Novel Fluorene-based Biphenolic Monomer: 9,9-Bis(4-hydroxyphenyl)-9-silafluorene

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A 9-silafluorene-containing biphenolic monomer, 9,9-bis(4hydroxyphenyl)-9-silafluorene, was prepared from 9,9-dichloro-9-silafluorene and employed for the synthesis of polyesters using a fluorene-based homoditopic acid chloride. Some properties of the polyesters were examined.

Fluorene-containing polymers, especially 9,9-diarylfluorene group-containing polymers, have recently collect much attention¹ because of their attractive properties coming from the socalled cardo structure which consists of rectangular two aromatic groups including the fluorene plane. The cardo structure often contributes to a variety of excellent properties such as high solubility, high refractive index, low birefringence, and high affinity toward carbon fillers enabling the fine dispersion into composite materials.² We reported the synthesis and unique properties of 9,9-diarylfluorene-containing polythioethers and polyethers accumpanied with excellent optical, physical, and/ or chemical properties.³ Recently, we have designed a siliconmodified 9,9-diarylfluorene monomer, 9,9-bis(4-hydroxyphenyl)-9-silafluorene (3), in order to endow some characteristic properties of silicon-containing polymers to fluorene-based polymers, such as high thermal stability, oxidation stability, low glass-transition temperature, and flame retardant.⁴ This paper describes the synthesis of a novel fluorene-based biphenolic monomer 3 possessing a silicon atom attached to four aromatic nuclei, which was used for the preparation of fluorene-rich polyesters (FPEs).

2,2'-Dibromobiphenyl **1** was treated with *n*-BuLi and successively with an ethereal solution of SiCl₄ at -100 °C to give 9,9-dichloro-9-silafluorene (**2**) in 44% yield. Biphenlic monomer **3** was prepared by the reaction of **2** with lithium 4-lithiophenolate at -78 °C (Scheme 1).⁵ By the purification by column chromatography, **3** was isolated as pale yellow solid in 60% yield.

The chemical structure of **3** was fully confirmed by FT-IR, ¹H, ¹³C, ²⁹Si NMR, and mass spectra, in addition to elemental analysis.⁶ Figure 1 shows the partial ¹H NMR spectrum which is well consistent with the structure of **3**. Namely, each aromatic signal was assignable as indicated in the spectrum where typical down field shift was confirmed in protons b and c of **3** in comparison with those of its carbon analog **4**.

A series of silicon-containing homo (FPE1) and copolyesters (FPE2–4) were synthesized from **3**, **4**, and fluorene-containing acid chloride 9,9-dimethyl-2,7-bis(chlorocarbonyl)fluorene





Figure 1. Partial ¹H NMR spectra of **3** (top) and its carbon analog **4** (bottom) for comparison (400 MHz, CD₃OD, 298 K).

(5) by the interfacial polycondensation in dichloromethanewater in the presence of benzyltriethylammonium chloride (BTEAC) as a phase-transfer catalyst and sodium hydroxide as a base (Scheme 2). Non-silicon-containing polymer FPE5 was similarly obtained from 4 and 5. The results are summarized in Table 1.

Although M_w of FPE1, a homopolymer, was less than 10,000, M_w of the copolyesters FPEs2–4 was sufficiently high (47,600–60,300) with polydispersity ranging from 2.1 to 2.7, depending slightly on the monomer feed ratio of **3** and **4**. The compositions of copolymers FPE2–4 determined from ¹H NMR integral ratio revealed that **3** was less reactive than the corresponding carbon analogue **4**.

The structures of FPEs were confirmed by ¹H NMR and IR spectra. The IR spectra of FPEs showed the characteristic absorptions around 1730 and 1220 cm⁻¹ which corresponded to the vibrational stretchings of the ester bond, while the absorption of the aromatic rings appeared around 1600 cm⁻¹. ¹H NMR spectra of FPEs also supported the polymer structures: all aro-



Scheme 2.

