From Terphenyl-Dendronized Macromonomers to Aromatic–Aliphatic Polyethers Bearing Two Pendant Dendrons per Repeating Unit

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ABSTRACT: Novel side chain dendritic aromatic—aliphatic polyethers are synthesized from aromatic terphenyl diols, disubstituted with Fréchet-type dendrons of the first and second generation and aliphatic dibromides of various lengths. High-molecular-weight soluble polymers were obtained in all cases. The bulk properties of the polymers were examined by means of thermal analyses (DSC), dynamic mechanical analyses (DMA), and X-ray diffractometry. Separation between the main chain and the dendritic side chains was evident due to the existence of two well-resolved glass transition temperatures, observed by both DSC and DMA measurements.

Introduction

Some of the most interesting macromolecular structures have appeared during the past years due to the unique combination of traditional polymers with the well-defined, monodisperse dendritic molecules.¹ Such dendronized or side chain dendritic polymers, bearing pendant dendritic wedges on every single repeating unit,² have mainly been constructed through grafting of the dendritic side groups on preformed linear polymeric chains,³ divergently developing the dendritic fragments onto suitable side groups of the polymeric backbones⁴ or polymerizing monomer units bearing the desired dendrons prior to polymerization.^{2a} The latter case accepted as the "macromonomer" approach has preferably been adopted for a variety of polymerization techniques,⁵⁻¹⁰ leading to the formation of perfectly substituted polymeric materials carrying dendrons onto each repeating unit, thus allowing the visualization of single macromolecular chains^{11,4b} as well as understanding the principles of stiffening classical polymers through the attachment of these bulky three-dimensional substituents.¹² Consequently, the final size, shape, rigidity, and conformation of these macromolecular systems should be directly controlled with the size or chemical structure of the pendant dendritic moieties. The best results have so far appeared in the literature either when a spacer has been introduced between the side dendrons and the polymerizable group, when selforganization of the dendritic monomers occurs, or when long reaction times have been adopted.² On the other hand, only a limited number of studies have, until now, dealt with the properties of these new polymeric features.¹⁰ Since high-molecular-weight polymers are always desirable, especially if solid-state properties of such unique macromolecules are to be examined, easily performed polymerization reactions should be employed with monomers that facilitate chain growth, without enhancing the overall rigidity, shape, and conformation of the final polymeric chains.

Herein we wish to report a synthetic pathway to dendronized polyethers consisting of aromatic-aliphatic

sequences and two Fréchet-type poly(benzyl ether) dendritic moieties^{13a} on every repeating unit. The general concept of our approach toward side chain dendritic polymers is to reduce the steric effect due to the space demanding dendrons. This was accomplished with the use of monomers that carry the polymerizable functionalities in less crowded sites that, moreover, do not undergo cleavage under the polymerization conditions. The introduction of the rigid terphenyl moieties along the main chain in combination with the aliphatic spacers, however, should allow less hindered conformations to be adopted, facilitating the completion of polymerization. Moreover, aliphatic segments with a variety in length were used, and together with the increase in dendrons' generation, their effect on the thermal and mechanical properties of these new dendronized polymers was tested. All following monomers, macromonomers, and dendronized polyethers were fully characterized through GPC, ¹H NMR, and ¹³C NMR, and their thermal and mechanical properties were investigated using DSC and DMA measurements.

Results and Discussion

Monomer and Polymer Syntheses. The synthetic procedure to macromonomers 8a and 8b, carrying firstand second-generation Fréchet-type dendrons, can be viewed in Schemes 1 and 2. The choice of the particular dendritic fragments relies on their well-established syntheses and the fact that their properties have been investigated probably more than any other homologous, and moreover they have been used preferably in most dendronized macromolecular systems allowing for safe correlations. The preparation of the doubly substituted aromatic dibromides 4a and 4b, and of the dendronized macromonomers themselves, can be performed in gram scale quantities, in an analogous procedure as in the convergent method for dendrimers.^{13b} Thus, polymerization can provide dendronized polymers in significant quantities.

