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Conjugated Polymers with Main Chain Chirality. 3. Synthesis of Optically Active Poly(aryleneethynylene)s

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ABSTRACT: Binaphthyl-based chiral poly(aryleneethynylene)s of different molecular weights have been synthesized. An optically active poly(aryleneethynylene), (*R*)-**9c**, is obtained by coupling an optically active binaphthyl molecule, (*R*)-2,2′-bis(octadecyloxy)-6,6′-diethynyl-1,1′-binaphthyl, (*R*)-**8**, with 1,4-diiodobenzene in the presence of tetrakis(triphenylphosphine)palladium(0) and cuprous iodide catalysts. GPC analysis of (*R*)-**9c** shows $M_w = 29\ 000$ and $M_n = 12\ 000$ (PDI = 2.4). Its specific optical rotation is $[\alpha]_D = -272.2°$ ($c = 0.5$, CH_2Cl_2). Coupling of (*R*)-**8** with 4,4′-diiodobiphenyl using tetrakis(triphenylphosphine)palladium(0) and cuprous iodide catalysts also generates an optically active poly(aryleneethynylene), (*R*)-**10c**. GPC analysis of (*R*)-**10c** shows $M_w = 37\ 000$ and $M_n = 18\ 000$ (PDI = 2.1). The specific optical rotation of (*R*)-**10c** is $[\alpha]_D = -281.7°$ ($c = 0.18$, CH_2Cl_2). A laser light scattering study of these polymers shows that the actual molecular weights (M_w) of these materials are higher (1.4−2.5 times) than those obtained from GPC analysis *vs* polystyrene standards. The repeat units of these polymers have been synthesized. UV spectroscopic studies of the repeat units and of the polymers demonstrate that the conjugation of the polymers is determined by the conjugation in their repeat units.

Introduction

The study of conjugated polymers is a very active research field, and these materials have exhibited a number of interesting properties including electroluminescence, optical nonlinearity, and high conductivity upon doping.[2] Although optically active conjugated polymers are also potentially useful materials, very few studies have been carried out in this area.[3] We have recently initiated a project to synthesize and study conjugated polymers that have a main chain chiral configuration.[4,5] In this new polymer system, optically active binaphthyl compounds are utilized as the chiral building blocks to construct the main chain of these novel materials. In the process of this study, we have developed a practical and efficient way to prepare optically active 1,1′-bi-2-naphthol.[6] From (*R*)-1,1′-bi-2-naphthol, a chiral binaphthyldiboronic acid monomer, (*R*)-**1**, has thus been conveniently synthesized. The Suzuki coupling of (*R*)-**1** with conjugated aryl dibromides leads to the formation of optically active poly(arylenevinylene)s and optically active polyarylenes such as (*R*)-**2** and (*R*)-**3** (Scheme 1).[4,5] The main chain of these polymers is inherently chiral because of the restricted rotation of the binaphthyl units. The nonplanarity of the polymer main chain and the flexible alkyl groups render these materials soluble in organic solvents. These materials are highly fluorescent and emit blue light when irradiated. They have also shown high thermal stability.

Poly(aryleneethynylene)s are rigid rod conjugated materials composed of aromatic rings and alkyne functions. They can be prepared by the palladium-catalyzed coupling of aryl halides and terminal alkynes (Scheme 2).[7] In the study carried out by Yamamoto *et al.*, these materials have exhibited photoluminescence as well as strong third harmonic generation.[7h] Recently, Swager *et al.* have incorporated cyclophane receptors into poly(aryleneethynylene)s to construct fluorescence sensors.[8] When these materials are used to detect paraquat, an aromatic cation, greatly enhanced sensitivity over the monomeric compounds is observed due to energy migration in the conjugated polymer backbone. As an integral part of our project to synthesize and study chiral conjugated polymers, we have prepared binaphthyl-based optically active poly(aryleneethynylene)s. Herein, our synthesis and study of these materials are reported.

Results and Discussion

1. Synthesis and Characterization of Chiral Poly(aryleneethynylene)s. The conjugated bisalkyne monomers 1,4-diethynylbenzene (**4**) and 4,4′-diethynylbiphenyl (**5**) are prepared as shown in Scheme 3.[9] The palladium-catalyzed coupling of 2-methyl-3-butyn-2-ol with 1,4-dibromobenzene or 4,4′-dibromobiphenyl generates compound **6** or **7**, which are converted to **4** or **5** respectively by a base-promoted deprotection. The polymerization of both **4** and **5** with binaphthyl halide monomers is studied.

When **4** is reacted with 2,2′-bis(hexyloxy)-6,6′-dibromo-1,1′-binaphthyl in the presence of palladium dichloride and cuprous iodide, polymerization occurs to give a solid which is found to be insoluble in organic solvent. A monomer with a longer alkyl group, 2,2′-bis(decyloxy)-6,6′-dibromo-1,1′-binaphthyl, is then synthesized and used to couple with **4**. The resulting polymer is still not soluble. In order to make a soluble polymer, 2,2′-bis(octadecyloxy)-6,6′-dibromo-1,1′-binaphthyl, (*R*)-**8**, a monomer with 18-carbon alkyl groups, is prepared from the reaction of (*R*)-6,6′-dibromo-1,1′-bi-2-naphthol with 1-iodooctadecane (Scheme 4). The specific optical rotation of (*R*)-**8** is $[\alpha]_D = +20.5°$($c = 1.0$, CH_2Cl_2). When (*R*)-**8** is polymerized with **4** in the presence of palladium dichloride and cuprous iodide, (*R*)-**9a** is obtained. (*R*)-**9a** is a low molecular weight polymer and can be dissolved in common organic solvents. GPC (THF, polystyrene standard) analysis shows $M_w = 7400$ and $M_n = 3800$ (PDI = 2.0). The specific optical rotation of (*R*)-**9a** is $[\alpha]_D = -154.9°$ ($c = 1.0$, CH_2Cl_2). *rac*-**9a** is also obtained from the polymerization of **4** with the racemic monomer *rac*-**8**. The molecular weight of *rac*-**9a** is $M_w = 8500$ and $M_n = 3200$ (PDI = 2.7).

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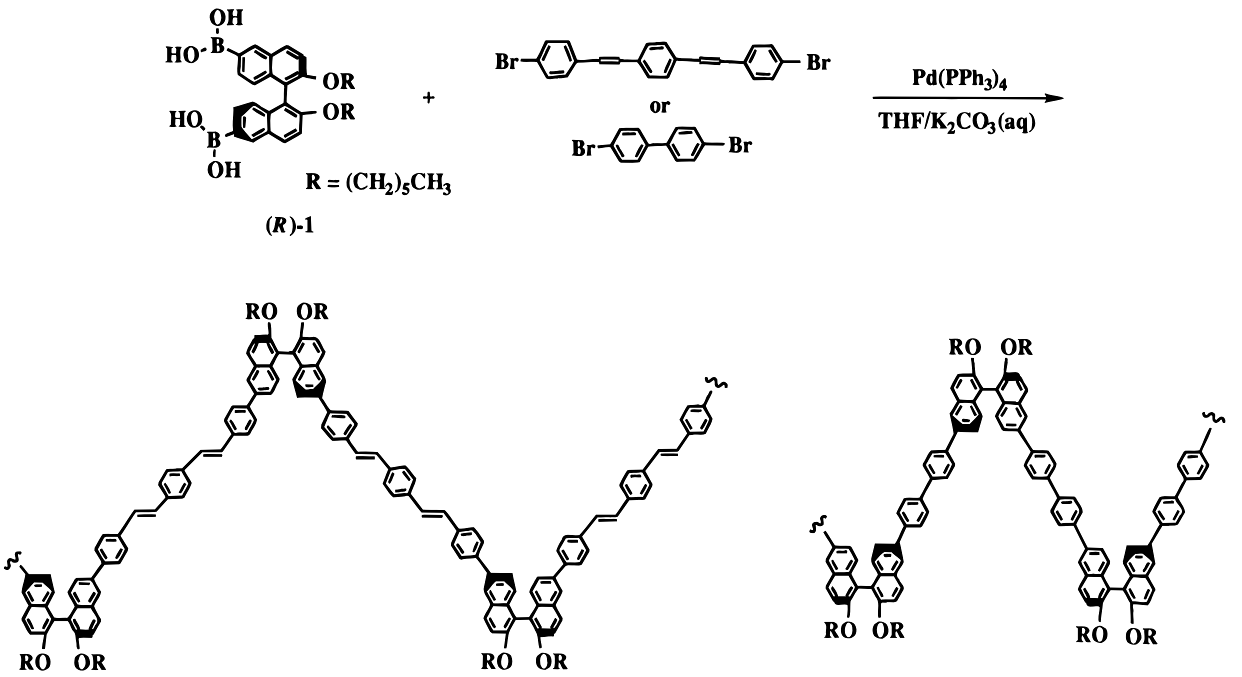
Scheme 1. Synthesis of a Chiral Poly(arylenevinylene), (*R*)-2, and a Chiral Polyarylene, (*R*)-3

