

Synthesis of a Novel [60]Fullerene Pearl-Necklace Polymer, Poly(4,4'-carbonylbisphenylene *trans*-2-[60]fullerenobisacetamide)

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Received 21 January 1999; accepted 14 May 1999

ABSTRACT: A novel [60]fullerene pearl-necklace polymer, poly(4,4'-carbonylbisphenylene *trans*-2-[60]fullerenobisacetamide), was synthesized by a direct polycondensation of *trans*-2-[60]fullerenobisacetic acid with 4,4'-diaminobenzophenone in the presence of large excesses of triphenyl phosphite and pyridine. In the present polymer, [60]fullerene pearls and diamine linkers were attached to each other by methanocarbonyl connectors. The molecular weight M_w of the polymer was determined to be 4.5×10^4 on the basis of the TOF-MS, and a GPC analysis of the polymer using polystyrene standards showed a weight-average molecular weight of 5.3×10^4 . The UV-vis spectrum of the resultant polymer in *N,N*-dimethylacetamide (DMAc) exhibited a broad absorption (λ_{\max} 310 nm, ϵ 2.1×10^4 L · mol⁻¹ · cm⁻¹), tailing to longer wavelengths, and a fluorescence peak centered at 550 nm was observed in DMAc. There was observed a large downfield-shift of the cyclopropane methyne proton in the ¹H-NMR spectra from 4.57 ppm of the ethyl ester to 5.78 ppm of the polyamide. These observations indicate that the present polyamide is a high-molecular-weight [60]fullerene pearl-necklace polymer and that the cyclopropane rings are efficient to make the [60]fullerene cages and the diamine components conjugatable. © 1999 John Wiley & Sons, Inc. *J Polym Sci A: Polym Chem* 37: 3632–3637, 1999

Keywords: *trans*-2; [60]fullerene; pearl-necklace polymer; polyamide; synthesis

INTRODUCTION

Because the electrons of [60]fullerene can bring about a highly delocalized state on the surface of [60]fullerene,¹ a polymer containing [60]fullerene molecules in the main chain is interesting from the viewpoint of the behavior of the electrons in the polymer as a result of the interplay between

the [60]fullerene clusters and the linkers. Along this line, the synthesis of so-called “pearl-necklace polymers,” in which [60]fullerene molecules are connected with each other by linkers, is of great interest. Although Loy and Assink² have reported the synthesis of a [60]fullerene pearl-necklace copolymer, the interplay could not be determined, because the polymer was insoluble in all solvents due to crosslinking. More recently, Taki et al.³ reported [60]fullerene pearl-necklace polymers in which the conjugation was interrupted on the introduction of functional groups to [60]fullerene.

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Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 37, 3632–3637 (1999)
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A [60]fullerene pearl-necklace polymer with delocalized electrons, not just confined on the cluster of [60]fullerene but extended into the linker, may exhibit interesting functions, such as nonlinear optical properties, electroluminescence, fluorescence, and even metallic conduction. Extended conjugation through the main chain in a [60]fullerene pearl-necklace polymer, however, would be rather difficult, because introducing functional groups onto the [60]fullerene cage usually results in a transformation of the sp^2 carbons of [60]fullerene into sp^3 carbons, and hence the conjugation is terminated at the sp^3 carbon. The functionalization of [60]fullerene by cyclopropanation is one possible approach to extend the conjugation out of a fullerene cage; the carbons of a cyclopropane are known to have a greater p -character than ordinary sp^3 carbons due to cyclopropane's highly distorted bond angle. The attempts described in our previous report⁴ were made along this line using equatorial-[60]fullerenobisacetic acid and 4,4'-diaminodiphenyl ether as components for polyamides. However, the reaction resulted in the formation only of oligomers, due to their low solubility in ordinary nonprotic polar solvents, although high-molecular-weight copolymers with a diacid could be prepared. In this article we report on the synthesis and properties of a high-molecular-weight [60]fullerene pearl-necklace polymer with elongated conjugation

EXPERIMENTAL

Materials

Sublimated [60]fullerene with a purity of 99.99% was used for syntheses. All of the reagents used were of reagent-grade, and the solvents were distilled and dried before use. The reactions were carried out under Ar.

