Alkyne-Bridged Carbazole Polymers by Alkyne Metathesis

Glen Brizius, Stephen Kroth, and Uwe H. F. Bunz*

Department of Chemistry and Biochemistry, The University of South Carolina, Columbia, South Carolina 29208

Received October 15, 2001
Revised Manuscript Received April 23, 2002

Introduction

We describe the metathesis of *N*-alkyl-3,6-dipropynylcarbazoles (**1**) into *N*-alkyl poly(carbazolyleneethynylene)s (**2**) (see Scheme 1). Metathesis was performed using the "shake-and-bake" system,[1] a mixture of $Mo(CO)_6$/*p*-chlorophenol in *o*-dichlorobenzene at 140 °C for 24 h.

The carbazole unit is known as a hole-transporting and electroluminescent structure;[2a] its simple functionalization[2b] has allowed the preparation of attractive polymers containing carbazole in the main chain[3a−d] (as building blocks) as well as polymers containing carbazoles as pendant groups in the side chains.[4] The results are blue-emitting polymers, polymers with tunable electroluminescence, blue-green electroluminescent polymers, and copolymers with improved materials properties.[5a−d]

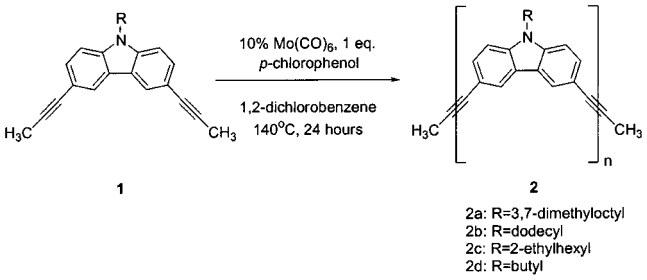
One example of polymers **2** has been reported in the literature;[6] however, the described *N*-hexyl polymer exhibited branched defects (attributed by the authors to palladium-catalyzed bond-opening polymerization), and no information regarding the polymers' fluorescence behavior was provided.

Alkyne metathesis using $Mo(CO)_6$/phenols allows the facile synthesis of a wide variety of alkyne-bridged materials, including organometallic polymers,[7a] fluorene polymers,[7b] PPV/PPE hybrids,[7c] and naphthalene-containing polymers.[7d] The catalytic system has also been found to be tolerant of heteroatoms providing they are positioned away from the alkyne unit.[7c,8] We are interested in broadening the scope of alkyne metathesis using the $Mo(CO)_6$/phenolic system and therefore report an alternative synthesis of **2** and an investigation of its optical properties as a step in that direction.

Monomer synthesis started with propynylation of commercially available 3,6-dibromocarbazole using $PdCl_2(PhCN)_2$/$P(t\text{-}Bu)_3$; this catalyst is reported to be active toward the alkynylation of "deactivated" (electron-rich) aryl bromides.[9] The 3,6-dipropynylcarbazole was isolated in an acceptable 54% yield and functionalized with a variety of alkyl groups (2-ethylhexyl, dodecyl, 3,7-dimethyloctyl, and butyl) using K_2CO_3/RBr in refluxing DMF. The resulting *N*-alkyl-3,6-dipropynylcarbazoles **1** were obtained in 65−70% yield. Polymerization of **1** using 10 mol % $Mo(CO)_6$/1 equiv of *p*-chlorophenol for 24 h in *o*-dichlorobenzene at 140 °C, followed by precipitation into methanol, yielded the polymers as beige powders.

