

Synthesis and Properties of Fluorine- and Siloxane-Containing Polybenzimidazoles for High Temperature Proton Exchange Membrane Fuel Cells

Steve Lien-Chung Hsu,¹ Yung-Chung Lin,¹ Tsung-Yu Tasi,¹ Li-Cheng Jheng,^{1,2} Cheng-Hsun Shen¹

¹Department of Materials Science and Engineering, Research Center for Energy Technology and Strategy, National Cheng-Kung University, Tainan City, 701 Tainan, Taiwan ROC

²Nano-Materials Center, ITRI-S, Industrial Technology Research Institute, Tainan, Taiwan ROC

Correspondence to: S.L.-C. Hsu (E-mail: lchsu@mail.ncku.edu.tw)

ABSTRACT: In this study, new fluorine–siloxane-containing polybenzimidazole (PBI) copolymers were synthesized by copolymerization of 3,3'-diaminobenzidine, 2,2-bis(4-carboxyphenyl)-hexafluoropropane (HFA), and 1,3 bis(carboxypropyl)tetramethyldisiloxane (BTMDS) with different molar ratios. PBI copolymer membranes were prepared by solution-casting and then doped with phosphoric acid. The structures of PBI copolymers were characterized by FTIR and X-ray diffraction. The solubility of the PBI copolymers was significantly increased by the introduction of the bulky HFA group and the flexible BTMDS group into the polymer backbone. The PBI copolymers still maintained good thermal stability and mechanical properties. Because of the introduction of the flexible and hydrophobic siloxane group in the polymer backbone, the methanol permeability was reduced and the proton conductivity under anhydrous condition at high temperatures was increased compared to the PBI without the siloxane group. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 4107–4112, 2013

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INTRODUCTION

Proton exchange membrane (PEM) is receiving increasing attention because it is one of the key parts in proton exchange membrane fuel cell (PEMFC). PEM functions as a conductive proton medium as well as a barrier to avoid direct contact between the fuel and oxidant. The current research on PEMFC is focused on the development of high temperature polymer electrolyte membranes for operation above 100°C to alleviate the effect of CO poisoning in electrodes and to improve the power density of the fuel cells.^{1–5} The perfluorosulfonic acid polymer membranes, such as Nafion, are typically used as the electrolyte in PEMFCs, because of their outstanding chemical stability and high proton conductivity. However, the Nafion membranes have three major drawbacks: (i) loss of proton conductivity at temperatures above 100°C due to dehydration phenomena; (ii) high methanol permeation, which causes loss of fuel and decrease cathode performance in PEMFCs; (iii) loss its mechanical and dimensional stability at high temperature due to its low glass transition (T_g) (80–120°C).^{6–12} Polybenzimidazole (PBI) is a very promising material for high-temperature (>100°C) fuel cell applications because of its high thermal stability and good