The need for a compound that could be employed in Suzuki coupling¹⁴ with the dibromides **4a** and **4b** producing the desired macromonomers was fulfilled by the tetrahydropyranyl ether of *p*-bromophenol. In particular, the tetrahydropyranyl group remained intact

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^a (a) K₂CO₃, acetone, reflux for 18 h, 97 and 80%.



^a (a) DHP, CH₂Cl₂, CSA, rt for 24 h. (b) *n*-BuLi, THF, -40 °C for 3 h, B(OMe)₃, rt for 18 h, H₂O, 88%. (c) 3 mol % Pd(PPh₃)₄, Na₂CO₃ 2 M, toluene, reflux for 18 h, 92%. (d) 4 mol % PdCl₂(dppf), NaOH 3 M, THF, reflux 48 h, 85%. (e) PTSA, DMA, MeOH, 80 °C, 42 h, 99%. (f) PTSA, THF, MeOH, 50 °C, 3 days, 80%.

both in the preparation of the corresponding boronic ester (6) and during the Suzuki coupling even when prolonged heating was required, as can be seen in Figure 1, where in the inset ¹H NMR of the THP-protected terphenyldiol-carrying dendrons of the second generation (7b), the characteristic peaks of the tetra-hydropyranyl protective groups are clearly viewed at 1.5-2, 3.55, 3.85, and 5.35 ppm. This protective group (3,4-dihydro-2*H*-pyran)¹⁵ gave best results, for the re-

quired applications, among other silyl ones, such as triiopropylsilyl chloride and *tert*-butyldiphenylsilyl chloride that produced aromatic boronic acids difficult to crystallize. On the other hand, selective cleavage of the protective groups, with the use of PTSA (*p*-toluenesulfonic acid), in the presence of the side dendrons was quantitative, as evident by the absence of their characteristic peaks in the ¹H NMR of the terphenyldiol macromonomer **8a** (Figure 1).

Polymerizations of dendronized macromonomers 8a and **8b** with α, ω -aliphatic dibromides were conducted under phase transfer conditions in a mixture of o-DCB/ NaOH (10 N) containing TBAH (*tert*-butylammonium hydrogen sulfate) as the phase transfer catalyst (Scheme 3).¹⁶ Polymerization conditions were only optimized for the polymerization time of the second-generation dendron-carrying polymers. Moreover, effort was devoted in accomplishing the correct stoichiometries due to great differences between the monomers' molecular weights. High-molecular-weight polymers were obtained in most cases (Tables 1 and 2) for both series $PETH-G_1$ and PETH-G₂, respectively. The molecular weights were initially determined by GPC using polystyrene standards, which is known to underestimate the molecular weight of dendronized polymers.¹² Thus, further measurements for those polyethers carrying second-generation dendrons, PETH-G₂, involved molecular weight determination through GPC equipped with a light scattering detector, which indeed measured higher molecular weights for all polymeric samples, compared to the GPC-UV detector system, as can be seen throughout the second column of Table 2. For PETH-



Figure 1. ¹H NMR spectra of the THP-protected macromonomer **7b** (inset) and of the dihydroxy-functionalized macromonomer **8b**.



 Table 1. GPC Data and Viscosimetric Characterization of PETH-G1 Samples

	time (h)	M _n ^a	$M_{ m w}{}^a$	$M_{ m n}/M_{ m w}{}^a$	[n] ^b (dL/g)
PETH-G ₁ -x=12	16	50 000	227 000	4.5	1.2
	12	30 500	60 200	2	
PETH-G ₁ - $x=11$	16	34 500	167 200	4.7	0.7
	12	27 000	55 000	2.1	
	192	28 900	69 500	2.4	
PETH-G1-x=10	16	25 000	96 000	3.8	0.61
PETH-G ₁ -x=9	16	13 300	34 600	2.6	0.35
PETH-G ₁ -x=8	16				0.4
PETH-G ₁ - $x=7$	16	15 600	37 160	2.4	
	16	13 700	29 370	2.2	

 a (a) o-DCB, NaOH 10 N, TBAH, 100 °C, 18 h. (b) Like (a), 7–12 days.