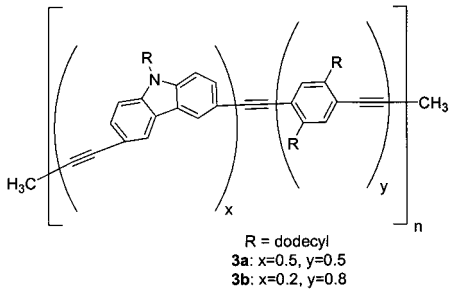
The butyl monomer **1d** was polymerized in dilute solution (approximately 6 mM) to test the possibility of ring-closing metathesis with these compounds. Mass spectral analysis of the crude product suggests the presence of the cyclic tetramer (*m*/*z* 980.5), although it

Scheme 1



was forming in too low of a yield to be isolated and characterized. To test the effects of incorporating these monomers into the poly(*p*-phenyleneethynylene)s,[10] two copolymers **3a**,**b** were prepared. *N*-Dodecyl-3,6-dipropynylcarbazole (**1b)** was copolymerized with 1 or 4 equiv of 1,4-dipropynyl-2,5-didodecylbenzene, yielding yellow polymers after precipitation into methanol. The polymers **2a**−**c** and **3a**,**b** are well soluble in chloroform and moderately soluble in dichloromethane. Table 1 shows some of the characterization data. The degree of polymerization increases with decreasing carbazole content, as is expected given the relatively sluggish activity of heteroatom-containing monomers in acyclic diyne metathesis (ADIMET) as compared with pure hydrocarbons utilizing this catalytic system.[7c,8] The IR alkyne signals for polymer **2c** are not visible for symmetry reasons (monomer alkyne stretching vibration 2227 cm^{-1}). This peak however can be easily distinguished in copolymers **3a** and **3b** as a band at 2204 cm^{-1}. No signal attributable to an "end-group" alkyne was found in the ^{13}C spectra, only one alkyne peak is seen in the polymer **2a** ^{13}C spectrum at δ 89.10 ppm.

Solution absorption spectra of **2** are unremarkable; addition of methanol does not induce a noticeable aggregation/planarization peak as seen in the PPEs.[10] Figure 1 compares the solution absorption spectra of a monomer to its corresponding polymer. Figure 2 shows the UV−vis and fluorescence spectra of a film of polymer **3b**. The fluorescence of polymers **2** exhibit a large Stokes shift, on the order of approximately 200 nm. Fluorescence studies on inceasingly dilute polymer solutions in chloroform, which displayed similar spectra, suggest that excimers are not responsible for this shift. The fluorescence spectra of PPE copolymers **3a** and **3b** show a bathochromic shift going from solution to the solid state, with polymer **3b** (80% PPE) having the larger shift of the two. This is reminiscent of the behavior seen in the parent PPE, that of forced planarization leading to increased conjugation and therefore a lower band gap. While this behavior in the parent PPE can be mimicked



* Corresponding author. E-mail: bunz@mail.chem.sc.edu.

10.1021/ma011788o CCC: $22.00
Published on Web 05/24/2002

Table 1. Characterization of Polymers 2a−c and 3a,b

polymer	% yield	M_w (P_n)[a]	M_w/M_n	λ_{max}, solution, nm	λ_{max}, film, nm	λ_{max}, emission, solution, nm	λ_{max}, emission, film nm	$\Phi_{f,\,sol}$
2a	86	9579 (31)	3.1	314, 354	318, 342	513		0.016
2b	98	5515 (24)	2.3	310, 348	345, 362	511		0.022
2c	94	9797 (26)	3.7	320, 356	344, 368	411, 508		0.015
3a	82	33152 (69)	4.7	366	400	421, 443	435, 467	0.362
3b	93	34416 (114)	3.0	374	412	423, 445	472, 500	0.555

[a] P_n is calculated by GPC, relative to polystyrene standard.