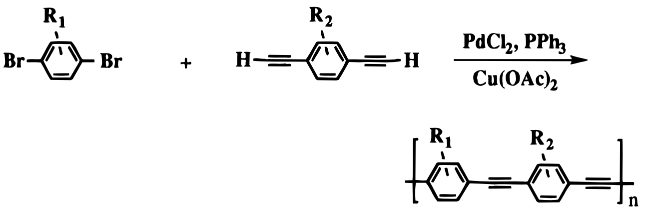


(*R*)-1

(*R*)-2

(*R*)-3

Scheme 2. Synthesis of Poly(aryleneethynylene)s

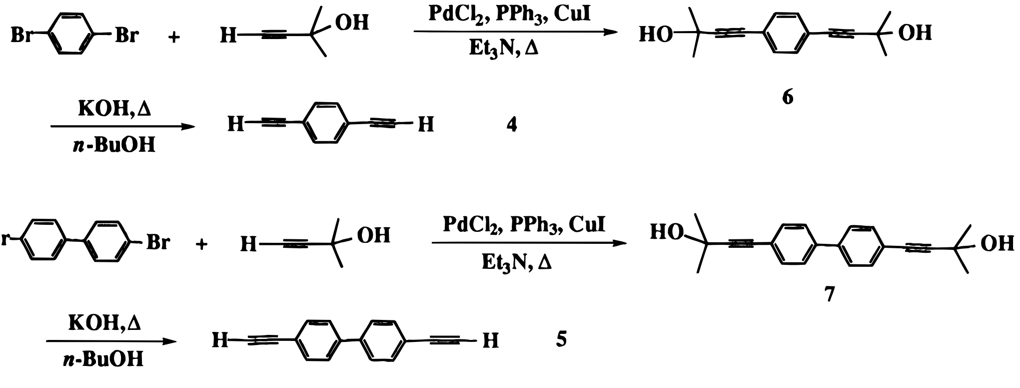


In a similar way, (*R*)-**8** is coupled with **5** to give (*R*)-**10a** (Scheme 5). (*R*)-**10a** is also a soluble low molecular weight material. GPC analysis of (*R*)-**10a** shows M_w = 9300 and M_n = 4800 (PDI = 1.9). Its specific optical rotation is $[\alpha]_D = -158.9°$ (c = 1.0, CH_2Cl_2). The coupling of **5** with *rac*-**8** produces *rac*-**10a**. The molecular weight of *rac*-**10a** is M_w = 6600 and M_n = 3900 (PDI = 1.7).

It is known that the reaction of terminal alkynes with aryl iodides proceeds faster than with aryl bromides.[7i] In order to obtain high molecular weight materials, (*R*)-2,2′-bis(octadecyloxy)-6,6′-diethynyl-1,1′-binaphthyl, (*R*)-**11**, is prepared to react with aryl iodides. As shown in Scheme 6, the cross-coupling of (*R*)-**8** with 2-methyl-3-butyn-2-ol gives (*R*)-**12**, which is then converted to (*R*)-**11** by a base-promoted deprotection. The specific optical rotation of (*R*)-**11** is $[\alpha]_D = -14.7°$ (c = 1.0, CH_2Cl_2), which is interesting because the optical rotation of (*R*)-**8** is positive. ^{1}H NMR of (*R*)-**11** shows a singlet at δ 3.08 (2H) for the two terminal alkyne protons. In the IR spectrum of (*R*)-**11**, the alkyne C−H stretch and the carbon−carbon triple-bond stretch are observed at 3310 (s) and 2108 (w) cm^{-1}, respectively. HPLC analysis on a chiralcel OD column shows that the optical purity of the molecule is greater than 99%. This demonstrates that no racemization occurs during the preparation of (*R*)-**11** from (*R*)-1,1′-bi-2-naphthol. Using palladium(II) dichloride and cuprous iodide as the catalysts, polymerization of (*R*)-**11** with 1,4-diiodobenzene generates (*R*)-**9b**. The molecular weight of (*R*)-**9b** is observed to be much higher than that of (*R*)-**9a**. GPC analysis of (*R*)-**9b** shows M_w = 21 000 and M_n = 15 000 (PDI = 1.4). The specific optical rotation of (*R*)-**9b** is $[\alpha]_D = -278.2°$ (c = 0.5, CH_2Cl_2), also significantly larger than that of (*R*)-**9a**. Polymerization of *rac*-**11** with 1,4-diiodobenzene produces *rac*-**9b**. GPC of *rac*-**9b** shows M_w = 13 000 and M_n = 8300 (PDI = 1.6).

(*R*)-**11** was also polymerized with 4,4′-diiodobiphenyl to give (*R*)-**10b**. GPC analysis of (*R*)-**10b** shows M_w = 29 000 and M_n = 15 000 (PDI = 1.9). The specific optical rotation of (*R*)-**10b** is $[\alpha]_D = -250.6°$ (c = 0.5,

Scheme 3. Preparation of 1,4-Diethynylbenzene (4) and 4,4′-Diethynylbiphenyl (5)