 G_1 polymers intrinsic viscosity measurements also revealed high values, especially for those polyethers having high molecular weights (Table 1). Polyethers PETH- G_1 were completely soluble, at room temperature, in chlorinated solvents like 1,1,2,2-tetrachloroethane (TCE) while their solubility increased with the length of the aliphatic segment along the main polymeric chain. For the GPC characterization of PETH- G_1 , the samples ^{*a*} Determined by GPC with a UV detector, $CHCl_3$ as eluent, and polystyrene standards. ^{*b*} In 1,1,2,2-tetrachloroethane at 30 °C.

were initially dissolved in TCE and afterward diluted with CHCl₃, which was used as eluent. However, PETH- G_1 -x=8 formed a stable gel under these conditions. On the other hand, all polyethers PETH- G_2 showed increased solubilities in common chlorinated solvents like chloroform.

Dendronized polyethers from both series, even those appendant with second-generation dendrons, were fully characterized by ¹H NMR, as can be viewed in Figure

Table 2. GPC Data for PETH-G₂ Samples

	time (h)	$M_{\rm w}{}^a$	$M_{\rm n}{}^b$	$M_{ m w}{}^b$	$M_{\rm n}/M_{\rm w}^{l}$
PETH-G2-x=12	16	24 300	13 600	18 950	1.8
	16	47 850	16 600	25 500	1.6
	96	119 300	18 100	74 300	4
PETH-G ₂ -x=11	168	281 000	48 600	135 070	2.8
PETH-G ₂ -x=10	60		23 700	64 500	2.7
	240	64 430	19 650	43 650	2.3
PETH-G ₂ -x=9	60		26 900	72 800	2.7
	240	283 900	$53\ 600$	132 000	2.5
PETH-G ₂ -x=8	192	195 000	47 300	127 900	2.7
PETH-G ₂ - $x=7$	288	155 500	15 100	52 600	3.5

 a Determined by GPC with a LS detector and CHCl₃ as eluent. b Determined by GPC with a UV detector, CHCl₃ as eluent, and polystyrene standards.



2, with complete assignment of all peaks, proving the proposed structures. In the ¹H NMR spectrum of both polyethers' groups, PETH-G₁ and PETH-G₂, respectively, no end groups throughout the polymeric chains were noticeable, since the aromatic protons neighboring to the hydroxyl functionalities are easily distinguished at 6.81 ppm moving up to 6.92 ppm for PETH-G₁ (from 6.85 to 6.91 ppm for PETH-G₂). Thus, the polymers' molecular weights could not be calculated using end group analyses, indicating at the same time their high molecular weights and complete monomer consumption.

Thermal and Mechanical Properties. Polyethers PETH- G_1 and PETH- G_2 were investigated for their thermal and mechanical properties through differential scanning calorimetry (DSC) and dynamic mechanical analyses (DMA) measurements.



Figure 3. DSC thermograms for PETH-G₁ samples: second heating runs (a) and after annealing at room temperature for 4 months (b).

The polyethers' thermal properties are presented in Figures 3 and 4. Polyethers pendant with dendrons of the first generation, PETH- \hat{G}_1 , revealed complex DSC thermograms with multiple transitions during the second heating runs (Figure 3a). In particular, those polymers having shorter spacers along the main chain revealed multiple endotherms in the temperature region from 100 to 170 °C, while only one endotherm at about 120 °C is present in the DSC traces of polyethers with longer spacers (x = 11, 12). Preliminary X-ray examination of the polyethers carrying first-generation dendrons supports the presence of ordered structures. Thus, the diffraction pattern of a film of PETH- G_1 -x = 8 displays at ambient temperature reflections at 2θ : 9.62, 12.915, 19.45, 22.52, and 26° corresponding to d = 9.183, 6.848, 4.558, 3.943, and 3.423 Å, respectively, as shown in Figure 5.