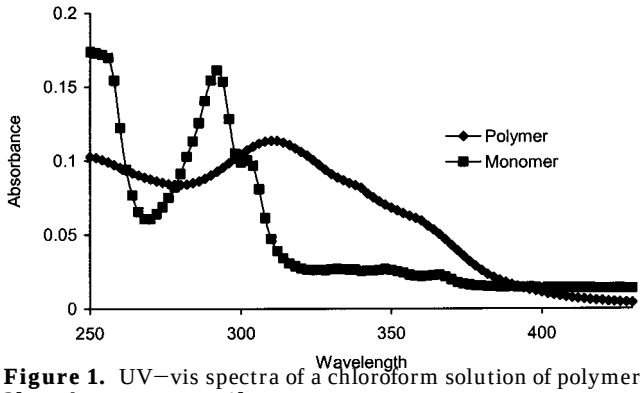


Figure 1. UV−vis spectra of a chloroform solution of polymer **2b** and its monomer **1b**.

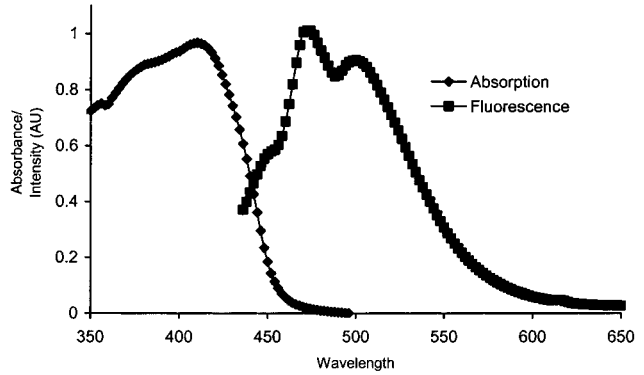


Figure 2. UV−vis/fluorescence spectra of a film of polymer **3b**. The excitation wavelength was 350 nm.

by the addition of a nonsolvent, in **2** the kinked disorder of the random carbazole units is apparently sufficient to minimize aggregation-induced planarization in solution, as has been noted[5d] in other carbazole copolymers.

The quantum yield of fluorescence of chloroform solutions of **2** and **3** increases with decreasing carbazole content, as expected given the break in conjugation with the 3,6-substitution on the carbazole unit.[5d] The solution quantum yields of fluorescence increase in a nonpolar solvent such as hexane as compared to chloroform (10.6% vs 1.5%). Addition of a few drops of trifluoroacetic acid to polymer solutions in chloroform efficiently quenches the fluorescence; even in a copolymer with only 20% carbazole units (polymer **3b**), addition of TFA quenches the fluorescence of the highly emissive PPE ($\phi = 0.0056$ after addition of acid). Washing with dilute base fully restores the fluorescence of the polymer solutions. Addition of a drop of concentrated HCl to **3b** leads to the same change in emission as TFA. While carbazoles of similar structure[6] are known to form remarkably stable radical cations, and despite the oxidizing ability of TFA, protonation and not oxidation is the source of the spectral changes of **3b** upon addition of acid.

Remarkably, polymers **2a−c** show a significant blue shift in their solution fluorescence upon addition of

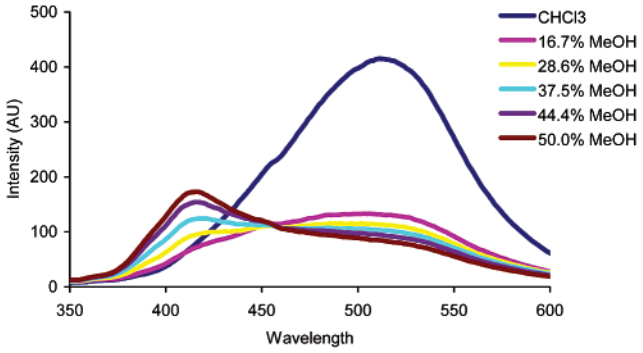


Figure 3. Fluorescence spectrum of polymer **2a** in $CHCl_3$/MeOH.

methanol to their chloroform solution, as demonstrated in Figure 3. The fluorescence spectrum of polymer **2a** in 1:1 MeOH/$CHCl_3$ (0.1 mg of polymer/100 mL of solvent) closely matches that of a more concentrated chloroform solution (4 mg/100 mL of solvent). Since self-absorption at this wavelength (under this concentration) is very low (less than 0.06), true aggregate formation appears to be responsible for the observed blue shift. Unfortunately, polymers **2a−c** are not sufficiently fluorescent in the solid state to obtain reliable fluorescence spectra.