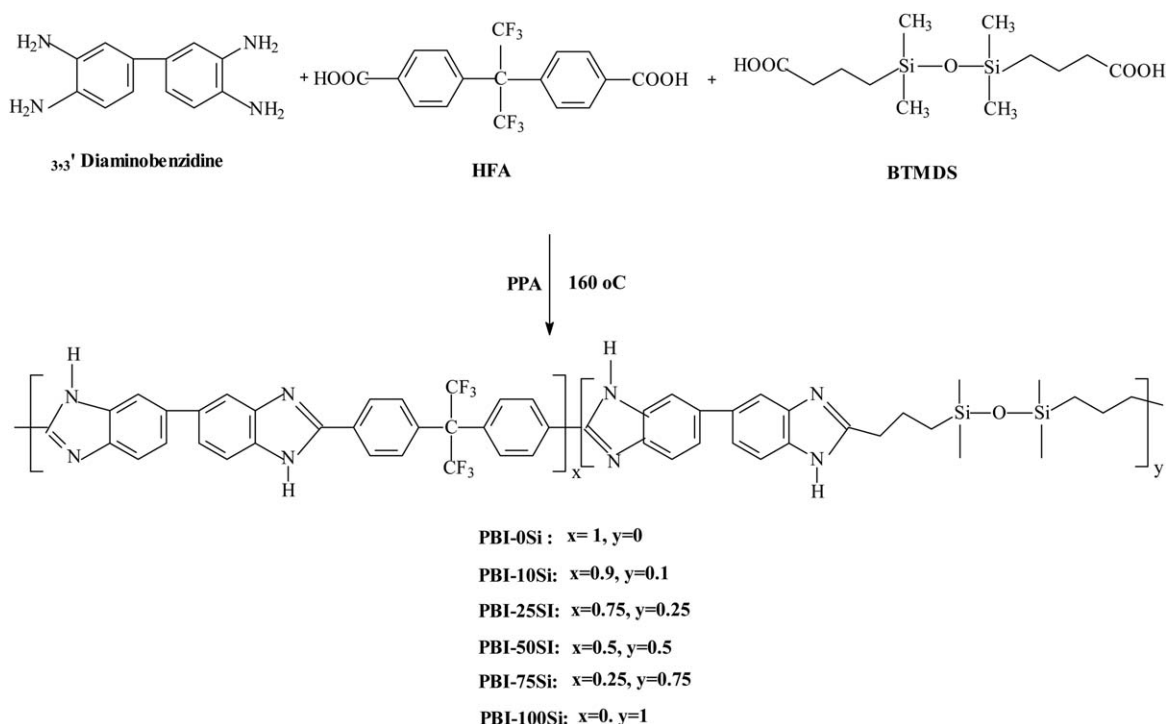
mechanical properties. In addition, PBI doped with strong acids has high proton conductivity at temperatures up to 200°C.^{13–21}

The commercially available PBI, poly[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole], has very good thermal and mechanical properties due to its rigid structure. However, it is difficult to dissolve in common organic solvents for the preparation of membranes by solution casting. In our previous research, we have synthesized organosoluble fluorine-containing PBI and its nanocomposites for direct methanol fuel cells applications.^{22–25} In this article, we report a new series of fluorine- and siloxane-containing PBI copolymers. The effects of the flexible and hydrophobic siloxane unit to the properties of PBI copolymer membranes used in fuel cell are discussed.

EXPERIMENTAL

Materials

2,2-Bis(4-carboxyphenyl)-hexafluoropropane (HFA) was purchased from TCI and purified by recrystallization from glacial acetic acid. 3,3'-Diaminobenzidine, dimethylacetamide (DMAc), and deuterated dimethylsulfone (d-DMSO) were obtained from Aldrich. 3,3'-Diaminobenzidine was used as received, and



Scheme 1. Synthesis of PBI copolymers.

DMAC was purified by distillation over calcium hydride. 1,3-Bis(carboxypropyl)-tetramethyldisiloxane (BTMDS) was obtained from Gelest. Reagent grade polyphosphoric acid (PPA) and phosphoric acid were obtained from Fluka and used as supplied. Other chemicals and solvents were used as received.

Synthesis of PBI Copolymers

The reaction is shown in Scheme 1. A typical preparation of the PBI-50Si ($x=0.5, y=0.5$) proceeds as follows: To a 500 mL three-necked round bottom flask equipped with a mechanical stirrer and a condenser, 2.678 g (12.5 mmol) of 3,3'-diaminobenzidine, 1.916 g (6.25 mmol) of BTMDS, 2.452 g (6.25 mmol) of HFA, 12.97 g of P_2O_5 , and 134 g of PPA (preheated at 120°C) were added. The solution was heated up to 160°C and stirred for 8 h under nitrogen. The resulting viscous solution was added dropwise to a 5 L of deionized water being stirred. The precipitated polymer was collected by filtration, and washed with 10 wt % NaOH. The polymer was further washed with deionized water five times. The polymer was dried under vacuum at 100°C for 24 h.

Preparation and Doping of PBI Copolymer Membranes

0.5 g of PBI copolymer powder was dissolved in 25 g of DMAC to make a 2% (w/w) solution. Films were cast from the viscous solution on glass plates by a doctor's knife. The films were dried under vacuum at 80°C for 24 h. The films were yellow and transparent. The films were doped by immersion in 9M phosphoric acid solution for 100 h. The amount of phosphoric acid in each film was calculated by weight analysis.