Synthesis of *Trans*-2-[60]fullereno-bisacetic acid

Trans-2-bisadduct, diethyl *trans*-2-[60]fullerenobisacetate (**1**), was synthesized by the reaction of [60]fullerene with dimethylsulfonium ethoxycarbonylmethylide⁵ $(CH_3)_2SCHCOOC_2H_5$ as follows.⁶ To a solution of [60]fullerene (360 mg, 0.5 mmol) in toluene (200 mL), kept at 0°C under Ar, was added a solution having a slight excess of sulfonium ylide (163 mg, 1.1 mmol) in toluene (20 mL) over a period of about 1 h. To remove away unre-

active pristine [60]fullerene and the monoadduct, as well as the trisadducts, from the resultant products, flash silica-gel chromatography was applied with hexane/toluene (3/2 and 2/3, respectively) as the elutions. A mixture of bisadducts was separated by a JAI LC908-C60 (Japan Analytical Industry Co., Japan) preparative HPLC, using Grom-Sil 100 Si NP-1, 5 μ m, 250 \times 20 column (GROM Analytik + HPLC GmbH, Germany) with toluene as an eluent. Bisadducts were eluted in the order of *trans*-2-, *trans*-3-, *trans*-4-, *equatorial*-, *cis*-3-, and then two stereoisomers of *cis*-2-bisadduct. Finally, *trans*-2-bisadduct (**1**) was isolated in 7% yield (32 mg). Then, **1** (89.2 mg, 0.1 mmol) was stirred with 10 equimolar amounts of NaH (48 mg, 2 mmol) in toluene (50 mL) at 60°C for 3 h under Ar. After the solution was treated with methanol (1 mL), the residual solid was washed successively with toluene (30 mL), hexane (15 mL), 2M H_2SO_4 (1 mL), and water to neutral pH.⁷ Finally, the residue was reprecipitated from a tetrahydrofuran (THF) solution with hexane, and dried under dynamic vacuum for 12 h to give 60 mg (72% yield) of brown-colored *trans*-2-[60]fullerenobisacetic acid (**2**).

ANAL. Calcd for $C_{64}H_4O_4 \cdot 2H_2O$: C, 88.08%; H, 0.92%. Found: C, 88.02%; H, 1.36%.

Polymerization

A direct polycondensation method with the aid of triphenyl phosphite and pyridine as condensing reagents, widely used in the preparation of aromatic polyamides,⁸ was applied in the present experiment. **2** (83.6 mg, 0.1 mmol), 4,4'-Diaminobenzophenone (**3**) (21.2 mg, 0.1 mmol) and LiCl (100 mg) were dissolved in a solution of triphenyl phosphite (0.25 mL) and pyridine (0.25 mL) in *N*-methyl- α -pyrrolidinone (NMP) (0.5 mL). The resultant solution was stirred under Ar at 115°C for 4 days. At 24-h intervals, additional triphenyl phosphite (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 (120 mL), boiled in methanol (40 mL) for 30 min to remove away unreacted starting monomers and by-products, and dried under vacuum for 12 h. Thus, poly(4,4'-carbonylbisphenylene *trans*-

2-[60]fullerenobisacetamide) (**4**) was obtained (98 mg, 97% yield).

ANAL. calcd for $C_{77}H_{12}N_2O_3 \cdot 4.5H_2O$: C, 84.54%; H, 1.94%; N, 2.56%. Found: C, 84.78%; H, 2.10%; N, 2.45%.

Characterization

Fourier-transform infrared spectra (FTIR) were obtained by a JASCO FT-IR 8900 using KBr pellets. Ultraviolet-visible (UV-vis) spectroscopy was performed with a Hitachi U-4000. Fluorescence was measured on a JASCO FP-777 W with excitation by a Xe lamp. Nuclear magnetic resonance (1H - and ^{13}C -NMR) spectra were recorded on a JEOL JNM-EX270 NMR spectrometer (270 MHz and 67.7 MHz, respectively). The average molecular weight and polydispersity were determined by gel permeation chromatography (GPC) using polystyrenes as calibration standards. The eluent was DMAc, containing 10mM LiCl. A Bruker Protein TOF was applied to obtain the Matrix-assisted laser desorption/ionization time-of-flight mass spectrum (MALDI-TOF-MS) using 3-indolacrylic acid as a matrix. The inherent viscosity was measured by a Sibata SO-96356 viscosimeter in DMAc at 30°C. Thermogravimetric analysis (TGA) was done with a ULVAC TGD 9600 under Ar at a flow rate of 100 mL/min and a heating rate of 10°C/min.

RESULTS AND DISCUSSION

From the resultant mixture of bisadducts, seven isomers were separated by HPLC in an eluent order of three kinds of *trans*-bisadducts, *equatorial*-bisadduct, and then three kinds of *cis*-bisadducts; the elution order was consistent with the order of the polarities of the bisadducts.