DSC analysis of the polymer **2a** shows no transitions, save a slow decomposition above 350 °C. Polymer **2b** shows two transitions at 168 °C (T_g) and 211 °C. Polymer **2c** shows a small transition (attributed to side chain melting) at 50 °C and a second-order transition at 142 °C. Both polymers **3a** and **3b** show a side chain melting at 46 and 42 °C, respectively. Neither **3a** nor **3b** shows DSC signals attributable to liquid crystalline states, which is reinforced by the failure of polarizing microscopy to detect either lyotropic or thermotropic liquid crystalline textures in samples of polymers **3a** and **3b.** Powder X-ray diffraction analysis of these polymers shows a broad and unstructured *d*-spacing around 4 Å, typical of amorphous carbon-containing materials.

In conclusion, we have demonstated the utility of alkyne metathesis with simple catalyst systems toward the preparation of alkyne-bridged carbazole polymers. These polymers show a blue shift in their fluorescence upon addition of a poor solvent. Making copolymers with PPE gives emissive polymers whose fluorescence can be reversibly quenched by the addition of TFA/mild base. Future work will include synthesis of the 2,7-propynyl analogues; these are predicted to be more highly conjugated, to yield polymers with even more interesting fluorescence properties.

Experimental Section

General Instrumentation. Gel permeation chromatography (GPC) was performed on a Shimadzu LC6AD with a SCL10A system controller utilizing a Waters Styragel HM-WGE 7.8 × 300 mm column with polystyrene standards and chloroform (flow rate 1 mL min^{-1}) as eluent. The ^1H and ^{13}C

NMR spectra were recorded with a Varian Mercury 400 MHz spectrometer operating at 400 MHz (^{1}H) and 100.6 MHz (^{13}C). The ^{1}H chemical shifts are referenced to the residual proton peaks of $CDCl_3$ at δ7.24 (vs TMS). The ^{13}C resonances are referenced to the central peak of $CDCl_3$ at δ77.0 (vs TMS). All NMR spectra were obtained in $CDCl_3$ solvent, except for some polymer carbon spectra which were obtained in TCE-d_2. The mass spectra were obtained on a Varian CH7a and a VG Instruments ZAB 2. UV−vis measurements were made with a Jasco V530 spectrometer. A Headway Research model PWM32 instrument was used to spin-coat dilute chloroform solutions onto either quartz or glass slides for thin film experiments. DSC was performed on a Mettler DSC 821^e. Powder diffraction was performed on a Rigaku D/Max 2200 powder X-ray diffractometer at 298 K.

3,6-Dipropynylcarbazole. An oven-dried 1000 mL Schlenk flask was charged under nitrogen with 5.00 g (15.4 mmol) of 3,6-dibromocarbazole, 230 mg (0.600 mmol) of $PdCl_2(PhCN)_2$, and 76.0 mg (0.402 mmol) of CuI. The flask was evacuated using a vacuum pump, and 0.15 mL of a 1 M P(*t*-Bu)$_3$ solution in dioxane, along with 5 mL of diisopropylamine and 10 mL of toluene, was added by syringe. The flask was then filled with propyne through the sidearm. Stirring and heating overnight to 60 °C followed by filtering through silica several times (dichloromethane eluent) and evaporation led to a beige solid. Recrystallization from 1:20 dichloromethane:hexane led to the pure product as a beige powder; yield 2.01 g (53.8%). ^{1}H NMR: δ 8.09 (s, 2H), 7.91 (bs, 1H), 7.45 (m, 2H), 7.17 (m, 2H), 2.12 (s, 6H). ^{13}C NMR: δ 138.81, 129.60, 123.56, 122.63, 115.00, 110.59, 83.84, 80.43, 4.31. HRMS: M^+ calc = 243.1048, obs = 243.1044. IR (cm^{-1}, thin film): 3482, 3404, 2910, 2358, 1653, 1624, 1479, 1283, 1323, 1130, 1021, 891, 810, 753.