Characterization

The IR spectra were recorded on a Jasco 460 FTIR Spectrometer. The inherent viscosity was measured using a Cannon-

Ubbelohde No. 100 viscometer at a concentration of 0.5 g/dL in DMAC at 30°C . The wide angle X-ray diffraction (WAXD) experiment was conducted on a Rigaku (Tokyo, Japan) D/MAX-III V X-ray diffractometer using $\text{Cu K}\alpha$ radiation. Thermo-oxidative stability was analyzed using a TA Instrument thermogravimetric analyzer (TGA) 2050 at a heating rate of $10^{\circ}\text{C}/\text{min}$ under air. The in-plane coefficients of thermal expansion (CTEs) and glass transition temperatures (T_g s) of PBI copolymer membranes were determined using a TA Instrument Thermal Mechanical Analyzer Q400EM. The CTEs were measured with an extension probe under 0.05 N tension force on the films in the temperature range of $100\text{--}250^{\circ}\text{C}$ at a heating rate of $5^{\circ}\text{C}/\text{min}$ under nitrogen. Tensile properties were determined from stress-strain curves obtained with a Shimadzu AG-SI universal testing machine at a strain rate of 5 mm/min at room temperature. The size of film specimens was 30 mm in length, 4.5 mm in width, and $40\text{ }\mu\text{m}$ in thickness. The oxidative stability of the membranes was examined by immersing the membranes in Fenton reagent (4 ppm FeSO_4 in 3 wt % H_2O_2) at 68°C for 96 h. The conductivity measurement was performed with an Autolab PGSTST 30 impedance analyzer in the frequency range of $100\text{--}10^5$ Hz with amplitude of 10 mV. The measurements were made at different temperatures in the range of $50\text{--}200^{\circ}\text{C}$. The conductivity (σ) was calculated from the equation:

$$\sigma = \frac{1}{R} \frac{L}{A}$$

where R , L , and A are the measured resistance, thickness, and the cross-sectional area of the membrane, respectively.²² The methanol permeability was measured by using a two-compartment glass cell. One source cell ($V_A = 100$ mL) was filled with a 6 wt %

Table I. Inherent Viscosity and H₃PO₄ Doping Level of PBI Copolymers

	Inherent viscosity (dL/g)	Doping level (doping for 100 h)
PBI-0Si	1.10	3.0
PBI-10Si	0.50	5.6
PBI-25Si	0.49	6.0
PBI-50Si	0.49	6.8

methanol aqueous solution. The other receiving cell ($V_B = 100$ mL) was filled with deionized water. The membrane was clamped between the two compartments. The concentration of methanol in the receiving cell was measured versus time by gas chromatography (HP 4890GC). The methanol concentration in the receiving cell is given by

$$C_B(t) = \frac{A}{V_B} \frac{P}{L} C_A(t - t_0)$$

where C_B and C_A are the methanol concentration in the receiving cell and the source cell, respectively, V_B is the volume of the receiving cell, P is the methanol permeability, L is the membrane thickness, and A is the cross-sectional area of the membrane. t_0 , also termed time lag, is related to the methanol diffusion coefficient (D) as $t_0 = L^2/6D$.^{19,20}

RESULTS AND DISCUSSION

Copolymer Synthesis

The fluorine- and siloxane-containing PBI copolymers were synthesized from 3,3'-diaminobenzidine, HFA, and BTMDA in PPA in different stoichiometric ratios as shown in Scheme 1. PAA was used as both solvent and catalyst for the condensation reaction. The reaction temperature and time are critical to the preparation of the copolymers. If the reaction temperature is higher than 160°C or the reaction time is longer than 8 h at 160°C, all copolymers except PBI-0Si are insoluble in any organic solvents. That could be due to the crosslinking through the methyl groups of the siloxanes under strong acid environment and high temperatures. Even though the reaction condition was kept at 160°C for 8 h, PBI-75Si and PBI-100Si were still insoluble in any organic solvents. It was skeptical that the probability of

