Regio- and Stereoselective Synthesis of a *trans*-4-[60]Fullerenobisacetic Acid Derivative by a Tether-Directed Biscyclopropanation: A Diacid Component Applicable for the Synthesis of Regio- and Stereo-regular [60]Fullerene Pearl-Necklace Polyamides

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A *trans*-4-[60]fullerenobisacetic acid derivative was easily obtained from its diethyl ester, which was regio- and stereoselectively prepared by the biscyclopropanation of [60]fullerene with a tethered bis(α-bromophenylacetate) derivative. The polycondensation of the resultant fullerenobisacetic acid with aromatic diamines proceeded smoothly to give the corresponding regio- and stereo-regular [60]fullerene pearl-necklace polyamides in excellent yields.

The fascinating structure and properties of fullerenes have led to rapid development of their chemistry.[1] In particular, the synthesis of fullerene polymers is highly intriguing from the standpoint of their potential technological applications. Among the fullerene polymers, polymers containing [60]fullerene (C_{60}) molecules in the main chain, so-called pearl-necklace polymers, are of great interest, because the electrons in the polymers are expected to show a unique behavior arising from their interplay between the fullerene cores and the linkers. Pearl-necklace polymers, however, have been rarely reported owing to difficulty to be prepared.[2,3]

Recently, we have succeeded in the synthesis of *trans*-2- and *equatorial*-[60]fullerenobisacetic acids and applied to the synthesis of the corresponding [60]fullerene pearl-necklace polyamides.[3] However, there is still great room for the improvement in the synthesis of the fullerenobisacetic acids, since the yields were very low (7–17%) due to the formation of many regioisomers and since a tedious separation by silica-gel chromatography, followed by preparative HPLC, was inevitably required. In addition, The stereochemistry of the substituents on the bridge-head carbon of the cyclopropane rings could not be controlled in a strict sense. Herein, we describe the regio- and stereoselective synthesis of a *trans*-4-[60]fullerenobisacetic acid derivative through a tether-directed biscyclopropanation and its application to the synthesis of regio- and stereo-regular pearl-necklace polyamides.

We first attempted the selective hydrolysis of both terminal ester groups of *trans*-4-adducts **1a–c**, prepared previously in a regioselective manner via a tether-directed biscyclopropanation (the double Bingel reaction[4]),[5] by conventional methods. However, all trials resulted in failure and gave complex mixtures, because the hydrolysis of the internal ester group took place more readily than that of the terminal ester group(s) presumably due to the strain of the bridge. This fact promoted us to apply the selective hydrolysis of the internal ester group to the preparation of the *trans*-4-adduct **4**; we designed and prepared the substrate **2** having phenylacetyl moieties, which are known to be applicable to the Bingel reaction as well as malonyl moieties, connected with


1a: R = -^tBu
1b: R = -CH₂CH₂TMS
1c: R = -Me
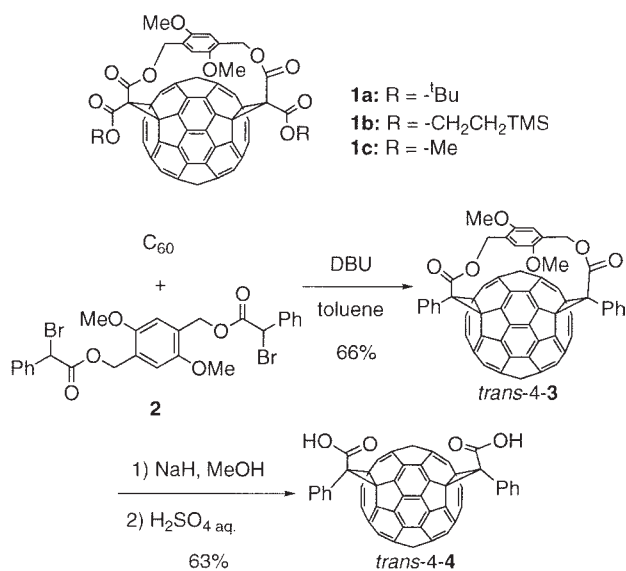
Scheme 1.

the same tether as that in **1**.

