CH_2Cl_2 was stirred at room temperature for 36 h. Then 30 mg of RCOOH (0.032 mmol) and 50 mg of DCC (0.25 mmol) were added into the mixture and continuously stirred for 1 day. After removing the solvent, the residue was washed with hot methanol three times. The obtained polymer was redissolved into 3 mL of CH_2Cl_2 and reprecipitated twice into 100 mL of methanol to obtain 160 mg of pure polymer with yield of 65%. $M_{n(GPC)} = 44\,400$, $M_w/M_n = 1.79$, $M_{n(NMR)} = 21\,400$. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.05$ (m, CH_3), 0.90 (m, CH_3), 1.05−2.20 (m, CH_2, CH), 2.94 and 2.95 (m, CH_2), 3.5, 3.8, and 4.1 (m, CH_2), 4.9−5.1 (m, CH_2O), 6.3 − 8.2 (m, phenyl and conjugated double bond). The weight fraction of the dendron with chromophores can be calculated as 37 wt %, and the chromophore loading level was then calculated to be 18 wt %. T_g: ~105 °C (PS phase) and ~119 °C (DCLD phase).

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