The TOF-MS spectrum indicated that the molecular weight of **1** was 892; **1** should be a bisadduct. The UV-vis spectrum (Fig. 1) of **1** in a toluene solution showed absorptions at 700, 630, 475, and 430 nm, which is very similar to that of a *trans*-2-bis-methano-[60]fullerene product reported by Schick et al.⁹ The 1H -NMR spectrum of **1** exhibited CH protons at 4.57 ppm as a singlet, CH_2 protons at 4.63 ppm as a quartet, and CH_3 protons at 1.64 ppm as a triplet. The ^{13}C -NMR spectrum (Fig. 2) of **1** showed 26 peaks for the sp^2 carbons of the [60]fullerene cage in the range of 134–148 ppm (two of them showed twice the intensities of the others), one peak at 165.42 ppm for the carboxyl carbons,

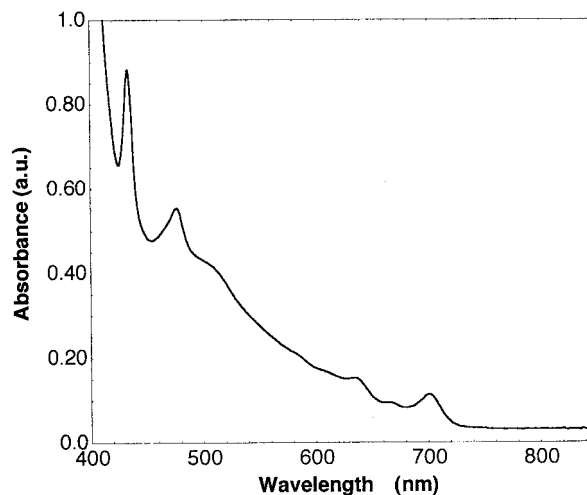


Figure 1. UV-vis absorption spectrum of *trans*-2-bisadduct **1** in toluene.

and two peaks at 69.63 and 70.14 ppm for the sp^3 carbons of the [60]fullerene cage. The cyclopropane bridge carbons appeared at 36.91 ppm, and the CH_2 and CH_3 carbons appeared at 62.07 and 14.53 ppm, respectively. From these spectra, it is deduced that **1** is a bisadduct of C_2 symmetry. Among the bisadducts, *trans*-2-, *trans*-3-, and *cis*-3-bisadducts are possible to be of C_2 symmetry. However, two kinds of bisadducts, eluted after **1** and after *equatorial*-bisadduct, respectively, were identified to be *trans*-3- and *cis*-3-bisadducts, according to the 1H - and ^{13}C -NMR spectra. On the basis of these observations, **1** was confirmed to be *trans*-2-bisadduct.

After the hydrogenolysis of **1** with NaH and methanol, the signals of the CH_2 and CH_3 protons completely disappeared in the 1H -NMR spectrum of **2**. Moreover, in its IR spectrum, the C-H absorption became highly weak, and the C=O absorption shifted to 1717 cm^{-1} from 1742 cm^{-1} of that in **1**. The TOF-MS spectrum showed the parent molecular signal at m/z 836. These observations indicate that complete hydrogenolysis occurred.

The procedure for synthesis of a polymer, poly(4,4'-carbonylbisphenylene *trans*-2-[60]fullerenobisacetamide) (**4**) from *trans*-2-[60]fullerenobisacetic acid (**2**) and 4,4'-diaminobenzophenone (**3**) is shown in Scheme 1. When polymerization was carried out using less than 30 mg of LiCl, only a mixture of oligomers was obtained; LiCl played a role in cleaving the intermolecular and intramolecular hydrogen bonds to improve polymer solubility, as generally observed in the synthesis of polyamides.⁸ In this condensation, a side reaction, such as the direct addition of 4,4'-diami-