The glass transition temperatures of the Fréchet-type poly(benzyl ether) dendrons have been reported in the temperature region from 30 to 50 °C.^{17a} In our case, on the other hand, there was some evidence of more than one T_{g} , in the same region, during the second heating runs. Thus, aging of the samples at room temperature was employed in order to facilitate development of the



Figure 4. DSC thermograms of the first heating runs for PETH-G₂ samples with x = 12, 11, 10, and 9.



Figure 5. X-ray diffraction pattern for PETH-G₁-*x*=8 in film form.

enthalpy relaxations. This method has been employed for the differentiation of the glass transition temperatures in polymer blends in those cases where the T_{g} 's of the two polymeric components are very close to each other and overlapped.¹⁸ For that purpose the DSC samples remained at room temperature for a period of 4 months, and their thermograms recorded afterward are presented in Figure 3b, where clearly separated enthalpy relaxation peaks can be seen for all polymeric samples. From the above, it is also reasonable to assume that the first transition at 35 °C is due to the dendron substituents, since it seems to be independent of the flexible spacer length and closer to the literature values. On the other hand, the second one at about 50 °C shows an "odd-even" effect, in agreement with our previous findings for the same type of rigid-flexible alternating polymers.¹⁹ This assignment of the two T_g 's is also supported by the fact that the respective macromonomer pendant with first-generation dendrons also exhibits a glass transition at 35 °C.

A similar behavior was observed for PETH-G₂ polymers during DSC measurements (Figure 4), which presented multiple transitions during the first heating runs of samples with no previous thermal treatment. Regarding their glass transition temperature, it is also probable that two T_g 's are present, though not clearly distinguished in their DSC traces.



Figure 6. DMA measurements for PETH- G_1 (a) and PETH- G_2 (b) samples.

Although the influence of parameters like the molecular weight, the chemical structure, and the type of chain ends on $T_{\rm g}$ has been studied in the case of dendrimers,¹⁷ so får there are no studies devoted to the mechanical properties of dendronized polymers. Since in our case we succeeded in synthesizing high-molecular-weight film forming dendronized polymers, it was a unique opportunity to examine their dynamic mechanical properties. Thus, the storage modules (E) and the loss modules (E') were recorded as a function of temperature in the region from -50 °C and up to 80 °C. The results for the first- and second-generation dendronized polyethers are presented in Figure 6. In the case of the PETH-G₁ polymers, the two transitions previously detected during the DSC measurements are also apparent here as two overlapping transitions. A broad secondary transition at about 10 °C is also obvious in most cases. On the basis of the assignment of the two T_{g} 's to the side dendrons and the main chain from DSC traces, more information can be obtained from the DMA measurements, as far as the contribution of these two glass transitions on the modulus of the materials is concerned. As expected for a transition due to the side chains, the first transition has a smaller effect on the E' decrease, while the second transition causes a more pronounced decrease on the E' value.

For the second-generation dendronized polyethers both transitions are dependent on the flexible spacer's length (Figure 6b). Comparing polymers PETH-G₁-*x*=8 and PETH- G_2 -x=8, we can easily notice the latter's lower $T_{\rm g}$. For these poly(benzyl ether) dendrons a small increase of the $T_{\rm g}$ has been observed with the generation number; however, it is accepted that the variation of T_{g} in the case of dendrimers can be unique, since it simultaneously depends on a number of various factors.¹⁷ On the other hand, comparison of the main chain $T_{\rm g}$ of these dendronized polyethers with substituted terphenyl- or quinquephenyl-containing aromaticaliphatic polyethers shows a weak increase probably due to the side dendritic moieties.¹⁹ Finally, on the basis of the thermal and mechanical properties of these polymers, we can see that, depending on the length of the flexible spacer, there is a significant change in the thermal properties. In all cases two low temperature transitions are observed which can be attributed to separately activated mobilities in the main chain and in the dendritic side groups. These observations demonstrate the effect the two side dendrons per repeating unit impose on the mechanical properties of the final polymers.