Scheme 1 shows the route for the synthesis of *trans*-4-[60]fullerenobisacetic acid derivative **4**. The substrate **2**[6] was easily prepared by the reaction of α-bromophenylacetic acid and 1,4-bis(hydroxymethyl)-2,5-dimethoxybenzene[7] in 66% yield. The biscyclopropanation of C_{60} with **2** in the presence of 1,7-diazabicyclo[5.4.0]undec-7-ene proceeded regioselectively to give the *trans*-4-[60]fullerenoadduct **3**[8] in 66% with a small amount of the *equatorial*-adduct (7%) as a regioisomer; pure **3** was isolated by a simple separation with single silica-gel column chromatography. The adduct **3** showed a very similar UV-vis spectrum to those in the library of *trans*-4-[60]fullereno-bisadducts reported by Dijojo et al.[9] The hydrolysis of **3** with NaH and methanol took place smoothly to give the *trans*-4-[60]fullerenobisacetic acid **4**[10] in 63% yield; upon the hydrogenolysis the proton signals of the tether part completely disappeared in the ^{1}H NMR spectrum, and in its IR spectrum the C=O absorption shifted to 1720 cm^{-1} from 1739 cm^{-1} of **3**. It is noteworthy that not only the regiochemistry (the formation of the *trans*-4-adduct) but also the stereochemistry (the formation of the in-in dicarboxylic acid) of the cyclopropane moieties on **4** is obviously controlled because of the formation of **3** through tether-directed biscyclopropanation of C_{60} with **2**.

In the next stage, the diacid component **4** was applied to the synthesis of *trans*-4-[60]fullerene pearl-necklace polyamides **6** (Scheme 2). The polycondensation of **4** with aromatic diamines **5a–c** took place easily by using (PhO)₃P and pyridine as
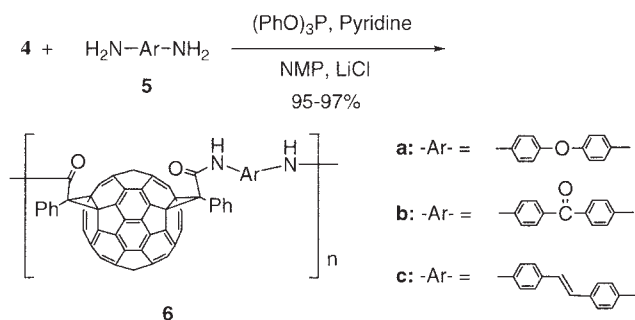
Scheme 2.

**Table 1.** The yield, IR stretching, and molecular weight of polymers **6**

Polymer	Yield/%[a]	IR stretching[b]		Mw[c]/10³ (g/mol)
		ν_{N-H}/cm⁻¹	$\nu_{C=O}$/cm⁻¹	
6a	97	3420	1660	9.6
6b	95	3420	1670	9.7
6c	95	3415	1670	9.9

[a]Polymerization was carried out in a 0.1 mmol scale by using 0.25 mL of (PhO)₃P and 0.25 mL of pyridine in the presence of 100 mg of LiCl at 115 °C for 4 days. [b]ν_{N-H} and $\nu_{C=O}$ represent the IR stretching of the corresponding groups in the polymer. [c]Mw represents the weight-average molecular weight.

condensating agents in *N*-methylpyrrolidinone (NMP) in the presence of LiCl to give the polyamides **6a–c** in excellent yields[11] (Table 1). Thus, regio- and stereo-regular [60]fullerene pearl-necklace polymers could be synthesized for the first time.

The IR absorptions of **6a–c**, corresponding to the C=O stretching, shifted from 1720 cm⁻¹ of **4** to about 1680 cm⁻¹ in all cases (in the case of polymer **6b**, overlapped with the C=O stretching of the 4,4′-diaminobenzophenone moiety). This shift clearly demonstrates the formation of amide linkages. GPC measurement indicated that the polyamides **6a–c** had a weight-average molecular weight (Mw) of 9.6–9.9 × 10³. The resultant polymers **6a–c** were soluble in aprotic polar solvents, such as *N*,*N*-dimethylacetamide (DMAc) and dimethylformamide as well as NMP, and slightly soluble in THF, but insoluble in methanol, toluene, and acetone.

Figure 1 shows the UV-vis spectra of **4** and **6a–c** in DMAc. These spectra are similar to those of *equatorial*-[60]fullerene pearl-necklace polyamides previously prepared,[5] which showed a tailing of the absorption to longer wavelengths. This means that
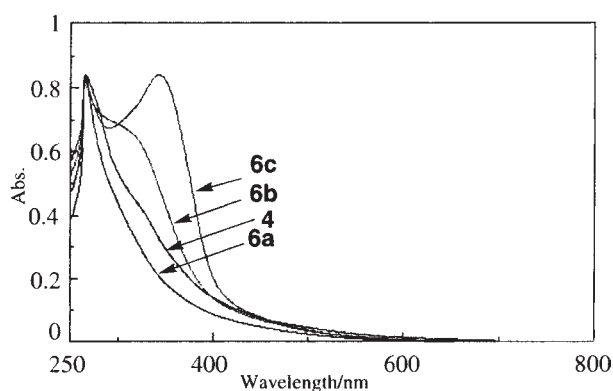
Figure 1. UV-vis spectra of monomer **4** and polymers **6a–c** in DMAc.

there is some electronic communication between the C₆₀ cores and the diamine moieties in the polyamides **6a–c**. Further investigation on the properties of **6a–c** is now in progress.