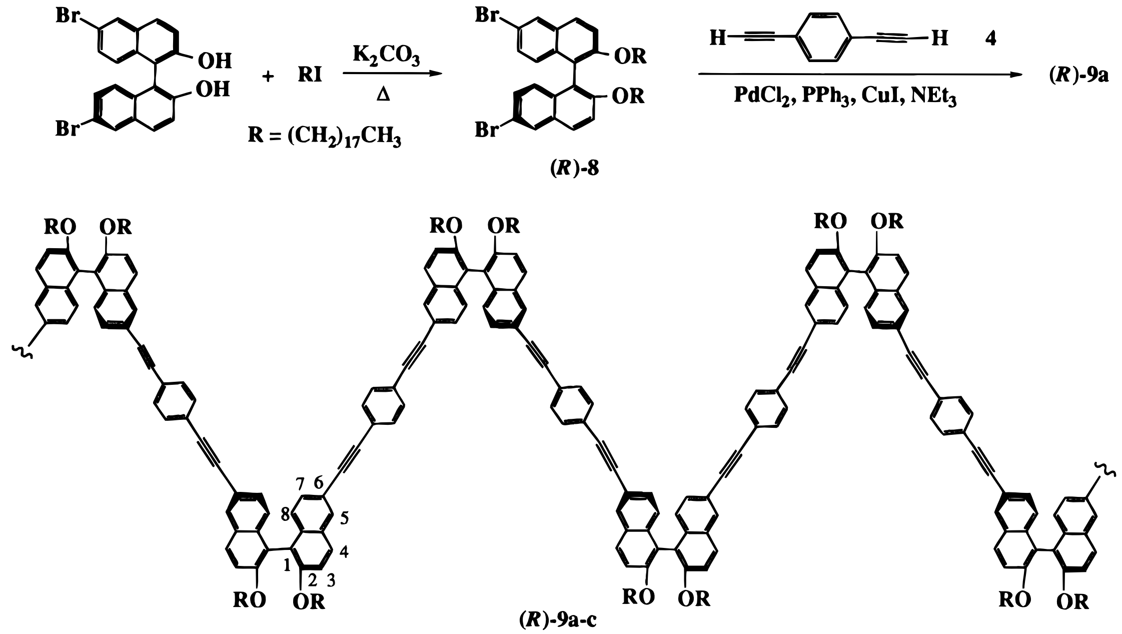
6

4

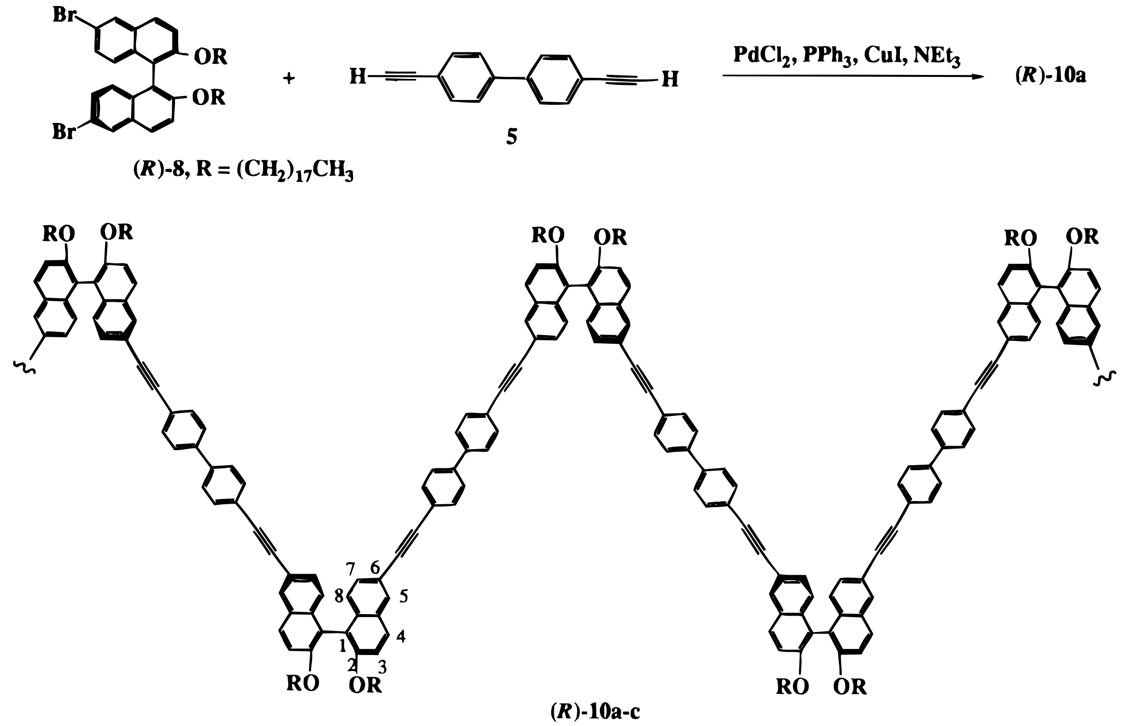
7

5

Scheme 4. Synthesis of (*R*)-9a



Scheme 5. Synthesis of (*R*)-10a



CH_2Cl_2). (*R*)-**10b** has a much higher molecular weight and a much larger optical rotation than (*R*)-**10a**. *rac*-**10b** is also obtained from the coupling of *rac*-**11** with 4,4′-diiodobiphenyl. GPC analysis shows that the molecular weight of *rac*-**10b** is M_w = 20 000 and M_n = 12 000 (PDI = 1.7).

When $Pd(PPh_3)_4$ and CuI are used as the catalysts in place of $PdCl_2$ and CuI, the polymerization of (*R*)-**11** with 1,4-diiodobenzene gives an even higher molecular weight polymer, (*R*)-**9c**. GPC analysis of (*R*)-**9c** shows M_w = 29 000 and M_n = 12 000 (PDI = 2.4). The specific optical rotation of the polymer is $[\alpha]_D = -272.2°$ (c = 0.5, CH_2Cl_2). The polymerization of *rac*-**11** with 1,4-diiodobenzene using $Pd(PPh_3)_4$ and CuI as the catalysts generates *rac*-**9c**, which has a molecular weight of M_w = 47 000 and M_n = 25 000 (PDI = 1.9) as measured by GPC. Polymerization of (*R*)-**11** with 4,4′-diiodobiphenyl using $Pd(PPh_3)_4$ and CuI as the catalysts generates (*R*)-**10c**. GPC analysis of (*R*)-**10c** shows M_w = 37 000 and M_n = 18 000 (PDI = 2.1). Its specific optical rotation is $[\alpha]_D = -281.7°$ (c = 0.18, CH_2Cl_2). *rac*-**10c** is also obtained with a molecular weight of M_w = 54 000 and M_n = 25 000 (PDI = 2.2).

Table 1 summarizes the polymerization conditions and the molecular weights of polymers **9a**−**c** and **10a**−**c**. As shown in Table 1, the best condition to achieve the highest molecular weights for the synthesis of the binaphthyl-based poly(aryleneethynylene)s is to use $Pd(PPh_3)_4$ and CuI as the catalysts to polymerize (*R*)-**11** or *rac*-**11** with aryl diiodides (1,4-diiodobenzene or 4,4′-diiodobiphenyl). From the monomers to the low molecular weight polymers and from the low molecular weight

Scheme 6. Synthesis of Monomer (*R*)-11 and Polymer (*R*)-9b

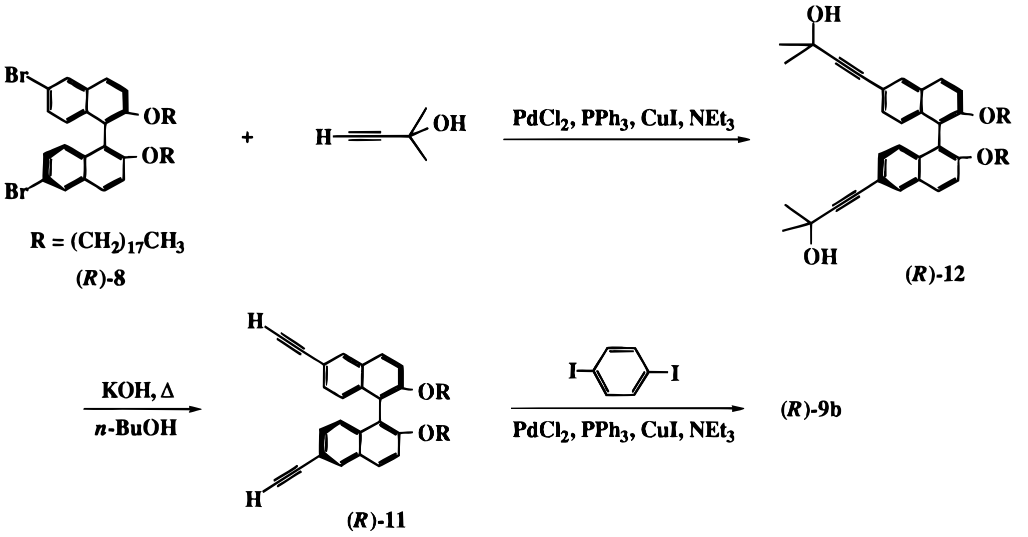


Table 1. Conditions To Prepare 9a−c and 10a−c and Their Molecular Weights Based on GPC Analysis

