Novel Copolyamides Containing [60]Fullerene in the Main Chain

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Novel copolymers, poly(1,4-oxybisphenylene fullerenobisacetamide-*co*-1,4-oxybisphenylene isophthalamide)s, which contained [60]fullerene in the main chain, were synthesized by the direct copolycondensation of a mixture of [60]fullerenobisacetic acid and isophthalic acid with 4,4'-diaminodiphenyl ether in the presence of triphenylphosphite and pyridine. Light scattering measurements for the copolymers showed a weight-average molecular weight Mw of about 5-6×10^4. The UV-visible spectra of the copolymers exhibited the characteristics of the parent fullerene derivative. The absorption edge red-shifted from 370 nm for poly(1,4-oxybisphenylene isophthalamide) to about 700 nm for the copolymers.

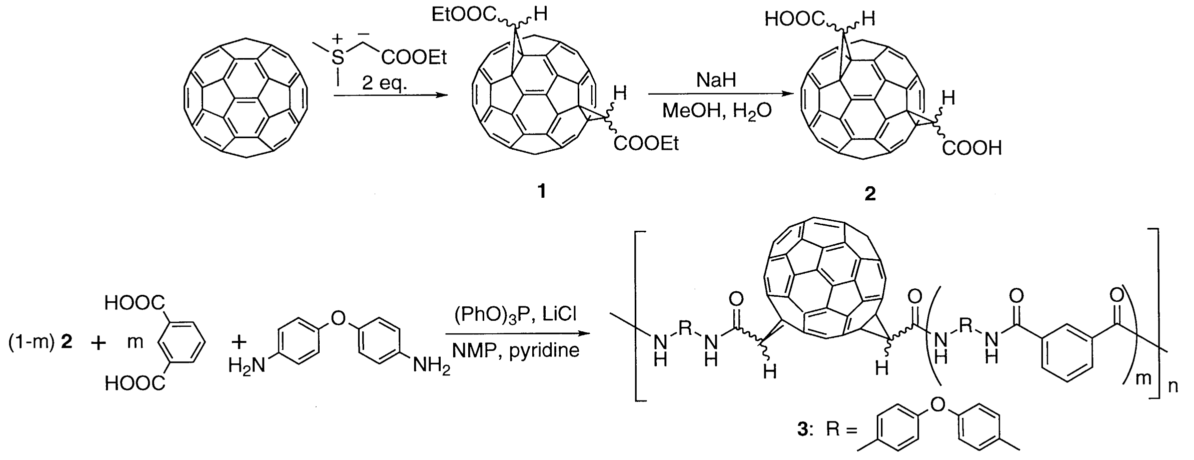
[60]Fullerene is easily attacked by nucleophiles and undergoes cycloaddition reactions.[1-3] Chemically modified [60]fullerene provides an efficient way to carry out polymerization or grafting of [60]fullerene onto a polymer chain or surface.[4,5] These polymeric fullerene-containing materials are expected to possess interesting electronic, optical, and catalytic properties arising from the unique features of the parent fullerene. A lot of efforts have been carried out in the past five years on the synthesis and characterization of fullerene polymers. Many types of polymers, including a dendritic polymer incorporating polyhydroxylated [60]fullerene[6] and pendant polymers with [60]fullerene attached on the side chain,[7-10] have been obtained by the ring-opening metathesis copolymerization of [60]fullerene with norbornene,[11] by the radical copolymerization of [60]fullerene with styrene,[12] and so on. Recently, fullerene-end-capped polystyrene with a star-like structure was reported by Cloutet *et al.*[13] and monosubstituted polymeric derivatives by Weis *et al.*[14] However, the synthesis of well-defined fullerene pearl necklace polymers (containing [60]fullerene in the main chain) is still a challenging goal. In this paper we report the synthesis and characterization of copolymers, poly (1,4-oxybisphenylene fullerenobisacetamide-*co*-1,4-oxybisphenylene isophthalamide) containing [60]fullerene in the main chain.