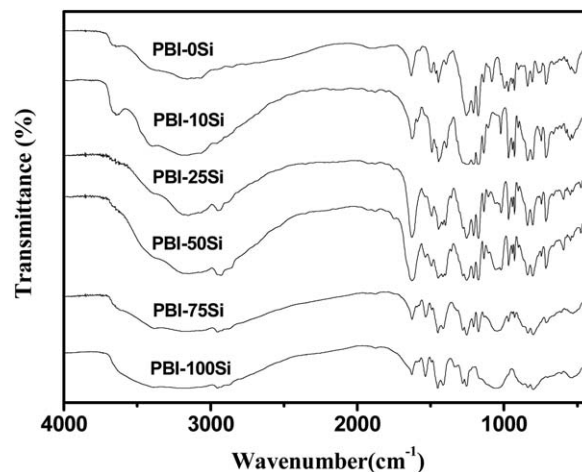


Figure 1. IR spectra of PBI copolymers.

crosslinking significantly increased in these two copolymers, which have much higher siloxane content. However, if the reaction temperature was lower than 160°C or the reaction time was shorter than 8 h at 160°C, we could not obtain high molecular weight polymers. The inherent viscosities of the copolymers were measured in DMAc at a concentration of 0.5 g/dL at 30°C and shown in Table I. The formation of PBI copolymers was confirmed by the IR spectra (Figure 1). The polymer exhibited characteristic absorption bands at 3450–3250 cm^{-1} and 1631 cm^{-1} due to the stretching vibration of the N–H groups and C=N groups.²¹

Table II summarizes the qualitative solubility of the PBI copolymers. PBI-0Si, PBI-10Si, PBI-25Si, and PBI-50Si are soluble in several organic solvents. This could be due to the introduction of bulky hexafluoropropylidene bridging groups and flexible siloxane groups in the PBI backbone, which reduces the rigidity and the intermolecular forces between polymer chains.

Membrane Fabrication

The PBI copolymer membranes were easily fabricated from the PBI copolymers solution in DMAc by solution casting. To increase the proton conductivity of the membranes, the membranes were doped with phosphoric acid by immersion in 9M

Table II. Solubility of PBI Copolymers at Room Temperature

	PBI-0Si	PBI-10Si	PBI-25Si	PBI-50Si	PBI-75Si	PBI-100Si
NMP	+	+	+	+	–	–
DMAc	+	+	+	+	–	–
DMSO	+	+	+	+	–	–
DMF	+	+	+	+	–	–
MSA	+	+	+	+	–	–
Methanol	–	–	–	–	–	–
THF	–	–	–	–	–	–
Chloroform	–	–	–	–	–	–
Acetone	–	–	–	–	–	–

NMP, N-methyl-2-pyrrolidone; DMAc, dimethylacetamide; DMSO, dimethylsulfoxide; DMF, dimethylformamide; MSA, methanesulfonic acid; THF, tetrahydrofuran; +, soluble; –, insoluble

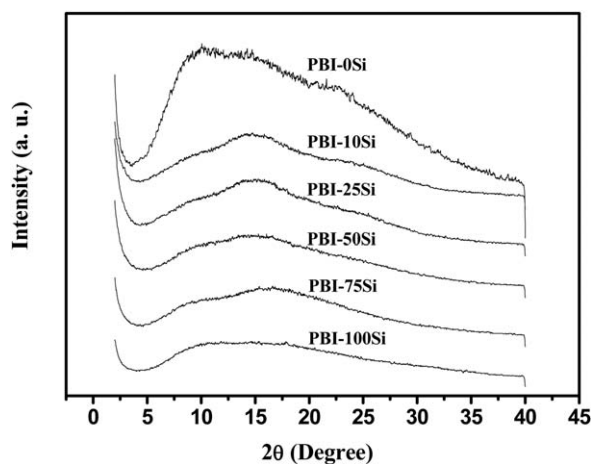


Figure 2. XRD patterns of PBI copolymers.

phosphoric acid solution for 100 h. The saturated doping level of the membranes is shown in Table I. It can be seen that PBI-10Si, PBI-25Si, and PBI-50Si much higher doping level than PBI-0Si. It could be due to that the siloxane-containing PBIs have larger free volumes because they have more flexible siloxane units.

Copolymer Characterization and Membranes Properties

To study the morphology of the PBI copolymers, the films prepared from the copolymers were examined by WAXD measurement. Figure 2 shows their WAXD patterns. A broad amorphous halo that appeared in these copolymers indicated the absence of crystallinity, which could be due to the bulky hexafluoropropylidene groups and flexible siloxane units in the backbone. The amorphous structure of the polymer is beneficial for proton transfer.