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Table 1. Synthesis of homo and copolyesters FPEs

Entry	Polymer	Feed	Intensity in copolymer ^a	Yield	Molecular weight ^b	
		3/4	3/4	/%	$M_{ m w} \times 10^4$	$M_{\rm w}/M_{\rm n}$
1	FPE1	100/0		75	0.84	2.3
2	FPE2	75/25	65/35	85	4.79	2.6
3	FPE3	50/50	40/60	85	6.03	2.7
4	FPE4	25/75	18/82	82	4.76	2.2
5	FPE5	0/100	_	92	5.10	2.1
6	FPE1 ^c	100/0	_	78	2.84	2.8

^aDetermined by ¹HNMR. ^bGel-permeation chromatography (GPC) data based on polystryrene standard (eluent: chloroform). ^cThe polycondensation of **3** and **5** was carried out at 185 ^oC in diphenyl ether for 2 h.

Table 2. Thermal properties of FPEs

Dolumor	$T_{\rm g}{}^{\rm a}$	Atmosphere: N2 ^b			Atmosphere: Air ^b		
Polymer	$/^{\circ}C$	Td_5	Td_{10}	Char ^d /%	Td_5	Td_{10}	Char/%
FPE1	ND ^c	469	503	55	437	493	25
FPE2	ND	474	487	61	422	443	21
FPE3	ND	482	498	59	442	462	15
FPE4	ND	490	502	53	443	464	14
FPE5	217	502	515	46	452	476	0.7

^aDSC measurement was conducted at a heating rate 10° C/min. ^bMeasured by TGA was carried out at a heating rate of 10° C/min. ^cND: Not detected. ^cChar yield (wt %) at 800 °C.

matic signals appeared at similar chemical shifts to those of the monomers, although the signals were broadened.⁷

Thermal property of FPEs was evaluated by means of thermogravimetric analysis (TGA) and differential scanning calorimetry analysis (DSC). All FPEs showed almost similar thermal degradation behavior. As summarized in Table 2, FPEs had good thermal stability with an onset of degradation temperature consistently higher than 460 and 420 °C in nitrogen and air atmosphere, respectively. The 10% weight loss temperature was in a range of 487-515 °C (in nitrogen). On the other hand, no glass-transition temperature (T_{σ}) was observed for FPEs1-4. None of them showed melting points, being consistent with that the results of the wide angle X-ray diffraction (WAXD). Copolymers FPEs2-4 had slightly lower thermal stability than their carbon analog (FPE5). Char yield at 800 °C for FPEs1-4 was in the range of 45-61% in nitrogen and 0.7-25% in air, indicating their high oxidation stability characteristic of silicon-containing polymers.4,8

FPEs1–4 exhibited good solubility similar to their carbon analog (FPE5). They were soluble in ordinary organic solvents such as chloroform, tetrahydrofuran, and dimethylformamide at room temperature.⁹ The high solubility can be attributed not only to the fluorene unit but also to the silicon atom introduced in the polymer main chain which reduces the chain stiffness.⁴ Self-standing films of FPEs obtained by casting from chloroform solution were transparent, flexible, and tough. Each silicon-containing FPE had adhesive nature to the substrate.

Thus, a novel biphenolic 9-silafluorene-containing monomer $\mathbf{3}$ was synthesized and utilized for the synthesis of polyesters FPEs as a typical application. The introduction of silicon atom to the key position of the fluorene skeleton actually induced some specific properties such as the oxidation stability. The potential utility of this new monomer will be clarified by successive studies on the synthesis of polymers and evaluation of their properties.