polymers	monomers	catalysts	M_w	M_n	PDI	$[\alpha]_D$/deg
(*R*)-**9a**	(*R*)-**8** + **4**	$PdCl_2$, CuI	7400	3800	2.0	−154.9
rac-**9a**	*rac*-**8** + **4**	$PdCl_2$, CuI	8500	3200	2.7	
(*R*)-**9b**	(*R*)-**11** + 1,4-diiodobenzene	$PdCl_2$, CuI	21000	15000	1.4	−278.2
rac-**9b**	*rac*-**11** + 1,4-diiodobenzene	$PdCl_2$, CuI	13000	8300	1.6	
(*R*)-**9c**	(*R*)-**11** + 1,4-diiodobenzene	$Pd(PPh_3)_4$, CuI	29000	12000	2.4	−272.2
rac-**9c**	*rac*-**11** + 1,4-diiodobenzene	$Pd(PPh_3)_4$, CuI	47000	25000	1.9	
(*R*)-**10a**	(*R*)-**8** + **5**	$PdCl_2$, CuI	9300	4800	1.9	−158.9
rac-**10a**	*rac*-**8** + **5**	$PdCl_2$, CuI	6600	3900	1.7	
(*R*)-**10b**	(*R*)-**11** + 4,4′-diiodobiphenyl	$PdCl_2$, CuI	29000	15000	1.9	−250.6
rac-**10b**	*rac*-**11** + 4,4′-diiodobiphenyl	$PdCl_2$, CuI	20000	12000	1.7	
(*R*)-**10c**	(*R*)-**11** + 4,4′-diiodobiphenyl	$Pd(PPh_3)_4$, CuI	37000	18000	2.1	−281.7
rac-**10c**	*rac*-**11** + 4,4′-diiodobiphenyl	$Pd(PPh_3)_4$, CuI	54000	25000	2.2	

materials to high polymers, there is a large increase of optical rotation. However, there is no significant difference in optical rotation between the higher molecular weight materials [(*R*)-**9b** *vs* (*R*)-**9c** and (*R*)-**10b** *vs* (*R*)-**10c**].

All of the polymers **9a−c** and **10a−c** are soluble in common organic solvents such as methylene chloride, chloroform, and THF and have been characterized by ^{1}H and ^{13}C NMR spectroscopy. The polymers *rac*-**9a−c** and *rac*-**10a−c** are most likely made of randomly distributed *R* and *S* binaphthyl units in the polymer chain. In the ^{13}C NMR spectrum of (*R*)-**9c**, two peaks at δ 91.9 and 88.9 are observed for the two different alkyne carbons of the polymer. The IR spectrum of (*R*)-**9c** shows a weak signal at 2205 cm^{-1} for the alkyne carbon−carbon triple-bond stretch. The ^{1}H NMR spectrum of (*R*)-**10c** is similar to that of (*R*)-**9c**. The alkyne carbon signals of (*R*)-**10c** are observed at δ 91.1 and 88.9 in the ^{13}C NMR spectrum. The IR spectrum of (*R*)-**10c** also displays a weak absorption at 2211 cm^{-1} for the carbon−carbon triple bond stretch.

Thermogravimetric analysis (TGA) of (*R*)-**9c** shows the onset decomposition temperature at 396 °C (Figure 1). At 486 °C, the polymer loses about 52% of its weight, which is approximately equivalent to the loss of the 18-carbon chain alkyl groups ($C_{18}H_{37}$ groups constitute 55.5% of the polymer mass). After the loss of the alkyl groups, the remaining material shows extremely high thermal stability, and no significant weight loss is observed up to 800 °C. TGA of (*R*)-**10c** shows a thermal stability similar to that of (*R*)-**9c** (Figure 2). The onset decomposition temperature of (*R*)-**10c** is about 395 °C. When the temperature is raised to 540 °C, the total weight loss of (*R*)-**10c** is about 50%, corresponding to the loss of the alkyl groups of the polymer ($C_{18}H_{37}$ groups constitute 51% of the polymer mass). No significant weight loss is observed at temperatures from 540 up to 800 °C.

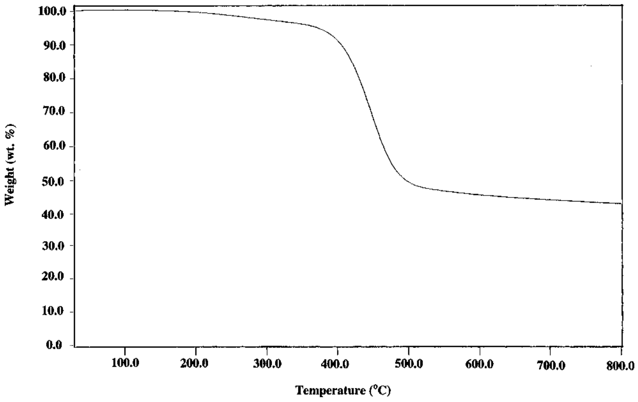


Figure 1. TGA plot of (*R*)-**9c** (N_2, heating rate 40.0 °C/min).

2. Laser Light Scattering Study of the Chiral Poly(aryleneethynylene)s. A laser light scattering (LLS) study has been carried out to measure the molecular weights of these polymers.[10−12] The LLS results for three of the polymer samples measured in THF at 25.0 °C are summarized in Table 2, wherein A_2 is the second virial coefficient, D is the translational diffusion coefficient, R_h is the hydrodynamic radius, and $\mu_2/\langle\Gamma\rangle^2$ is the width of the line-width distribution. The GPC data are also included for comparison. When the polymer size is too small ($<\sim$10 nm), we are unable to determine an accurate value of the radius of gyration R_g. The positive value of A_2 indicates that THF is a good solvent for these polymers at room temperature. The

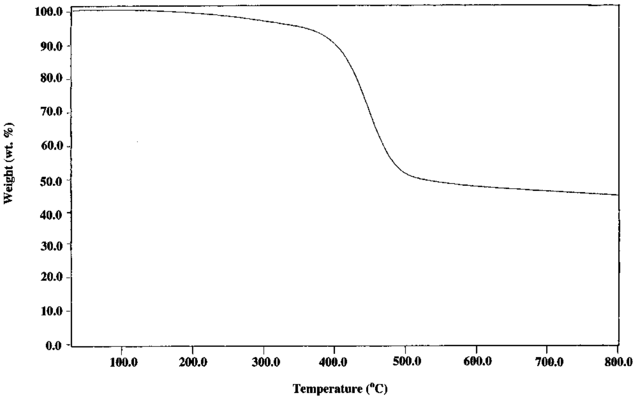
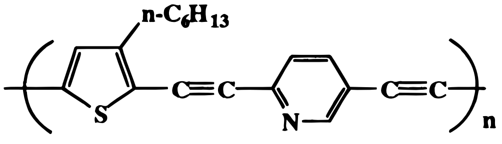


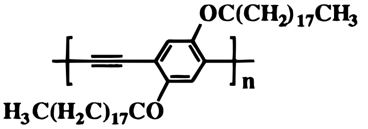
Figure 2. TGA plot of (*R*)-**10c** (N_2, heating rate 40.0 °C/min).

relatively large value of $\mu_2/\langle\Gamma\rangle^2$ demonstrates that the polymer samples are broadly distributed. The polydispersity index M_w/M_n estimated from $\mu_2/\langle\Gamma\rangle^2$, i.e., $M_w/M_n \sim (1 + 4\mu_2/\langle\Gamma\rangle^2)$, is in the range of 2–3.5. As shown by the LLS study, the actual molecular weights of this class of polymers are normally higher (ca. 1.4–2.5 times) than what are measured by GPC analysis relative to polystyrene standards. LLS studies on other poly(aryleneethynylene)s, e.g. **13a**, have been reported which in some cases have also given significantly higher molecular weight data than those obtained from GPC analysis (*vs* polystyrene).[13]



13a

3. UV Spectroscopic Study of the Chiral Poly(aryleneethynylene)s and Their Repeat Units. The UV spectrum of (*R*)-**9c** displays λ_{max} = 238, 300, 354, and 384 (sh) nm. The fluorescence spectrum shows emissions at 401 (sh), 419, and 461 (sh) nm for the polymer. Polymers (*R*)-**9a–c** and *rac*-**9a–c** give very similar UV and fluorescence spectra. In the UV spectrum of (*R*)-**10c**, λ_{max} is observed at 234, 305, and 352 nm. The fluorescence spectrum of the polymer exhibits emissions at 407 (sh), 420, and 460 (sh) nm. Polymers (*R*)-**10a–c** and *rac*-**10a–c** also have similar UV and fluorescence spectra. All of the polymers **9a–c** and **10a–c** emit strong blue light under a UV lamp. The electronic absorptions of these binaphthyl-based conjugated polymers appear at much shorter wavelengths compared to an ordinary poly(aryleneethynylene), **13b**. The UV spectrum of **13b** (M_w > 10 000, GPC) shows an absorption maximum at λ = 410 nm.[14] This indicates that the nonplanar polymers **9a–c** and **10a–c** have much larger π–π* bandgaps than the planar poly(aryleneethynylene)s. The chiral conjugated polymers (*R*)-**9c** and (*R*)-**10c** display strong Cotton effects in their circular dichroism spectra (Figures 3 and 4). In Figures 3 and 4, the molar ellipiticity, [θ], is calculated using the molecular weight of the polymer repeat unit.