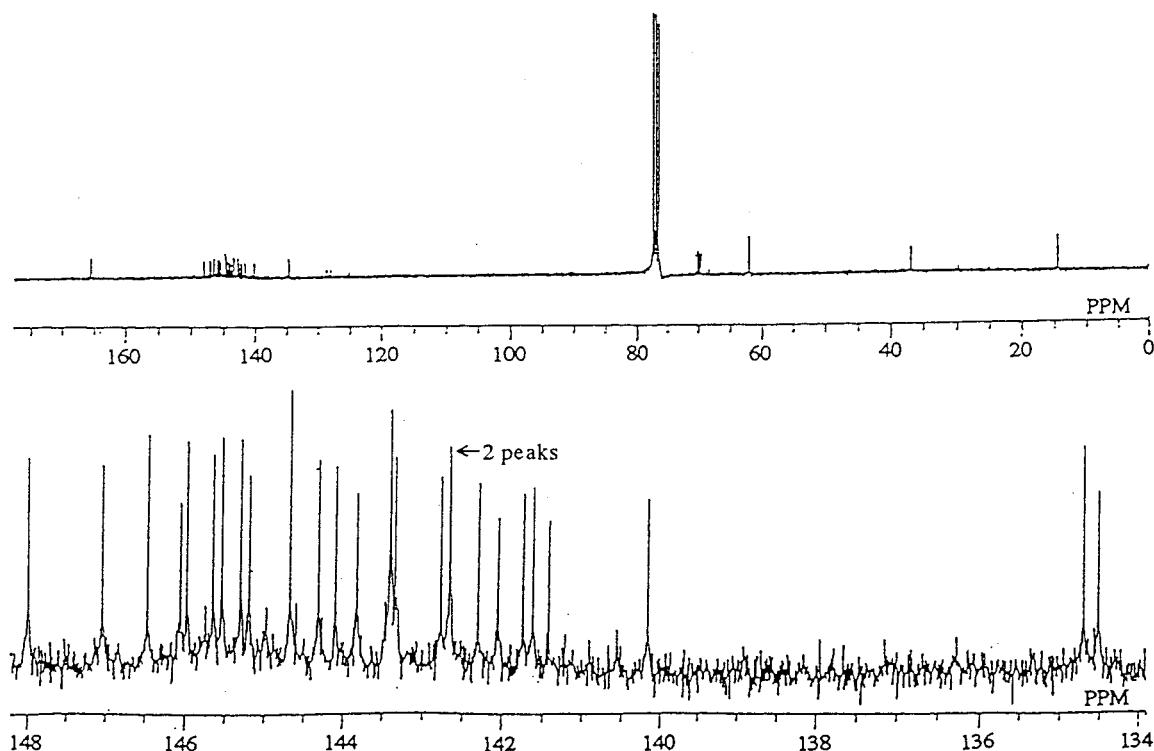
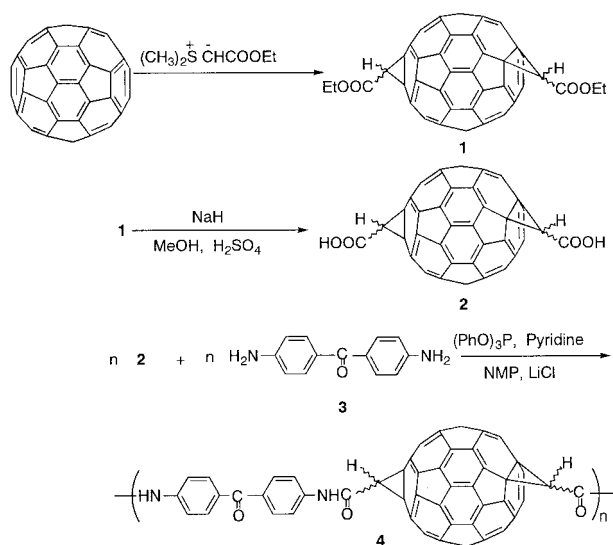


Figure 2. ^{13}C -NMR spectrum of trans-2-bisadduct **1** in $\text{CS}_2/\text{CDCl}_3$ (9:1)(a) and expanded 134–48 ppm region in the ^{13}C -NMR spectrum of **1** (b).

nobenzophenone (**3**) to the carbon-carbon double bond of [60]fullerenobisacetic acid (**2**), would be possible, because the carbon-carbon double bond of **2** is susceptible to a nucleophilic addition.¹⁰



Scheme 1. Reaction scheme for the preparation of polymer **4**.

Actually, in the absence of condensing reagents, triphenyl phosphite and pyridine, the reaction of **2** with **3** gave a product that exhibited strong absorption around 1115 cm^{-1} in its FTIR spectrum and a broad peak around 6.60 ppm in its ^1H -NMR spectrum; these observations strongly indicate the existence of the $\text{C}_{60}\text{-NH}$ -group.¹⁰ Thus, a direct amination of **2** with **3** in the absence of condensing reagents was observed. In contrast, when the condensation was carried out using large excesses of the condensing reagents (20-times excess of the functional groups), these absorption peaks were not observed in the FTIR spectrum or the ^1H -NMR spectrum. This means that the side reaction could be prevented by using the condensing reagents in large excesses.