Conclusions

Side chain dendritic aromatic-aliphatic polyethers bearing two Fréchet-type dendrons of the first and second generation have been synthesized from terphenyldiols carrying the dendritic moieties and α, ω -aliphatic dibromides under phase transfer polymerization conditions. High molecular weights and complete monomer consumption were detected from GPC and NMR. The thermal and dynamic mechanical properties of the polymers were investigated, which revealed a phase separation tendency between the dendritic fragments and the main polymeric chains. Two distinct T_{g} 's were noticeable during DSC measurements, with the first one attributed to the side dendrons and the second one to the main chain. The above assignment is in agreement with the DMA measurements of the film-forming samples, where the former T_g had a smaller effect on the \vec{E} decrease while the latter one a more pronounced effect on the loss modules. Moreover, for the PETH-G₂ polymers two well-distinguished E' transitions were observed in contrast to the PETH-G₁ samples, pointing out the increased effect these larger dendritic groups impose on the polymer properties. Preliminary X-ray characterization further supported the existence of ordered structures, which was initially indicated by the complexity of the DSC thermograms.

Experimental Section

Materials. Dendrons **2** and **3**,^{13a} 1,4-dihydroxy-2,5-dibromobenzene (**1**),²⁰ and catalysts Pd(PPh₃)4²¹ and PdCl₂(dppf)²² were prepared according to literature procedures. Trimethylborate was dried over lithium chloride and distilled prior to use. Tetrahydrofuran (THF) was distilled from sodium in the presence of benzophenone prior to use. All chemicals and solvents were purchased from Aldrich or Merck and used without purification unless otherwise noted. All reactions were carried out under an atmosphere of argon. ¹H and ¹³C NMR spectra were obtained on a Bruker Avance DPX 400 and 100 MHz, respectively, spectrometer with deuterated CHCl₃, DMSO, and 1,1,2,2-tetrachloroethane with TMS as internal standard. Gel permeation chromatography (GPC) measurements were carried out using a Polymer Lab chromatographer with two Ultra Styragel linear columns (104, 500 Å), UV detector (254 nm), polystyrene standards, and CHCl₃ as eluent, while for the PETH-G₂ samples a Shimadzu-10A chromatographer was also used, equipped with three Ultra Styragel linear columns $(10^5, 10^4, 500$ Å), a Wyatt LS detector operating at 30°, 90°, and 120°, and CHCl₃ as eluent. Viscosity measurements of the polymers were performed in 1,1,2,2-tetrachloroethane solutions at 30 °C with an Ubbelohde-type viscometer in a Scott Gerate AVS 310. Differential scanning calorimetry (DSC) thermograms were obtained using an SP plus calorimeter equipped with the Autocool accessory from Rheometrics Scientific Ltd. The heating rate was 10 °C min-1, and the temperature region was from -50 to 250 °C. DMA measurements were carried out with a solid-state analyzer RSA II, Rheometrics Scientific Ltd., at 10 Hz.

1,4-Di[3,5-bis(benzyloxy)benzyloxy]-2,5-dibromobenzene (4a). A mixture of 1,4-dihydroxy-2,5-dibromobenzene (1) (0.95 g, 3.545 mmol), **2** (3.4 g, 8.86 mmol), and K_2CO_3 (1.22 g, 8.86 mmol) in acetone (50 mL) was refluxed for18 h. Filtration and washing with acetone and water gave a white solid, which was recrystallized from toluene to give **4a** as a white solid. Yield 3 g (97%); mp 164–165 °C. Anal. Calcd for $C_{48}H_{40}O_6Br_2$ (872): C, 66.05; H, 4.58. Found: C, 66.18; H, 4.68. ¹H NMR (CDCl₃): 5 (s, 4H), 5.05 (s, 8H), 6.57 (t, 2H), 6.7 (d, 4H), 7.13 (s, 2H), 7.29–7.38 (m, 20H). ¹³C NMR (CDCl₃): 70.55,72.11, 102.26, 106.4, 112.0, 119.55, 127.94, 128.42, 129.0, 137.17, 138.98, 150.34, 160.59.