13b

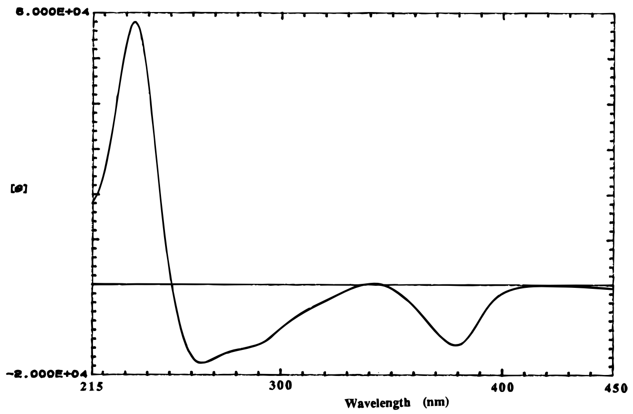


Figure 3. CD spectrum of (*R*)-**9c** in methylene chloride.

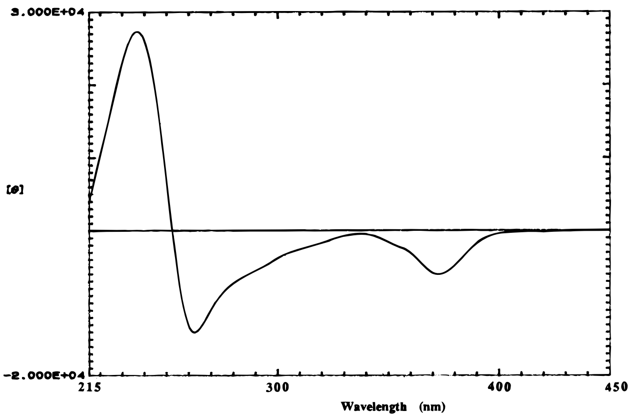
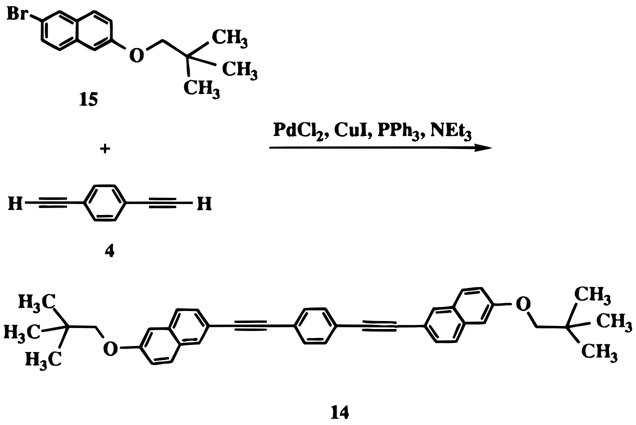


Figure 4. CD spectrum of (*R*)-**10c** in methylene chloride.

Scheme 7. Synthesis of 14 as the Repeat Unit for Polymers 9a–c



In order to determine the degree of extended conjugation in polymers **9a–c**, a conjugated molecule **14** has

Table 2. Static and Dynamic LLS Results for Polymers (*R*)-10a,b and *rac*-10c

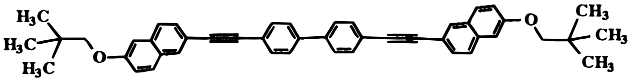
polymer	M_w (GPC)	M_w (LLS data)	A_2/(mol mL/g^2)	D/(cm^2/s)	R_h/nm	$\mu_2/\langle\Gamma\rangle^2$	M_w/M_n
(*R*)-**10a**	9300	23000		9.00×10^{-7}	5.1	~0.67	~3.7
(*R*)-**10b**	20000	32000	1.5×10^{-3}	9.00×10^{-7}	5.1	~0.62	~3.5
rac-**10c**	54000	73000	5.2×10^{-4}	5.00×10^{-7}	9.2	~0.27	~2.1

Table 3. UV Absorptions of the Chiral Polymers (*R*)-9c and (*R*)-10c and the Repeat Units 14 and 16

UV absorption (CH_2Cl_2) λ_{max} (nm)			
(*R*)-**9c**	(*R*)-**10c**	**14**	**16**
238, 300, 354, 384 (sh)	234, 306 (sh), 352	236, 290, 350, 374 (sh)	236, 296 (sh), 348

been synthesized from the reaction of **15**[5] with **4** as the repeat unit of polymers **9a**–**c** (Scheme 7). A weak absorption at 2210 cm^{-1} is observed for the carbon–carbon triple-bond stretch. In the ^{13}C NMR of **14**, the alkyne carbons are observed at δ 91.1 and 88.8. Both the IR and NMR signals of **14** are very similar to what are observed in polymers **9**, which supports the structure described for these polymers. The UV spectrum of **14** shows maximum absorptions at $\lambda_{max} = 236$, 290, 340, and 374 (sh) nm. These UV absorptions of **14** are very close to those of polymers **9**, indicating essentially no conjugation between adjacent repeat units. The conjugation of the polymer is therefore determined by the conjugation in its repeat unit.

The conjugated molecule **16** has also been synthesized from the coupling of **15** with **5** as the repeat unit of polymers **10**. The carbon–carbon triple bonds of **16** show a weak absorption at 2210 cm^{-1} in the IR spectrum. The ^{13}C NMR spectrum shows the alkyne carbon signals at δ 91.9 and 88.8. The UV spectrum of **16** displays absorption maxima at $\lambda_{max} = 236$, 296 (sh), and 348 nm which are almost the same as those of the polymers **10**. A main difference is observed when the UV spectrum of **16** is compared with that of **14**. In the UV spectrum of **14**, there is an absorption at 374 (sh) nm, which is absent in **16**. This indicates that even though **16** has an extra phenyl ring, its effective conjugation length may be shorter than that of **14**. Thus, the nonplanarity of the biphenyl unit in **16** might have disrupted the conjugation, leading to a shorter absorption wavelength than **14**. A similar phenomenon is also observed when comparing the UV spectra of polymers **10** with polymers **9**. Table 3 summarizes the UV absorption data of the chiral polymers and the repeat units.



16

Summary

In summary, optically active poly(aryleneethynylene)s have been synthesized and characterized. Conditions to prepare these polymers of different molecular weights have been explored. With the introduction of 18-carbon alkyl substituents at the oxygen atoms of the binaphthyl units, these polymers are made soluble and easy to process. A laser light scattering study of these polymers reveals that the molecular weights (M_w) obtained from GPC analysis of these polymers versus polystyrene standard are generally lower (by 1.4–2.5 times) than their actual molecular weights. With the preparation of the repeat units for these polymers, it is demonstrated that the conjugation of these binaphthyl-based materials is determined by the conjugation in their repeat units. The electroluminescence property and optical nonlinearity of these new materials will be investigated.

Experimental Section

General Data. NMR spectra were recorded on JEOL 270 MHz and JEOL 400 MHz spectrometers. Infrared spectra were recorded on a 2020/Galaxy Series FT-IR spectrometer by preparing KBr pellets of the materials. Elemental analyses were carried out using a Perkin-Elmer 2400 Series II CHN S/O analyzer. Mass spectra were obtained using a Hewlett-Packard 5890 Series II GC/DIP MS. Thermogravimetric analyses were carried out using a Perkin-Elmer TGA 7 analyzer. Gel permeation chromatography (GPC) utilized a Waters 510 HPLC pump, a Waters 410 differential refractometer, and Ultrastyragel Linear GPC columns. THF was used as the solvent for the GPC analysis, and polystyrene standard was used. UV–vis spectra were recorded on a Hewlett-Packard 8451A diode array spectrophotometer. Emission spectra were taken using a Spex Fluorolog spectrofluorometer. Circular dichroism spectra were recorded using a JASCO J-710 spectropolarimeter. Optical rotations were measured on a JASCO polarimeter at 589 nm. Differential scanning calorimetry studies were carried out using a Perkin-Elmer DSC 7. THF and ether were dried with sodium benzophenone. Triethylamine was dried with calcium hydride. 1,4-Diiodobenzene, 4,4′-diiodobiphenyl, 1,4-dibromobenzene, 4,4′-dibromobiphenyl, and 2-methyl-3-butyn-2-ol were purchased from Aldrich and used directly. Tetrakis(triphenylphosphine)palladium(0), palladium chloride, and cuprous iodide were purchased from Strem and used directly.