The thermo-oxidative stabilities of the PBI copolymers were studied by using TGA technique under air. The TGA thermograms are shown in Figure 3, and the data are listed in Table III. It was found that the thermo-oxidative stability decreased with the increasing amounts of siloxanes due to the weak Si-CH₃ bonding. However, PBI-50Si still had good thermo-

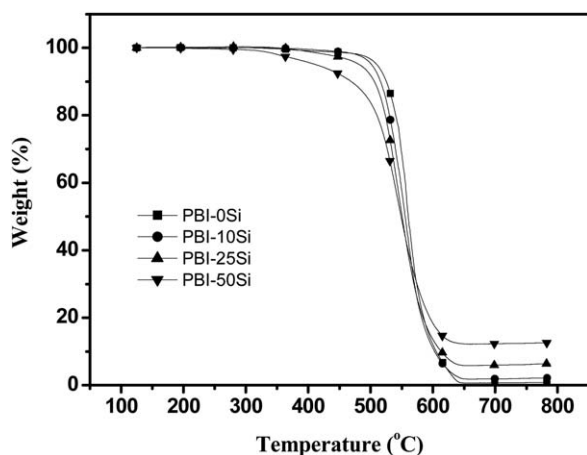


Figure 3. TGA thermograms of PBI copolymers in air atmosphere.

Table III. Thermal Properties of PBI Copolymers

	T_d (°C) ^a	W_{ex} (%) ^b	W_{th} (%) ^c	CTE (μm/m °C)	T_g (°C)
PBI-0Si	510	0.71	0	34.84	441
PBI-10Si	502	1.89	2.28	39.03	382
PBI-25Si	482	5.96	5.85	49.61	346
PBI-50Si	413	12.29	12.22	57.79	288

^aThe 5% weight loss temperature.

^bThe measured residual weight percentage.

^cThe theoretical residual weight percentage.

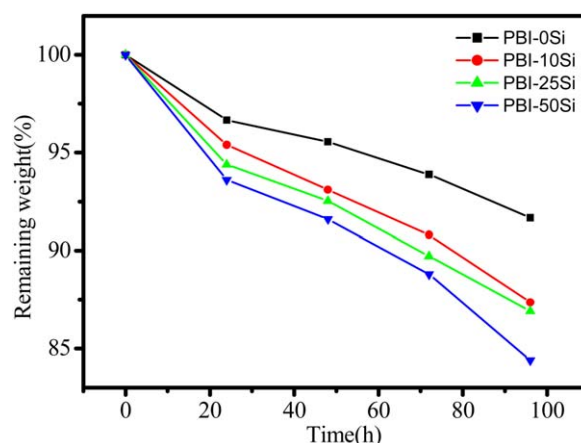


Figure 4. Oxidative stability of PBI copolymers with time in 3% H₂O₂ containing 4 ppm Fe²⁺ at 68°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

oxidative stability because its 5% weight loss temperature (T_d) was over 400°C. From the TGA thermograms, we can see that the more the siloxane units in the copolymer, the higher the residual SiO₂ content. Compared the measured residual weight percentage (W_{ex}) and the theoretical residual weight percentage (W_{th}), we found that the molar ratios of the resulting copolymers were close to the feed ratios of monomers. The chemical oxidative stability of the membranes was tested by immersing them into Fenton reagent (4 ppm FeSO₄ in 3 wt % H₂O₂) at 68°C. Figure 4 gives the weight change of the copolymers. The chemical oxidative stability also decreased with the increasing amounts of the siloxane content as the thermo-oxidative stability, which was owing to the same reason.

The in-plane CTEs of PBI copolymer membranes are listed in Table III. It was found that the CTEs of PBI copolymer

Table IV. Mechanical Properties of PBI Membranes Before Doping with Phosphoric Acid

	Modulus (GPa)	Stress (MPa)	Elongation (%)
PBI-0Si	2.53 ± 0.28	114.4 ± 4.8	6.2 ± 1.5
PBI-10Si	2.33 ± 0.31	101.9 ± 3.2	7.4 ± 1.3
PBI-25Si	1.72 ± 0.27	72.8 ± 2.1	9.9 ± 2.0
PBI-50Si	1.52 ± 0.30	62.0 ± 2.6	11.5 ± 1.8

membranes increased with increasing amounts of siloxanes but the T_g s of PBI copolymer membranes decreased with increasing amounts of siloxanes. That is due to the increasing flexibility of the copolymers with higher siloxane content. Nevertheless, the PBI-50Si still has a high T_g of 288°C.