Although [60]fullerene is a fully π-conjugated nanomolecule, the introduction of a functional group onto [60]fullerene should result in the conversion of the sp^2 carbon of [60]fullerene into a sp^3 carbon, which interferes π-conjugation of the [60]fullerene sphere. On the other hand, the carbons of cyclopropane derivatives are well-known to have p-character to a considerable extent. This means that [60]fullerenobisacetic acid (**2**) would be a component for the synthesis of conjugated polymers having [60]fullerene moieties in the main chains. On the basis of the consideration, we tried to prepare copolyamides having **2** as a diacid component.

The reaction pathway for the preparation of poly(1,4-oxybisphenylene fullerenobisacetamide-*co*-1,4-oxybisphenylene isophthalamide) (**3**) is shown in Scheme 1. The reaction of [60]fullerene with the sulfonium ylide gave a mixture of the monoadduct, bisadducts, and trisadducts, from which 1,2:18,36-bisadduct **1** was isolated in 17% yield by silica-gel column chromatography (hexane/toluene = 1/1). The starting monomer **2** was obtained by hydrogenolysis of **1** with NaH and methanol.[2,3]

In the FAB mass spectra, the corresponding parent peaks were observed at m/z 892 for **1** and at m/z 836 for **2**, respectively. In the ^{1}H NMR spectrum of **1**, in addition to the peaks for the protons of the ethyl groups, two other peaks at δ 4.48 and 4.66 were observed, which may be attributed to the two kinds of methyne protons having different stereo-orientation.

A direct polycondensation method in the presence of triphenylphosphite and pyridine was applied in order to prepare the [60]fullerene copolyamides. To a solution of 0.2 mmolar



Scheme 1.

amount of a mixture of **2** and isophthalic acid (molar ratio: 1/50, 1/5 and 1/1, respectively), 0.2 mmolar amount of 4,4'-diaminodiphenyl ether, and 0.4 mmolar amount of triphenyl phosphite in *N*-methyl-2-pyrrolidinone (NMP) (1 mL) was added a solution of 0.6 mmolar amount of LiCl in pyridine (0.1 mL) under N_2. The solution was stirred under N_2 at 110 °C for 3 h to give a viscous solution. The solution was diluted by adding NMP (10 mL), and poured into methanol (150 mL). The fiber-like precipitate appeared was washed with methanol three times and then boiled in methanol for 30 min to remove NMP, pyridine, and other by-products. The precipitate thus obtained was dried under reduced pressure for 12 h at 60 °C to give the corresponding copolymer (abbreviated [1/50]-, [1/5]-, and [1/1]-copolymer, respectively). The yields were 90-95%.[15]

The copolymers obtained were soluble in NMP and *N,N*-dimethylacetamide. Both [1/50]- and [1/5]-copolymers formed clear brown films when coated on glass plates from their *N,N*-dimethylacetamide solutions. However, the film of [1/1]-copolymer was brittle.

After polymerization, the IR absorption originated from the carbonyl shifted from 1720 cm^{-1} of **2** to 1660 cm^{-1} of the copolymers due to the formation of amide bonds (Figure 1). The intrinsic viscosities of the copolymers varied from 1.4 dL/g for [1/50]-copolymer to 1.2 dL/g for [1/5]-copolymer and to 0.7 dL/g for [1/1]-copolymer. On the basis of light scattering measurements the Mw of the copolymers was estimated to be about 50,000 for [1/50]-copolymer and 60,000 for [1/5]-copolymer. Thermogravimetric analyses showed that the degradation of the copolymers started at about 260 °C. The [1/5]-copolymer lost about 36% of its weight until 700 °C to give a black residue. The UV-visible spectrum of poly(1,4-oxybisphenylene isophthalamide) (without [60]fullerene) showed an absorption edge at about 370 nm as shown in Figure 2. However, the UV-visible spectra of the copolymers exhibited a red-shift of the absorption edge upto about 700 nm, which is beyond that of the parent [60]fullerene derivative. These data indicate the formation of copolymers with elongated π-conjugation.