The IR absorption of the $\text{C}=\text{O}$ stretching shifted from 1717 cm^{-1} of **2** to 1670 cm^{-1} for **4** (overlapped with the $\text{C}=\text{O}$ stretching of the 4,4'-diaminobenzophenone moiety) due to a mesomeric effect (Fig. 3). This clearly demonstrates the formation of amide linkages.

The UV-vis spectrum of **4** in DMAc exhibited a broad absorption (λ_{max} 310 nm) with a high absorbance coefficient (ϵ) of $2.1 \times 10^4\text{ L} \cdot \text{mol}^{-1}$

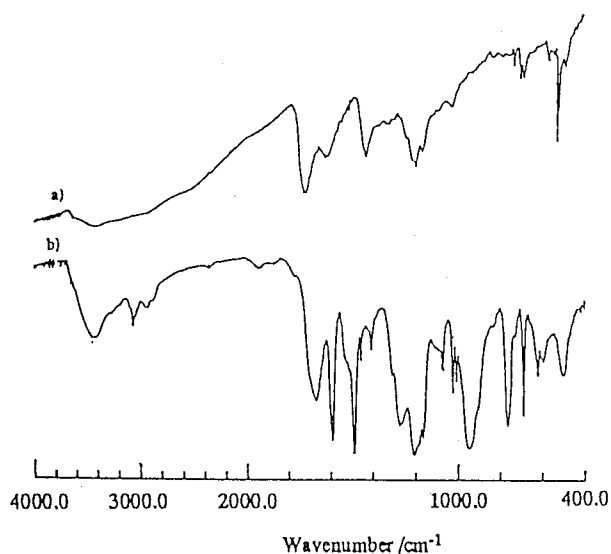


Figure 3. FTIR spectra of (a) monomer **2** and (b) polymer **4**.

$\cdot \text{cm}^{-1}$ tailing to longer wavelengths (to about 760 nm) (Fig. 4); the λ_{max} red-shifted by 25 nm, compared to that of the previously prepared copolymers,⁴ poly(1,4'-oxybisphenylene equatorial-[60]fullerenobisacetamide-co-1,4-oxybisphenylene isophthalamide), of which the tailing end extended to about 700 nm. A model polyamide, derived from isophthalic acid and 4,4'-diaminobenzophenone, showed an absorption peak at around 310 nm and tailing to shorter wavelengths (to about 380 nm). Moreover, a fluorescence peak at around 550 nm for **4** in DMAc was

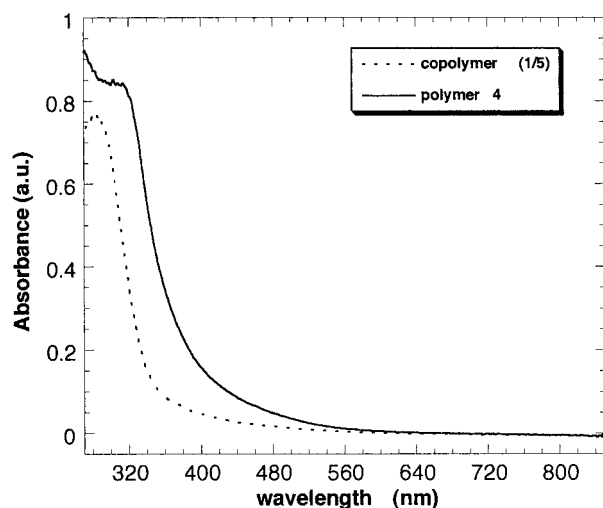


Figure 4. UV-vis absorption spectra of polymer **4** ($c = 4.0 \times 10^{-5}$ mol/L) and copolymer (1/5)⁴ in DMAc.