Laser Light Scattering (LLS) Experiment. The excess absolute scattered light intensities and intensity–intensity time correlation functions were measured with a modified commercial LLS spectrometer (ALV/SP-150 equipped with an ALV-5000 multi-τ digital time correlator). A He–Ne laser (Spectra-Physics Model 127, ~40 mW at $\lambda_0 = 632.8$ nm) was used as the light source. The incident beam was vertically polarized with respect to the scattering plane. The details of the LLS instrumentation and theory can be found elsewhere.[10–12] A precise value of the specific refractive index increment dn/dC is important for determining the weight-average molecular weight M_w of a given polymer because $M_w \propto (dn/dC)^{-2}$. In this study, the refractive index increment Δn was measured by using a novel differential refractometer,[12] wherein the laser light was split into one strong beam (~1%) and one weak beam (~99%) which were used as the light source for LLS and refraction, respectively. In this way, we were able to measure Δn and the scattered light intensity under identical conditions, so that the wavelength correction was eliminated. The dn/dC value calculated from the slope of Δn versus the concentration C is 0.244 ± 0.001 mL/g for the poly(aryleneethynylene)s in THF at $T = 25.0$ °C and $\lambda_0 = 632.8$ nm. All light scattering solutions were clarified by a 0.5 μm filter in order to remove dust.

Preparation of (*R*)-2,2′-Bis(octadecyloxy)-6,6′-dibromo-1,1′-binaphthyl ((*R*)-8). A mixture of (*R*)-6,6′-dibromo-2,2′-dihydroxy-1,1′-binaphthyl (1.50 g, 3.38 mmol), 1-iodooctadecane (2.70 g, 7.10 mmol), and K_2CO_3 (1.59 g, 11.5 mmol) in acetone (40 mL) was heated under nitrogen at reflux for 36 h. The solvent was then evaporated, and the mixture was washed with water (3 × 70 mL) and dried under vacuum for 24 h. The residue was purified by flash column chromatography (silica gel, 10% ethyl acetate in hexane) to give (*R*)-**8** as a yellow solid (2.87 g, 90%). Mp 49–50 °C. $[\alpha]_D = +20.5°$ (c = 1.0, CH_2Cl_2). ^1H NMR (270 MHz, $CDCl_3$) δ 7.99 (d, J = 1.5 Hz, 2H, H-5), 7.83 (d, J = 8.8 Hz, 2H), 7.40 (d, J = 8.8 Hz, 2H), 7.26 (dd, J = 1.5, 8.8 Hz, 2H, H-4), 6.97 (d, J = 8.8 Hz, 2H, H-8), 3.94–3.91 (m, 4H, OCH_2), 1.39–0.90 (m, 64H, CH_2), 0.87 (t, J = 7.3 Hz, 6H, CH_3). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 154.7, 132.5, 130.1, 129.7, 129.4, 128.3, 127.1, 120.0, 117.2, 116.3, 69.5, 31.9, 29.7, 29.5, 29.4, 29.3, 29.2, 29.1, 25.6, 22.7, 14.1. MS m/z 948 (M^+). Anal. Calcd for $C_{56}H_{84}Br_2O_2$: C, 70.89; H, 8.86. Found: C, 70.85; H, 8.84.

Preparation of *rac*-8. A procedure similar to the preparation of (*R*)-**8** was used to make *rac*-**8** (91% yield) from the reaction of *rac*-6,6′-dibromo-2,2′-dihydroxy-1,1′-binaphthyl and 1-iodooctadecane. *rac*-**8** was recrystallized from hexane. Mp 97–98 °C. ^1H NMR (270 MHz, $CDCl_3$) δ 7.99 (d, J = 2.2 Hz, 2H), 7.85 (d, J = 8.8 Hz, 2H), 7.40 (d, J = 8.8 Hz, 2H), 7.26 (dd, J = 2.2, 8.8 Hz, 2H), 6.98 (d, J = 9.5 Hz, 2H), 3.94–3.91 (m, 4H, OCH_2), 1.39–0.91 (m, 64H, CH_2), 0.87 (t, J = 6.6 Hz, 6H, CH_3). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 154.7, 132.5, 130.2, 129.7, 129.4, 128.3, 127.1, 120.0, 117.2, 116.4, 69.5, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.1, 25.7, 22.7, 14.1. MS *m/z* 948 (M^+). Anal. Calcd for $C_{56}H_{84}Br_2O_2$: C, 70.89; H, 8.86. Found: C, 70.58; H, 8.90.

Preparation of (*R*)-2,2′-Bis(octadecyloxy)-6,6′-bis(3″-hydroxy-3″-methylbutynyl)-1,1′-binaphthyl (*R*)-12. To a solution of (*R*)-**8** (2.50 g, 2.60 mmol) in dry triethylamine (25 mL) was added 2-methyl-3-butyn-2-ol (0.66 g, 7.8 mmol). After the solution was degassed with nitrogen for 30 min while stirring, it was taken into a drybox, and palladium(II) chloride (23 mg, 0.13 mmol), triphenylphosphine (0.35 g, 1.35 mmol), and cuprous iodide (89 mg, 0.47 mmol) were added. The reaction mixture was then refluxed under nitrogen for 22 h. After the reaction was complete, the crude mixture was filtered at room temperature to remove triethylammonium bromide precipitate. The precipitate was rinsed with diethyl ether, and the combined filtrates were evaporated to dryness. The residue was purified by flash column chromatography (silica gel, 20% ethyl acetate in hexane) to give (*R*)-**12** (2.13 g, 85%) as an orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, $J = 1.6$ Hz, 2H), 7.87 (d, $J = 9.1$ Hz, 2H), 7.40 (d, $J = 9.1$ Hz, 2H), 7.18 (dd, $J = 1.6$, 8.6 Hz, 2H), 7.04 (d, $J = 9.1$ Hz, 2H), 3.94−3.91 (m, 4H, OCH_2), 2.06 (s, 2H, O*H*), 1.64 (s, 12H, CH_3), 1.39−1.02 (m, 64H, CH_2), 0.88 (t, $J = 6.6$ Hz, 6H, CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 155.2, 133.5, 131.5, 129.0, 128.6, 128.5, 125.3, 120.0, 117.3, 115.9, 93.3, 82.7, 69.4, 65.6, 31.9, 31.5, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 25.5, 22.6, 14.1.

Preparation of *rac*-12. The procedure to prepare *rac*-**12** is similar to that of (*R*)-**12** by coupling *rac*-**8** with 2-methyl-3-butyn-2-ol. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, $J = 1.6$ Hz, 2H), 7.87 (d, $J = 9.1$ Hz, 2H), 7.40 (d, $J = 9.1$ Hz, 2H), 7.18 (dd, $J = 1.6$, 8.6 Hz, 2H), 7.04 (d, $J = 8.6$ Hz, 2H), 3.95−3.91 (m, 64H, CH_2), 2.02 (s, 2H, O*H*), 1.64 (s, 12H, CH_3), 1.39−1.02 (m, 64H, CH_2) , 0.88 (t, $J = 7.0$ Hz, 6H, CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 155.2, 133.5, 131.5, 129.0, 128.6, 128.5, 125.3, 120.0, 117.3, 115.9, 93.3, 82.7, 69.4, 65.6, 31.9, 31.5, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 25.6, 22.7, 14.1.