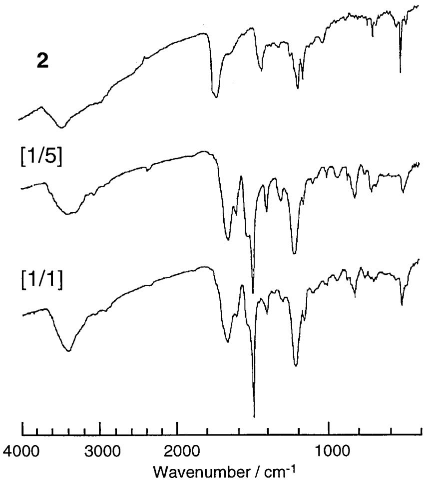


Figure 1. IR spectra of monomer **2** and the copolymers.

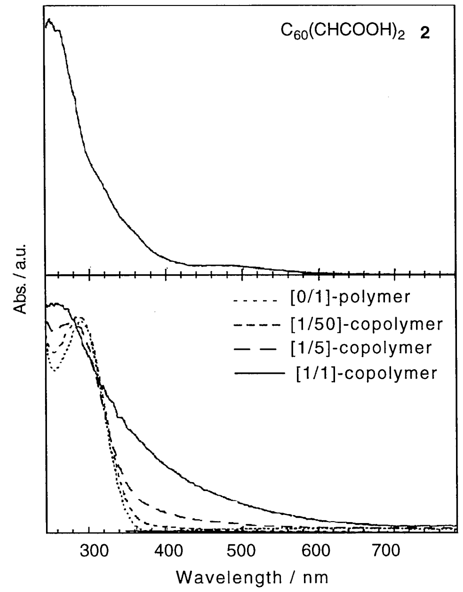


Figure 2. UV-Visible spectra of monomer **2**, poly(1,4-oxybisphenylene isophthalamide), and the copolymers.

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References and Notes

1 A. Hirsch, "The Chemistry of the Fullerenes," Georg Thieme Verlag, Stuttgart: New York (1994), pp. 79-112.
2 A. Hirsch, I. Lamparth, and H. R. Karfunkel, *Angew. Chem. Int. Ed. Engl.*, **33**, 437 (1994).
3 I. Lamparth and A. Hirsch, *J. Chem. Soc., Chem. Commun.*, **1994**, 1727.
4 I. Amato, *Science*, **254**, 30 (1991).
5 A. Hirsch, *Adv. Mater.*, **5**, 859 (1993).
6 L. Y. Chiang, L. Y. Wang, and C.-S. Kuo, *Macromolecules*, **28**, 7574 (1995).
7 S. Shi, K. C. Khemani, Q. Li, and F. Wudl, *J. Am. Chem. Soc.*, **114**, 10656 (1992).
8 A. O. Patil, G. W. Schriver, B. Carstensen, and R. D. Lundberg, *Polym. Bull.*, **30**, 187 (1993).
9 C. J. Hawker, *Macromolecules*, **27**, 4836 (1994).
10 M. Berrada, Y. Hashimoto, and S. Miyata, *Chem. Mater.*, **6**, 2023 (1994).
11 N. Zhang, S. R. Schricker, and F. Wudl, *Chem. Mater.*, **7**, 441 (1995).
12 T. Cao and S. E. Webber, *Macromolecules*, **28**, 3741 (1995); T. Cao and S. E. Webber, *Macromolecules*, **29**, 3826 (1996); A. G. Camp, A. Lary, and W. T. Ford, *Macromolecules*, **28**, 7959 (1995); E. T. Samulski, J. M. DeSimone, M. O. Hunt, Jr., Y. Z. Mencelogu, R. C. Jarnagin, G. A. York, K. B. Labat, and H. Wang, *Chem. Mater.*, **4**, 1153 (1992).
13 E. Cloutet, Y. Gnanou, J.-L. Fillaut, and D. Astruc, *J. Chem. Soc. Chem. Commun.*, **1996**, 1565.
14 C. Weis, C. Friedrich, R. Mulhaupt, and H. Frey, *Macromolecules*, **28**, 403 (1995).

15 The exact ratio of **2** and isophthalic acid parts in these copolymers could not be determined by the ^{1}H NMR, IR, and other analytical methods.