References and Notes

- a) X. Y. Shang, D. Shu, S. J. Wang, M. Xiao, Y. Z. Meng, J. Membrane. Sci. 2007, 291, 140. b) R. S. Ashraf, H. Hoppe, M. Shahid, G. Gobsch, S. Sensfuss, E. Klemm, J. Polym. Sci., Part A: Polym. Chem. 2006, 44, 6952. c) G. Klärner, J.-I. Lee, V. Y. Lee, E. Chan, J.-P. Chen, A. Nelson, D. Markiewicz, R. Siemens, J. C. Scott, R. D. Miller, Chem. Mater. 1999, 11, 1800.
- a) S. Setayesh, A. C. Grimsdale, T. Weil, V. Enkelmann, K. Müllen, F. Meghdadi, E. J. W. List, G. Leising, J. Am. Chem. Soc. 2001, 123, 946. b) T. Inada, H. Masunaga, S. Kawasaki, M. Yamada, K. Kobori, K. Sakurai, Chem. Lett. 2005, 34, 524. c) K. Sakurai, M. Fuji, Polym. J. 2000, 32, 676. d) S. Kawasaki, M. Yamada, K. Kobori, T. Kakumoto, F. Jin, A. Tarutani, T. Takata, Polym. J. 2007, 39, 115.
- 3 a) S. Seesukphronrarak, T. Takata, J. Polym. Sci., Part A: Polym. Chem., 2007, 37, 0000. b) S. Kawasaki, M. Yamada, K. Kobori, F. Jin, Y. Kondo, H. Hayashi, Y. Suzuki, T. Takata, Macromolecules, in press.
- 4 a) L. A. Mercado, M. Galiá, J. A. Reina, *Polym. Degrad. Stab.*2006, 91, 2588. b) C. Hamciuc, E. Hamciuc, T. Pakula, L. Okrasa, *J. Appl. Polym. Sci.* 2006, 102, 3062. c) M. Bruma, B. Schulz, *J. Macromol. Sci.* 2001, C41, 1.
- 5 W. Davidsohn, B. R. Laliberte, C. M. Goddard, M. C. Henry, J. Organometal. Chem. 1972, 36, 283.
- A dry THF solution (134 mL) of p-bromophenol (9.7 g, 6 50 mmol) was added slowly under argon atmosphere at -78 °C to a hexane solution of n-BuLi (70.4 mL, 1.5 M, 0.100 mol). The mixture was warmed up to +5 °C and stirred at that temperature for 1 h. To the mixture cooled to -50 °C was added a dry THF solution of 2 (0.015 mol, 15 mL). The mixture was warmed up to +10 °C and stirred for 1 h. Then, the mixture was hydrolyzed by adding 5% HCl until obtaining a yellow solution. The resulting mixture was evaporated and the residue was dissolved in diethyl ether, washed with water, concentrated, dried, filtered, and evaporated to dryness. The residue was triturated with dry pentane for 20 min. The crude product obtained by decantation of pentane was chromatographed on silica gel with chloroform/ethyl acetate (1:1) as eluent to give 3 as semi-solid (3.15 g, 60%). Mp 103-105 °C; IR (KBr, cm⁻¹): 825, 1176, 1501, 1595, 3348. ²⁹Si NMR (CD₃OD, 60 MHz) $\delta - 11.6$ ppm. ¹H NMR (CD₃OD, 400 MHz) δ 7.81 (d, J = 8 Hz, 2H), 7.59 (d, J = 8 Hz, 2H), 7.34 (m, 2H), 7.30 (d, J = 8.5 Hz, 4H), 7.18 (m, 2H), 6.67 (d, J = 8.5 Hz, 4H). ¹³C NMR (CD₃OD, 100 MHz) δ 115.3, 121.1, 123.7, 127.7, 130.5, 133.8, 136.5, 137.3, 148.0, 157.3. MALDI-TOF-MS (m/z): Calcd for C₂₄H₁₈O₂Si 366.46, Found 366.90. Anal. Calcd for C24H18O2Si: C, 78.65; H, 4.95%; Found: C, 78.40; H, 5.01%.
- 7 **FPE1**; ¹H NMR (C₄D₈O, 400 MHz) δ 8.35 (s, 2H), 8.23 (d, J = 8 Hz, 2H), 8.04 (d, J = 8 Hz, 2H), 7.98 (d, J = 8 Hz, 2H), 7.88 (d, J = 8 Hz, 2H), 7.78 (d, J = 8 Hz, 2H), 7.51–7.48 (m, 2H), 7.40–7.29 (m, 6H).
- 8 S. F. Thames, K. G. Malone, J. Polym. Sci., Part A: Polym. Chem. 1993, 31, 521.
- 9 Solubility of FPEs was evaluated by using 3 mg of polymer and 1 mL of solvent.