Preparation of (*R*)-2,2′-Bis(octadecyloxy)-6,6′-diethynyl-1,1′-binaphthyl ((*R*)-11). A mixture of (*R*)-**12** (2.0 g, 2.1 mmol) and pulverized potassium hydroxide (0.59 g, 10.5 mmol) in 1-butanol (20 mL) was heated at reflux under nitrogen with vigorous stirring for 30 min. The solvent was then removed with a rotoevaporator, and the residue was washed with water (3 × 50 mL). The remaining solid was dried under vacuum and purified by flash column chromatography (silica gel, 10% ethyl acetate in hexane) to give (*R*)-**11** as a yellow solid (1.38 g, 78%). Mp 39−40 °C. $[\alpha]_D = -14.7°$ ($c = 1.0$, CH_2Cl_2). FT-IR (KBr pellet, cm^{-1}) 3310 (m), 2931 (s), 2856 (s), 2108 (w), 1620 (m), 1591 (m), 1467 (s), 1340 (s), 1267 (s), 1248 (s), 1091 (s), 1053 (m), 887 (m), 825 (m). ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.04 (d, $J = 1.5$ Hz, 2H), 7.89 (d, $J = 9.5$ Hz, 2H), 7.41 (d, $J = 8.8$ Hz, 2H), 7.26 (dd, $J = 1.5$, 8.8 Hz, 2H), 7.07 (d, $J = 8.8$ Hz, 2H), 3.96−3.93 (m, 4H, OCH_2), 3.08 (s, 2H, alkyne-*H*), 1.39−1.01 (m, 64H, CH_2), 0.88 (t, 6H, CH_3). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 155.4, 133.8, 132.4, 129.2, 128.8, 128.5, 125.4, 119.9, 116.8, 115.8, 84.3, 76.6, 69.4, 31.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.1, 25.7, 22.7, 14.1. Anal. Calcd for $C_{60}H_{86}O_2$: C, 85.92; H, 10.26. Found: C, 85.71; H, 10.25.

Preparation of *rac*-11. A procedure similar to the preparation of (*R*)-**11** was used to make *rac*-**11** (white powder, 90% yield) from the reaction of *rac*-**12** with base. Mp 88−89 °C. FT-IR (KBr, cm^{-1}) 3315 (m), 2918 (s), 2852 (s), 2104 (w), 1620 (m), 1585 (m), 1489 (m), 1469 (s), 1340 (m), 1267 (s), 1242 (s), 1093 (s), 887 (m), 814 (m). ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.04 (d, $J = 1.5$ Hz, 2H), 7.89 (d, $J = 9.5$ Hz, 2H), 7.41 (d, $J = 8.8$ Hz, 2H), 7.25 (dd, $J = 2.2$, 10.3 Hz, 2H), 7.06 (d, $J = 8.1$ Hz, 2H), 3.96−3.93 (m, 4H, OCH_2), 3.08 (s, 2H, alkyne-*H*), 1.39−1.01 (m, 64H, CH_2), 0.88 (t, $J = 6.6$ Hz, 6H, CH_3). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 155.4, 133.7, 132.3, 129.2, 128.8, 128.4, 125.4, 119.9, 116.7, 115.9, 84.3, 76.7, 69.4, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 25.6, 22.7, 14.1. Anal. Calcd for $C_{60}H_{86}O_2$: C, 85.92; H, 10.26. Found: C, 85.67; H, 10.27.

Three Polymerization Methods. (A) Coupling of (*R*)-8 or *rac*-8 with 4 or 5 To Prepare (*R*)-9a, *rac*-9a, (*R*)-10a, or *rac*-10a. A typical polymerization procedure is described below. In a flame-dried Schlenck flask, a mixture of (*R*)-**8** (237 mg, 0.25 mmol), **5** (50 mg, 0.25 mmol), triethylamine (20 mL), and THF (10 mL) was degassed with nitrogen for 30 min. The flask was then taken into a drybox, and palladium(II) chloride (4.4 mg, 0.025 mmol), triphenylphosphine (68 mg, 0.26 mmol), and cuprous iodide (16 mg, 0.085 mmol) were added. After the reaction mixture was refluxed under nitrogen for 60 h, it was filtered at room temperature to remove triethylammonium bromide precipitate. The salt was rinsed with ethyl ether, and the combined filtrates were evaporated to dryness. The residue was dissolved in the minimum amount of methylene chloride which was poured into methanol (75 mL) to precipitate out the polymer twice. After centrifuge separation, the resulting polymer was dried under vacuum to give (*R*)-**10a** as a yellow solid (240 mg, 97% yield). Polymers (*R*)-**9a**, *rac*-**9a,** and *rac*-**10a** were obtained in a similar way.

(B) Coupling of (*R*)-11 or *rac*-11 with 1,4-Diiodobenzene or 4,4′-Diiodobiphenyl Using $PdCl_2$ and CuI_2 as the Catalysts To Prepare (*R*)-9b, *rac*-9b, (*R*)-10b, or *rac*-10b. A typical polymerization procedure is described below. In a 50 mL flame-dried Schlenck flask, a mixture of (*R*)-**11** (210 mg, 0.25 mmol), 1,4-diiodobenzene (83 mg, 0.25 mmol), triethylamine (5 mL), and toluene (10 mL) was degassed for 30 min. The flask was then taken into a drybox, and palladium(II) chloride (2.2 mg, 0.013 mmol), triphenylphosphine (34 mg, 0.13 mmol), and cuprous iodide (8 mg, 0.043 mmol) were added. After the reaction mixture was refluxed under nitrogen for 48 h, it was filtered at room temperature to remove triethylammonium bromide precipitate. The salt was rinsed with diethyl ether, and the combined filtrates were evaporated to dryness. The residue was dissolved in the minimum amount of methylene chloride which was then poured into methanol (75 mL) to precipitate out the polymer twice. After centrifuge separation, the resulting polymer was dried under vacuum to give (*R*)-**9b** as a yellow solid (80% yield). (*R*)-**10b** and *rac*-**10b** were prepared in a similar way. The preparation of *rac*-**9b** used THF instead of toluene as the cosolvent, which gave a lower molecular weight material.

(C) Coupling of (*R*)-11 or *rac*-11 with 1,4-Diiodobenzene and 4,4′-Diiodobiphenyl Using $Pd(PPh_3)_4$ and CuI, as the Catalysts To Prepare (*R*)-9c, *rac*-9c, (*R*)-10c, or *rac*-10c. A typical polymerization procedure is described below. In a 50 mL flame-dried Schlenck flask, a mixture of (*R*)-**11** (210 mg, 0.25 mmol), 1,4-diiodobenzene (83 mg, 0.25 mmol), triethylamine (2 mL), and toluene (8 mL) was degassed for 30 min. The flask was then taken into a drybox and tetrakis(triphenylphosphine)palladium(0) (14.4 mg, 0.013 mmol) and cuprous iodide (2.4 mg, 0.013 mmol) were added. After the reaction mixture was refluxed under nitrogen for 48 h, it was filtered at room temperature to remove triethylammonium bromide precipitate. The salt was rinsed with diethyl ether, and the combined filtrates were evaporated to dryness. The residue was dissolved in the minimum amount of methylene chloride which was then poured into methanol (75 mL) to precipitate out the polymer. This process was repeated one more time. The resulting polymer was then separated by centrifugation and was dried under vacuum to give (*R*)-**9c** as a yellow solid (220 mg, 96% yield). GPC (THF, polystyrene standards): $M_w = 29\,000$ and $M_n = 12\,000$ (PDI = 2.4). $[\alpha]_D = -272.2°$ ($c = 0.5$, CH_2Cl_2). FT-IR (KBr, cm^{-1}) 2922 (s), 2852 (s), 2204 (w), 1620 (m), 1520 (s), 1482 (s), 1342 (s), 1265 (s), 1242 (s), 1088 (m), 1049 (m). UV−vis (CH_2Cl_2, nm) 238, 300, 354, 384 (sh). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (br s, 2H, H-5), 7.92 (d, $J = 8.6$ Hz, 2H, H-4), 7.52 (br, 4H, *p*-phenylene-*H*), 7.43 (d, $J = 8.6$ Hz, 2H, H-3), 7.32 (d, $J = 9.1$ Hz, 2H, H-7), 7.11 (d, $J = 9.1$ Hz, 2H, H-8), 3.98−3.94 (br, 4H, OCH_2), 1.47−1.01 (br, 64H, CH_2), 0.94−0.85 (br, 6H, CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 155.3, 133.6, 131.5, 129.2, 128.6, 125.4, 123.1, 120.0, 117.7, 115.9, 91.9, 88.9, 69.4, 31.9, 29.7, 29.5, 29.3, 29.2, 29.1, 25.6, 22.7, 14.1. Anal. Calcd for $C_{66}H_{88}O_2$: C, 86.84; H, 9.65. Found: C, 85.26; H, 9.83.