General Alkylation Procedure. 1 equiv of 3,6-dipropynylcarbazole, 2 equiv of potassium carbonate, and 1.5 equiv of the alkyl bromide were heated to reflux in DMF for 24 h. Water and ether were then added, followed by ether extraction. The combined organic layers were dried over anhydrous $MgSO_4$, and the solvent was removed in vacuo. The resulting oils were purified using column chromatography with silica slurry packed in 10% NEt_3/90% hexane. Eluting with 10% EtOAc/hexane gave the pure monomers as colorless to light yellow viscous oils.

Characterization. ***N*-(3,7-Dimethyloctyl)-3,6-dipropynylcarbazole.** 58.8% yield. ^{1}H NMR: δ 8.11 (s, 2H), 7.52 (m, 2H), 7.25 (m, 2H), 4.16 (m, 2H), 2.13 (s, 6H), 0.89−1.78 (m, 19H). ^{13}C NMR: δ 139.66, 129.27, 123.66, 122.27, 114.38, 108.47, 93.48, 80.51, 41.15, 39.09, 36.93, 35.39, 30.76, 27.86, 24.53, 22.60, 22.52, 19.58, 4.35. HRMS: M^+ calc = 383.2613, obs = 383.2621. IR (cm^{-1}, thin film): 2954, 2917, 2867, 2336, 1697, 1624, 1479, 1370, 1283, 1203, 1145, 883, 803.

***N*-Dodecyl-3,6-dipropnylcarbazole.** 93.1% yield. ^{1}H NMR: δ 8.12 (s, 2H), 7.51 (s, 2H), 7.24 (s, 2H), 4.16 (t, 3H), 2.13 (s, 6H), 1.76−1.82 (m, 2H), 1.05−1.78 (m, 18H), 0.89−0.94 (t, 3H). ^{13}C NMR: δ 139.84, 129.38, 123.63, 122.24, 114.40, 108.63, 83.48, 80.50, 43.05, 31.87, 29.55, 29.49, 29.30, 28.84, 27.15, 22.65, 14.08, 4.33. HRMS: M^+ calc = 411.2926, obs = 411.2916. IR (cm^{-1}, thin film): 2925, 2852, 1733, 1603, 1479, 1385, 1348, 1261, 1152, 876, 803.

***N*-(2-Ethylhexyl)-3,6-dipropynylcarbazole.** 82.2% yield. ^{1}H NMR: δ 8.13 (s, 2H), 7.52 (s, 2H), 7.25 (s, 2H), 3.94 (d, 2H), 2.14 (s, 6H), 1.93−1.97 (m, 1H), 1.23−1.33 (m, 8H), 0.84−1.08 (m, 6H). ^{13}C NMR: δ 140.10, 129.20, 123.38, 122.04, 114.31, 108.75, 83.34, 80.46, 47.03, 39.07, 30.71, 28.50, 24.12, 22.83, 13.79, 10.61, 4.17. HRMS: M^+ calc = 355.2300, obs = 355.2305. IR (cm^{-1}, thin film): 3048, 2954, 2859, 2754, 2227, 2046, 1871, 1704, 1601, 1479, 1385, 1348, 1283, 1210, 1174, 1065, 891, 882, 803, 759, 694, 665.