1,4-Di[3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyloxy]2,5-dibromobenzene (4b). A mixture of **1** (0.4 g, 1.5 mmol), **3** (3.01 g, 3.73 mmol), K_2CO_3 (0.515 g, 3.73 mmol), and 18-crown-6 (0.08 g, 0.3 mmol) in acetone (70 mL) was refluxed for 18 h. The suspension was filtrated and washed with acetone. The solvent was evaporated under reduce pressure, and the brownish glassy solid recrystallized from toluene to give a white powder. Yield 2.05 g (80%); mp 112–114. Anal. Calcd for $C_{104}H_{88}O_{14}Br_2$ (1720): C, 72.55; H, 5.12. Found: C, 71.94; H, 5.3. ¹H NMR (CDCl₃): 4.98 (s, 12H), 5.03 (s, 16H), 6.55 (m, 6H), 6.67 (m, 12H), 7.12 (s, 2H), 7.28–7.42 (m, 40H). ¹³C NMR (CDCl₃): 70.42, 70.52, 72.03, 102.02, 102.27, 106.7, 106.8, 111.87, 119.45, 127.97, 128.4, 128.98, 137.19, 138.98, 139.64, 150.3, 160.47, 160.59.

1,3-Propanediol Ester of 2-Tetrahydropyranyloxy-4phenylboronic Acid (6). To a solution of 4-bromophenol (5) (8.2 g, 47.4 mmol) and 3,4-dihydro-2*H*-pyran (DHP) (8.65 mL, 94.8 mmol) in 40 mL of CH_2Cl_2 at 0 °C was added camphorosulfonic acid (CSA) (0.05 g, 0.22 mmol). The solution was stirred at room temperature for 24 h, diluted with ether, washed several times with water and NaOH (1 N),and dried over MgSO₄, and the organic layer evaporated to dryness. The crude product was purified by silica gel column chromatography with hexane/ether 5:1 as eluent to give the 2-tetrahydropyranyloxy-4-bromobenzene as white crystals; mp 56–57 °C (Commercial product mp 56–58 °C). ¹H NMR (CDCl₃): 1.55–2 (three m, 6H), 3.5 (m, 1H), 3.8 (m, 1H), 5.3 (t, 1H), 6.94 (d, 2H), 7.35 (d, 2H). ¹³C NMR (CDCl₃): 19.05, 25.54, 30.65, 62.4, 96.68, 114.22, 118.7, 132.4, 156.57.

2-Tetrahydropyranyloxy-4-bromobenzene (5 g, 19.46 mmol) was placed under a continues stream of argon in a previously flamed round flask and diluted with THF (50 mL), distilled prior to use. The solution was cooled to -80 °C, and a solution of *n*-BuLi 1.6 M in hexane (30.4 mL, 48.64 mmol) was added dropwise. The solution was then stirred at -40 °C for 3 h, cooled again to -80 °C for the addition of B(OMe)₃ (21.76 mL, 194.46 mmol), and afterward stirred at room temperature for 18 h. Addition of H₂O (40 mL), stirring for 2 h, extraction with ethyl acetate, evaporation of the organic layer under reduced pressure, and subsequent work-up with hexane gave **6** as a white powder.²³ Yield 2.3 g (88%). ¹H NMR (CDCl₃): 1.55–2 (three m, 6H), 3.64 (m, 1H), 3.9 (m, 1H), 5.46 (t, 1H), 6.98 (d, 2H), 7.69 (d, 2H). ¹³C NMR (CDCl₃): 19.10, 25.58, 30.67, 62.47, 96.36, 116.19, 135.54, 137.78, 161.11.