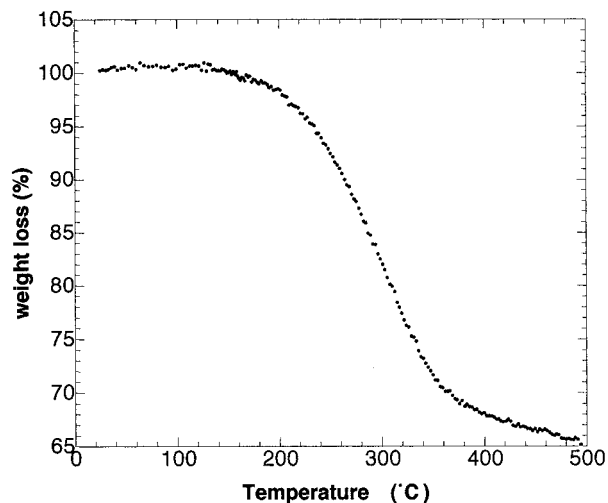


Figure 5. TGA of polymer **4**.

observed, which was shifted to a longer wavelength compared to that of the model polyamide (455 nm). A solvent effect was also observed; the fluorescence peak shifted from 550 nm in DMAc to 560 nm in dimethyl sulfoxide (DMSO) and 540 nm in NMP. There was a downfield shift of 1.21 ppm in the ¹H-NMR chemical shift of the cyclopropane methyne proton in the polymer from 4.57 ppm for that of the corresponding ethyl ester (**1**). All of these results indicate that the conjugation of the present polymer **4** is more extended than the previous copolymers, and that it is possible to obtain a more conjugated polymer by introducing the [60]fullerene component into a polymer chain.

The MALDI-TOF-MS of **4** showed a maximal peak at $m/z 4.5 \times 10^4$ when 3-indolacrylic acid was used as the matrix. GPC measurement indicated that **4** had a weight-average molecular weight (M_w) of about 5.3×10^4 with a polydispersity of 2.2; the intrinsic viscosity of the polymer was 0.35 dL/g in DMAc at 30°C.

These observations indicate that a high-molecular-weight [60]fullerene pearl-necklace polymer with a structure as shown in Scheme 1 is obtained without any chain-growth nor any crosslinking by direct amination, and that the conjugation of the polymer is more extended than that of the copolymers.⁴

TGA revealed that **4** started to decompose at about 200°C and lost 29% of its weight before reaching 380°C, which corresponded to the weight of the nonfullerene parts (Fig. 5). This result shows that the polymer is stable below 200°C and that polymer scission occurs on the cyclopropane rings to sustain [60]fullerene.

The resultant polymer was soluble in nonprotic polar solvents, such as DMAc, dimethylformamide, NMP, and DMSO, and slightly soluble in THF, but insoluble in methanol, toluene, acetone, and hexane.

CONCLUSIONS

We prepared a [60]fullerene pearl-necklace polyamide from *trans*-2-[60]fullerenobisacetic acid and 4,4'-diaminobenzophenone. In the presence of large excesses of triphenyl phosphite and pyridine, the polycondensation proceeded smoothly to give a high-molecular-weight [60]fullerene pearl-necklace polyamide, which was expected to exhibit elongated conjugation.

The authors thank Takuzo Aida and Dong-Lin Jiang of the University of Tokyo for help with the TOF mass and PL measurements. A part of this work was supported by CREST, Japan Science and Technology Corp., and the Japan Society for the Promotion of Science (JSPS-RFTF 97R11601).

REFERENCES AND NOTES

1. Kroto, H. W.; Allaf, A. W.; Balm, S. P. *Chem Rev* 1991, 91, 1213.
2. Loy, D. A.; Assink, R. A. *J Am Chem Soc* 1992, 114, 3977.
3. Taki, M.; Takigami, S.; Watanabe, Y.; Nakamura, Y.; Nishimura, J. *Polym J* 1997, 29, 1020.
4. Ozawa, M.; Li, J.; Nakahara, K.; Xiao, L.; Sugawara, H.; Kitazawa, K.; Kinbara, K.; Saigo, K. *J Polym Sci, Polym Chem Ed* 1998, 17, 3139.
5. Ratts, K. W.; Yao, A. N. *J Org Chem* 1966, 31, 1185.
6. Wang, Y.; Cao, J.; Schuster, D. I.; Wilson, S. R. *Tetrahedron Lett* 1995, 36, 6843.
7. Hirsch, A.; Lamparth, I.; Karfunkel, H. R. *Angew Chem, Int Ed Engl* 1995, 33, 437; *J Chem Soc, Chem Commun* 1994, 1727.
8. Imai, Y.; Kajiyama, M.; Ogata, S. I.; Kakimoto, M. *J Polym Sci, Polym Chem Ed* 1984, 22, 3183.
9. Schick, G.; Hirsch, A.; Mauser, H.; Clark, T. *Chem Eur J* 1996, 12, 1537.
10. Hwu, J. R.; Kuo, T.-Y.; Chang, T. M.; Patel, H. V.; Yong, K.-T. *Fullerene Sci & Tech* 1996, 3, 407.