General Polymerization Procedure. The monomers were dissolved in 1,2-dichlorobenzene along with 1 equiv of *p*-chlorophenol and 0.1 equiv of $Mo(CO)_6$. Heating to 140 °C for 24 h under N_2 purge followed by multiple precipitations into methanol yielded the polymers as beige to yellow solids in 80−90% yield. The comonomer 1,4-dipropynyl-2,5-didodecylbenzene was synthesized according to the literature method.[1]

Polymer 2a. ^{1}H NMR: δ 8.38 (s, 2H), 7.69 (d, 2H), 7.33 (d, 2H), 4.29 (bm, 2H), 0.85−1.86 (bm, 19H). ^{13}C NMR: δ 177.66, 139.95, 129.61, 129.24, 123.78, 122.64, 114.56, 108.67, 89.10, 41.42, 39.10, 36.97, 35.47, 30.91, 29.46, 27.73, 24.41, 22.46, 22.41, 19.57. IR (cm^{-1}, thin film): 3407, 3057, 2954, 2926, 2867, 1627, 1600, 1570, 1290, 1382, 1355, 1283, 1211, 1148, 1132, 1059, 1023, 881, 803, 733, 655.

Polymer 2b. ^{1}H NMR: δ 8.25 (s, 2H), 7.62 (d, 2H), 7.23 (d, 2H), 4.05 (d, 2H), 2.02 (m, 1H), 0.82−1.58 (bm, 14H). ^{13}C NMR: δ 140.83, 129.47, 124.10, 122.84, 114.63, 109.41, 89.31, 47.84, 39.62, 31.22, 28.98, 24.64, 23.27, 14.26, 11.15. IR (cm^{-1}, thin film): 3403, 2922, 2851, 1628, 1599, 1569, 1290, 1383, 1351, 1284, 1254, 1216, 1149, 1101, 882, 803, 722, 654.

Polymer 2c. ^{1}H NMR: δ 8.33 (s, 2H), 7.65 (d, 2H), 7.31 (d, 2H), 4.22 (m, 2H), 1.81 (m, 2H), 0.65−1.45 (bm, 21H). ^{13}C NMR: δ 140.09, 129.22, 123.74, 122.57, 114.56, 108.78, 89.10, 43.22, 31.69, 29.38, 29.33, 29.27, 29.12, 29.07, 28.76, 27.07, 22.44, 13.85. IR (cm^{-1}, thin film): 2956, 2926, 2871, 1600, 1490, 1379, 1350, 1284, 1203, 1140, 1131, 879, 803, 666.

Polymer 3a. ^{1}H NMR: δ 8.22 (bs, carbazole), 7.58 (bd, carbazole), 7.19 (bm, carbazole plus benzene ring), 4.23 (bs, carbazole alkyl), 2.11 (bm), 0.76−1.78 (bm, alkyl chains). ^{13}C NMR: δ 141.86, 141.75, 140.39, 132.23, 131.99, 129.66, 123.73, 122.50, 14.33, 108.90, 95.03, 87.28, 43.33, 34.10, 31.65, 30.43, 29.46, 29.42, 29.34, 29.21, 29.06, 29.04, 28.75, 27.05, 22.40, 13.79. IR (cm^{-1}, thin film): 2923, 2852, 2356, 2204, 1628, 1496, 1466, 1380, 1351, 1284, 1232, 1119, 1010, 881, 804, 721, 654.

Polymer 3b. ^{1}H NMR: δ 8.29 (s, H), 7.66 (d, 2), 7.25−7.35 (bm, 4H), 4.31 (bm, 2H), 2.85 (bm, 6H), 1.20−1.83 (bm, 33H), 0.85 (bm, 9H). ^{13}C NMR: δ 141.87, 141.76, 140.43, 132.24, 131.99, 129.65, 123.73, 122.51, 114.31, 108.93, 95.29, 93.15, 43.34, 34.05, 31.67, 30.43, 29.46, 29.42, 29.34, 29.22, 29.08, 29.04, 28.75, 27.05, 22.41, 13.80. IR (cm^{-1}, thin film): 2922, 2852, 1498, 804.

Acknowledgment. We thank the Petroleum Research Fund and the National Science Foundation (NSF CHE 0138-659) for financial support and K. Stitzer for collection of the diffraction data.

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MA011788O