Compound **6** was further treated with 1.04 equiv of 1,3propanediol, producing the corresponding 1,3-propanediol ester of 2-tetrahydropyranyloxy-4-phenylboronic acid.²⁴

2',5'-Di[3,5-bis(benzyloxy)benzyloxy]-p-triphenylene-4',4"-di(tetrahydropyranyloxy) (7a). To a carefully degassed mixture of 4a (1.6 g, 1.84 mmol), 6 (1.63 g, 7.34 mmol), and Pd(PPh₃)₄ (0.09 g, 0.078 mmol) were added toluene (25 mL) and Na₂CO₃ (2 M) (3.7 mL, 7.4 mmol) under a continuous stream of argon. The mixture was vigorously stirred at reflux for 18 h. Subsequent addition of MeOH precipitated a white solid, which was then filtrated, washed carefully with MeOH and hexane, and dried, providing 7a which was used without further purification. Yield 1.8 g (92%); mp 213-215 °C. ¹H NMR (CDCl₃): 1.5-2 (three m, 12H), 3.55 (m, 2H), 3.85 (m, 2H), 4.96 (d, 12H), 5.36 (t, 2H), 6.5 (t, 2H), 6.57 (d, 4H), 7.03 (s, 2H), 7.1 (d, 4H), 7.3-7.4 (m, 20H), 7.55 (d, 4H). ¹³C NMR (CDCl₃): 19.12, 25.6, 30.7, 62.33, 70.46, 71.7, 96.68, 102.05, 105.98, 116.4, 117.2, 127.99-128.94, 131.06-131.92, 137.28, 140.81, 150.48, 156.73, 160.4.

2',5'-**Di**[3,5-**bis**(3,5-**bis**(**benzyloxy**)**benzyloxy**]**-***p*-**triphenylene-4'**,4"-**di**(**tetrahydropyranyloxy**) (7**b**). With the same procedure as in 7**a**, 4**b** (2 g, 1.16 mmol), 6 (1.03 g, 4.64 mmol), PdCl₂(dppf) (0.07 g, 0.093 mmol), THF (50 mL), and NaOH (3 N) (4 mL, 0.012 mmol) were refluxed with vigorous stirring for 48 h. The resulting mixture was diluted with THF and filtrated before the addition of MeOH that precipitated a white solid, which was then filtrated, dried, and used without further purification. Yield 1.88 g (85%); mp 163–165 °C. ¹H NMR (CDCl₃): 1.5-2 (three m, 12H), 3.55 (m, 2H), 3.85 (m, 2H), 4.9 (s, 8H), 6.68 (s, 8H), 7.05 (s, 2H), 6.52 (s, 2H), 6.58 (s, 8H), 6.68 (s, 8H), 7.05 (s, 2H), 7.12 (d, 4H), 7.3-7.45 (m, 40H), 7.55 (d, 4H). ¹³C NMR (CDCl₃): 19.14, 25.58, 30.66, 62.38, 70.36, 70.51, 71.72, 96.72, 101.97, 102.1, 105.92, 106.84, 116.42, 117.19, 127.98-128.98, 130.99-131.98, 137.2, 139.69, 140.33, 150.5, 156.76, 160.31, 160.55

2',5'-**Di**[**3**,5-**bis**(**benzyloxy**)**benzyloxy**]-*p*-**triphenylene 4'**,**4''**-**dio**] (**8a**). To a solution of **7a** (1.8 g, 1.69 mmol), DMA (140 mL), and MeOH (3 mL) was added PTSA (0.86 g, 7.9 mmol). Stirring at 80 °C for 24 h and addition of H₂O precipitated a white solid, which was recrystallized from CHCl₃. Yield 1.07 g (70%); mp 211 °C. Anal. Calcd for C₆₀H₅₀O₈ (898): C, 80.18; H, 5.568. Found: C, 80.3; H, 5.445. ¹H NMR (DMSO-*d*₆): 5 (d, 12H), 6.53 (t, 2H), 6.59 (d, 4H), 6.81 (d, 4H), 7.03 (s, 2H), 7.28–7.4 (m, 20H), 7.43 (d, 4H). ¹³C NMR (DMSO*d*₆): 70.23, 71.25, 102.19, 106.87, 115.75, 117.01, 128.4–131.3, 137.83, 140.94, 150.27, 157.49, 160.37.