In a similar way, *rac*-**9c**, (*R*)-**10c**, and *rac*-**10c** were obtained.

rac-**9c**. GPC: $M_w = 47\,000$ and $M_n = 25\,000$ (PDI = 1.9). FT-IR (KBr, cm^{-1}) 2920 (s), 2850 (s), 2210 (w), 1620 (m), 1591 (m), 1465 (s), 1342 (m), 1287 (s), 1244 (s), 1091 (m), 1037 (m), 835 (m). UV−vis (CH_2Cl_2, nm) 238, 300, 356, 381 (sh). ^{1}H

NMR (400 MHz, $CDCl_3$) δ 8.05 (br, 2H), 7.90 (d, $J = 9.1$ Hz, 2H), 749 (br, 4H), 7.40 (d, $J = 9.1$ Hz, 2H), 7.29 (d, $J = 8.6$ Hz, 2H), 7.10 (d, $J = 9.1$ Hz, 2H), 3.95−3.89 (br, 4H, OCH_2), 1.42−0.98 (br, 64H, CH_2), 0.85−0.82 (br, 6H, CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 155.3, 133.6, 131.6, 131.4, 129.2, 128.6, 125.4, 123.1, 120.0, 117.7, 115.9, 91.9, 88.9, 69.4, 31.9, 29.7, 29.5, 29.3, 29.2, 29.1, 25.6, 22.7, 14.1. Anal. Calcd for $C_{66}H_{88}O_2$: C, 86.84; H, 9.65. Found: C, 85.15; H, 9.59.

(*R*)-**10c**. GPC: $M_w = 37\,000$ and $M_n = 18\,000$ (PDI = 2.1). $[\alpha]_D = -299.6°$ ($c = 0.5$, CH_2Cl_2). FT-IR (KBr, cm^{-1}) 2955 (s), 2850 (s), 2210 (w), 1620 (m), 1599 (s), 1462 (s), 1342 (s), 1267 (s), 1242 (s), 1099 (m), 1045 (m), 821 (m). UV−vis (CH_2Cl_2, nm) 234, 306 (sh), 352. ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (br, 2H, H-5), 7.92 (d, $J = 8.8$ Hz, 2H, H-4), 7.62 (br, 8H, *p*-biphenylene-*H*), 7.44 (d, $J = 8.8$ Hz, 2H, H-7), 7.34 (d, $J = 8.8$ Hz, 2H, H-3), 7.14 (d, $J = 8.8$ Hz, 2H, H-8), 3.99−3.93 (br, 4H, OCH_2), 1.46−1.02 (br, 64H, CH_2), 0.89−0.85 (br, 6H, CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 155.3, 139.8, 133.6, 132.1, 132.0, 129.2, 128.8, 126.7, 125.4, 122.7, 120.0, 117.8, 115.9, 91.1, 88.9, 69.4, 31.2, 29.7, 29.6, 29.3, 29.2, 29.1, 25.6, 22.7, 14.1. Anal. Calcd for $C_{72}H_{92}O_2$: C, 87.45; H, 9.31. Found: C, 85.64; H, 9.19.

rac-**10c**. GPC: $M_w = 54\,000$ and $M_n = 25\,000$ (PDI = 2.1). FT-IR (KBr, cm^{-1}) 2918 (s), 2850 (s), 2204 (w), 1620 (m), 1589 (s), 1467 (s), 1344 (s), 1273 (s), 1242 (s), 1091 (m), 1037 (m), 821 (m). UV−vis (CH_2Cl_2, nm) 236, 310 (sh), 354. ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (br, 2H), 7.93 (d, $J = 8.6$ Hz, 2H), 7.62 (br, 8H), 7.45 (d, $J = 9.1$ Hz, 2H), 7.34 (d, $J = 8.6$ Hz, 2H), 7.15 (d, $J = 8.6$ Hz, 2H), 3.99−3.95 (br, 4H, OCH_2), 1.43−1.02 (br, 64H, CH_2), 0.89−0.86 (br, 6H, CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 155.3, 139.8, 133.6, 132.1, 132.0, 129.2, 128.7, 126.8, 125.5, 122.8, 120.1, 117.9, 115.9, 91.2, 88.9, 69.4, 31.9, 29.8, 29.7, 29.6, 29.4, 29.3, 29.2, 25.6, 22.7, 14.1. Anal. Calcd for $C_{72}H_{92}O_2$: C, 87.45; H, 9.31. Found: C, 85.13; H, 8.92.

Preparation of the Repeat Unit 16. In a 50 mL flame-dried Schlenck flask, a mixture of 6-bromo-2-(neopentyloxy)-naphthene (145 mg, 0.49 mmol), **5** (50 mg, 0.25 mmol), and triethylamine (10 mL) was degassed with nitrogen for 30 min. The flask was then taken into a drybox and palladium(II) chloride (2.2 mg, 0.012 mmol), triphenylphosphine (6.48 mg, 0.025 mmol), and cuprous iodide (2.4 mg, 0.013 mmol) were added. The reaction mixture was refluxed under nitrogen, for 26 h during which the product precipitated out with triethylammonium bromide. The mixture was filtered at room temperature and the solid was washed with diethyl ether, water, 3 M HCl, and water. After drying under vacuum, the solid was recrystallized from THF. After filtration and washing with hexane, **16** was obtained as a bright yellow solid in 45% yield. Mp > 300 °C. FT-IR (KBr, cm^{-1}) 2953 (s), 2903 (m), 2866 (m), 2210 (w), 1624 (s), 1599 (s), 1473 (s), 1396 (s), 1257 (s), 1209 (s), 1016 (s), 821 (s). UV−vis (CH_2Cl_2, nm) 236, 296 (sh), 348. ^1H NMR (270 MHz, $CDCl_3$) δ 8.01 (s, 2H), 7.75−7.54 (m, 14H), 7.21 (dd, $J = 2.2, 8.8$ Hz, 2H), 7.12 (s, 2H), 3.74 (s, 4H, OCH_2), 1.10 (s, 18H, CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 158.3, 139.9, 134.2, 132.1, 131.3, 129.2, 128.9, 128.4, 126.9, 126.8, 122.8, 119.9, 117.8, 106.5, 91.1, 88.8, 77.5, 31.9, 26.7. MS m/z 626 (M^+).

In a similar way, the repeat unit **14** was obtained as a light brown solid (78% yield). UV−vis (CH_2Cl_2, nm) 236, 290, 350, 374 (sh). FT-IR (KBr, cm^{-1}) 2955 (s), 2899 (m), 2864 (m), 2210 (w), 1624 (s), 1601 (s), 1499 (s), 1473 (s), 1390 (s), 1257 (s), 1209 (s), 1188 (s), 1138 (s), 1016 (s), 854 (s). ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 2H), 7.74−7.69 (m, 4H), 7.56 (s, 4H), 7.54 (d, $J = 1.6$ Hz, 2H), 7.21 (dd, $J = 2.2, 8.6$ Hz, 2H), 7.12 (d, $J = 2.2$ Hz, 2H), 3.74 (s, 4H, OCH_2), 1.10 (s, 18H, CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 158.3, 134.3, 131.5, 131.4, 129.2, 128.8, 128.3, 126.8, 123.1, 119.9, 117.6, 106.4, 91.9, 88.8, 77.9, 31.9, 26.7. MS m/z 550 (M^+).

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