References and Notes
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6   **2**: ¹H NMR (CDCl₃, 300 MHz) δ 3.60 (s, 6H), 5.23 (s, 4H), 5.41 (s, 2H), 6.71 (s, 6H), 7.34–7.38 (m, 6H), 7.55–7.60 (4H, m); ¹³C NMR (CDCl₃, 75 MHz) δ 46.77, 55.90, 63.19, 111.71, 124.06, 128.67, 128.74, 129.22, 135.66, 150.92, 167.95; FAB-Mass *m/z* 592 (M⁺).
7   B. Wang and M. R. Wasielewski, *J. Am. Chem. Soc.*, **119**, 12 (1997).
8   **3**: ¹H NMR (CDCl₃/CS₂, 300 Mz) δ 3.68 (s, 3H), 3.73 (s, 3H), 4.68 (d, *J* = 11.1 Hz, 1H), 5.16 (d, *J* = 10.7 Hz, 1H), 5.73 (d, *J* = 10.7 Hz, 1H), 6.34 (d, *J* = 11.1 Hz, 1H), 6.67 (s, 1H), 6.86 (s, 1H), 7.38–7.60 (m, 3H), 8.01–8.17 (m, 2H); ¹³C NMR (CDCl₃/CS₂, 75 MHz) δ 52.03, 52.90, 55.42, 55.61, 61.36, 63.27, 73.44, 74.00, 74.14, 74.31, 114.31, 114.64 (×2), 114.88, 124.58, 125.89, 128.62 (2C), 128.73 (2C), 129.13 (2C), 129.22 (2C), 131.17 (2C), 131.47 (2C), 131.66 (2C), 131.97 (2C), 132.25, 132.36, 138.50, 138.61 (2C), 138.81, 140.90, 141.06 (2C), 141.29 (2C), 141.59 (2C), 142.13 (2C), 142.28, 142.47, 142.55, 142.66 (2C), 142.81 (2C), 142.90, 142.96 (2C), 143.88, 143.96 (2C), 144.44, 144.59, 144.70, 144.79, 144.99, 145.06 (2C), 145.09, 145.20, 145.29, 145.49 (2C), 145.75, 145.94 (2C), 146.14, 146.31, 146.41, 146.52, 146.57, 146.90, 147.74, 151.40, 152.69, 166.46, 167.08; IR (KBr) ν 1739 (C=O) cm⁻¹; UV-vis (ε): 417 (3900), 473 (2500), 634 (650), 700 (260) nm; FAB-Mass *m/z* 1150 (M⁺).
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10 **4**: ¹H NMR (THF-d₈, 300 MHz) δ 7.69–7.82 (m, 6H), 8.35 (d, *J* = 6.9 Hz, 4H); ¹³C NMR (THF-d₈, 75 MHz): δ 55.89 (2C), 76.68 (2C), 79.66 (2C), 129.37 (4C), 129.81 (4C), 132.65 (4C), 132.89 (4C), 133.36 (4C), 134.60 (2C), 135.94 (2C), 138.48 (2C), 138.94 (2C), 140.63 (2C), 141.50 (2C), 142.18 (2C), 142.66 (2C), 142.90 (2C), 143.06 (2C), 143.37 (2C), 143.77 (2C), 144.61 (2C), 144.77 (2C), 145.71 (2C), 145.95 (4C), 146.19 (2C), 146.50 (2C), 147.20 (2C), 147.76 (2C), 147.82 (2C), 147.89 (2C), 148.66 (2C), 167.78 (2C); IR (KBr) ν 1720 (C=O) cm⁻¹; FAB-Mass *m/z* 988 (M⁺).
11 A typical polymerization procedure: The diacid **4** (98.8 mg, 0.1 mmol), the diamine **5a** (20.0 mg, 0.1 mmol), and LiCl (100 mg) were dissolved in a solution of (PhO)₃P (0.25 mL), pyridine (0.25 mL), and NMP (0.5 mL). The resultant solution was stirred under Ar at 115 °C for 4 days. At 24 h intervals, additional (PhO)₃P (0.25 mL) and pyridine (0.25 mL) were added to the reaction mixture. When the solution became too viscous to be stirred, NMP (0.5 mL) was added. Finally, the reaction mixture was diluted with NMP (5 mL) and poured into methanol (40 mL). The precipitate that appeared was collected by centrifugation, washed with methanol (90 mL), boiled in methanol (80 mL) for 30 min to remove the unreacted starting monomers and the by-products, and dried under vacuum for 12 h. Thus, the polyamide **6a** was obtained in 97% yield. Found: C, 84.05; H, 2.76; N, 2.11%. Calcd for C₈₈H₂₀N₂O₃·6H₂O: C, 83.80; H, 2.56; N, 2.22%.