2',5'-**Di**[3,5-**bis**(3,5-**bis**(**benzyloxy)benzyloxy)benzyloxy**]*p*-**triphenylene**-4',4"'-**diol (8b).** To a solution of **7b** (1.88 g, 0.98 mmol), THF (50 mL), and MeOH (3 mL) was added PTSA (0.98 g, 8.99 mmol) and stirred at 60 °C for 3 days. Precipitation with MeOH, filtration, and recrystallization from toluene afforded **8b** as a white solid. Yield 1.37 g (80%); mp 170.5 °C. Anal. Calcd for C₁₁₆H₉₈O₁₆ (1746): C, 79.72; H, 5.61. Found: C, 78.9; H, 5.57. ¹H NMR (DMSO-*d*₆): 4.93 (s, 8H), 5.01 (s, 4H), 5.05 (s, 16H), 6.52 (s, 2H), 6.6 (s, 8H), 6.66 (s, 8H), 6.82 (d, 4H), 7.05 (s, 2H), 7.27-7.42 (m, 40H), 7.45 (d, 4H). ¹³C NMR (DMSO-*d*₆): 69.9, 70.18, 71.1, 102, 106.52, 107.23, 115.7, 116.78, 128.56-129.25, 130.37-131.36, 137.76, 140.19, 140.91, 150.18, 157.47, 160.2, 160.41.

General Procedure for Phase Transfer Polymerization. A mixture of aliphatic dibromide (0.1 mmol), dendronized macromonomer (0.1 mmol), and TBAH (0.04 mmol) was carefully degassed before *o*-DCB (0.5 mL) and NaOH (10 N) (0.5 mL) were added. The mixture is vigorously stirred at 100 °C for 18 h or up to 10 days. 1,1,2,2-Tetrachloroethane or CHCl₃ was then added, and the solution was filtrated, precipitated into a 10-fold amount of MeOH, and dried under vacuum.

PETH-G₁-*x***=12.** ¹H NMR (TCE- d_2): 1.2–1.4 (broad, 16H), 1.66 (broad, 4H), 3.8 (broad, 4H), 4.89 (s, 8H), 4.95 (s, 4H), 6.5 (s, 2H), 6.57 (s, 4H), 6.92 (d, 4H), 7.01 (s, 2H), 7.26–7.4 (m, 20H), 7.55 (d, 4H). ¹³C NMR (TCE- d_2): 25.93, 31.13–31.4, 69.87, 71.89, 73.12, 103.55, 107.6, 115.95, 118.6, 129.4–130.47, 132.08–132.48, 138.63, 141.8, 151.9, 160.2, 161.8. **PETH-G₂-x=12.** ¹H NMR (CDCl₃): 1.1–1.3 (broad, 16H), 1.65 (broad, 4H), 3.8 (broad, 4H), 4.85 (s, 8H), 4.94 (s, 4H), 4.99 (s, 16H), 6.45 (s, 2H), 6.54 (s, 8H), 6.64 (s, 8H), 6.91 (d, 4H), 7.02 (s, 2H), 7.26–7.37 (m, 40H), 7.54 (d, 4H). ¹³C NMR (CDCl₃): 26.47, 29.72–30.07, 68.43, 70.32, 70.47, 71.76, 101.97, 106, 106.8, 114.45, 117.23, 127.94–128.96, 130.74–131.1, 137.18, 139.66, 140.35, 150.54, 158.84, 160.29, 160.54.

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