Table IV summarizes the tensile properties of PBI copolymers before doping with phosphoric acid. As expected, the tensile modulus and strength of the films decreased with the increasing siloxane content. However the PBI-50Si still had enough mechanical properties. It had a tensile modulus of 1.52 GPa, tensile strength of 62 MPa, and elongation at break of 11.5%.

PBIs are known to have low methanol permeability due to their low electro-osmotic drag coefficient and high density of the membrane matrix.²⁶ The methanol permeability data of PBI copolymer membranes are shown in Table V. It can be seen that the methanol permeability decreased with the increasing siloxane content. For PBI-50Si, the methanol permeability was nearly zero (it could not be detected by the instrument). It could be due to that the siloxane group is hydrophobic and less polar, so the hydrophilic and polar methanol molecules are expelled from the membranes.

Figure 5 shows the proton conductivity of PBI copolymer membranes doped with phosphoric acid up to a saturation level as described in Table I. The conductivity measurement was conducted under anhydrous condition between 50 and 200°C. Combining the doping level and conductivity data, we found that the conductivity of PBI copolymer membranes was dependent on the doping level. PBI-10Si, PBI-25Si, and PBI-50Si have similar conductivity because their doping levels are very close. The PBI-50Si has the highest conductivity of 4.6×10^{-3} (S/cm) at 160°C, because it has the highest doping level of 6.8. As shown in the previous section, the T_g s of PBI copolymers decreased as the siloxane content increased. The decrease of T_g implied the increase of free volume. Vehicle mechanism is one of the explanations described on how to transport protons within the polyelectrolyte, which is highly relevant to the free volume involved in Vogel-Tamman-Fulcher behavior. A higher free volume would lead to more efficient proton transportation. Therefore, the PBI-50Si has the highest conductivity.

CONCLUSIONS

In this work, a new series of amorphous, organosoluble fluorine- and siloxane-containing PBI copolymers were synthesized from 3,3'-diaminobenzidine, HAF, and BTMDS with different molar ratios. Due to the bulky HFA groups and flexible siloxane groups, the PBI copolymers have good solubility in common organic solvents. PBI copolymer membranes can be easily pre-

Table V. Methanol Permeability of PBI Copolymers

	PBI-0Si	PBI-10Si	PBI-25Si	PBI-50Si	Nafion 117
Permeability (10^{-8} cm ² /s)	1.84	0.26	0.08	— ^a	130

^a Could not be detected.

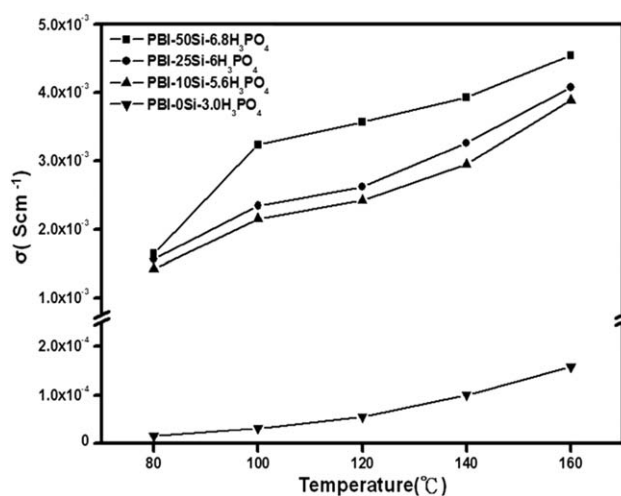


Figure 5. Conductivity of PBI copolymers doped with H_3PO_4 for 100 h.

pared from the copolymers by solution casting in DMAc. The PBI copolymer membranes still have good thermo-oxidative stability and mechanical properties. The methanol permeability decreased with the increasing siloxane content. The methanol permeability of PBI-50Si was nearly zero. The PBI-50Si also has the highest conductivity of 4.6×10^{-3} (S/cm) at 160°C under anhydrous condition, because it has the highest doping level of 6.8.

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