Polymerization procedure of diblock copolymer P1-P2(*m*-141) by catalyst transfer polymerization.

All reactions were performed in a dry box under Ar atmosphere. To **P2(141)** THF solution, the second monomer, **1** treated with ^{i}PrMgCl·LiCl complex (1.3 M solution in THF) was added and stirred at room temperature for 30 h. The reaction was quenched with HCl aq./methanol. The insoluble material was washed with methanol and collected by suction filtration. The residue was reprecipitated from chloroform solution into acetone/methanol to give **P1-P2(*m*-141)** as a pale pink solid. Detailed synthetic condition was shown in Table S1.

Table S1. Synthesis condition of **P1-P2(*m*-141)**.

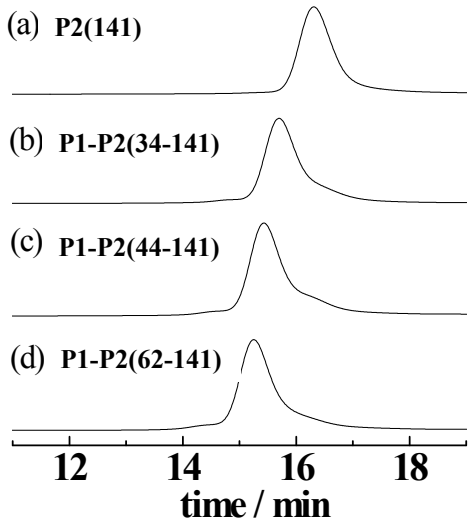
Sample	Monomer / mmol	Ni(dppe)Cl_2 / g (mmol)	THF / ml	Monomer/ Ni(dppe)Cl_2	Yield / g (%)
P1-P2(*34*-141)	5.40	0.0758	300	71	2.63 (47)
P1-P2(*44*-141)	5.40	0.0606	300	89	1.88 (48)
P1-P2(*62*-141)	6.48	0.0530	300	122	2.44 (48)

Synthesis of diblock copolymer ionomers SP1-P2(*m*-141).

The neopentyl protected sulfonyl group in **P1-P2(*m*-141)** was cleaved with an *N*-methylpyrrolidone solution of diethylamine hydrobromide at 120 ºC for 48 h to obtain the acid form of the copolymer **SP1-P2(*m*-141)**. After cooling to room temperature, the reaction mixture was poured into diethyl ether. The insoluble material was collected by suction filtration. The product was stirred in 1 M HCl aq for 48 h and in water for 24 h to give **SP1-P2(*m*-141)** as a brown solid.

Table S2. Synthesis condition of S**P1-P2(*m*-141)**.

Sample	**P1-P2** / g	$(C_2H_5)_2$NH HBr / g (mmol)	NMP / ml	Yield /g (%)
SP1-P2(*34*-141)	2.10	1.88 (12.2)	40.0	1.22 (63)
SP1-P2(*44*-141)	1.60	1.58 (10.3)	20.0	0.716 (49)
SP1-P2(*62*-141)	1.90	2.45 (15.9)	20.0	1.47 (88)



(a) M_n = 34,800、 M_w = 39,100
M_w / M_n = 1.12

(b) M_n = 51,000、 M_w = 61,700
M_w / M_n = 1.21

(c) M_n = 58,700、 M_w = 68,900
M_w / M_n = 1.17

(d) M_n = 67,200、 M_w = 80,500
M_w / M_n = 1.20

Figure S1. GPC profiles of **P2(141)** and **P1-P2(*m*-141)** in THF.

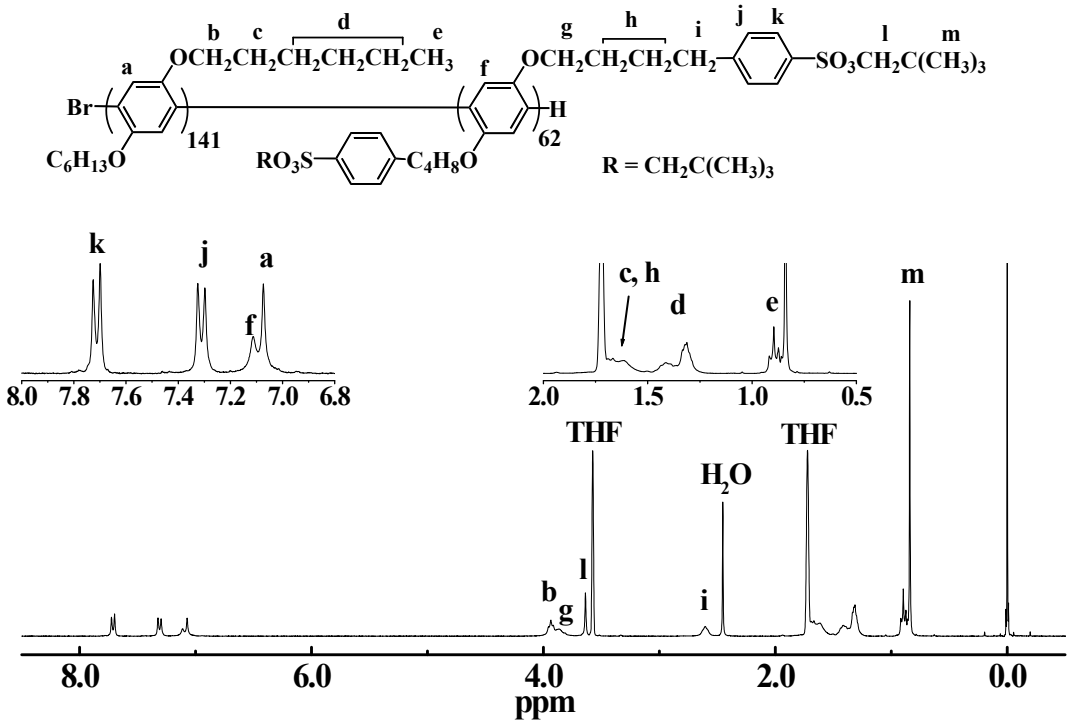


Figure S2. ^{1}H NMR spectrum of **P1-P2(62-141)** in THF-d_8.

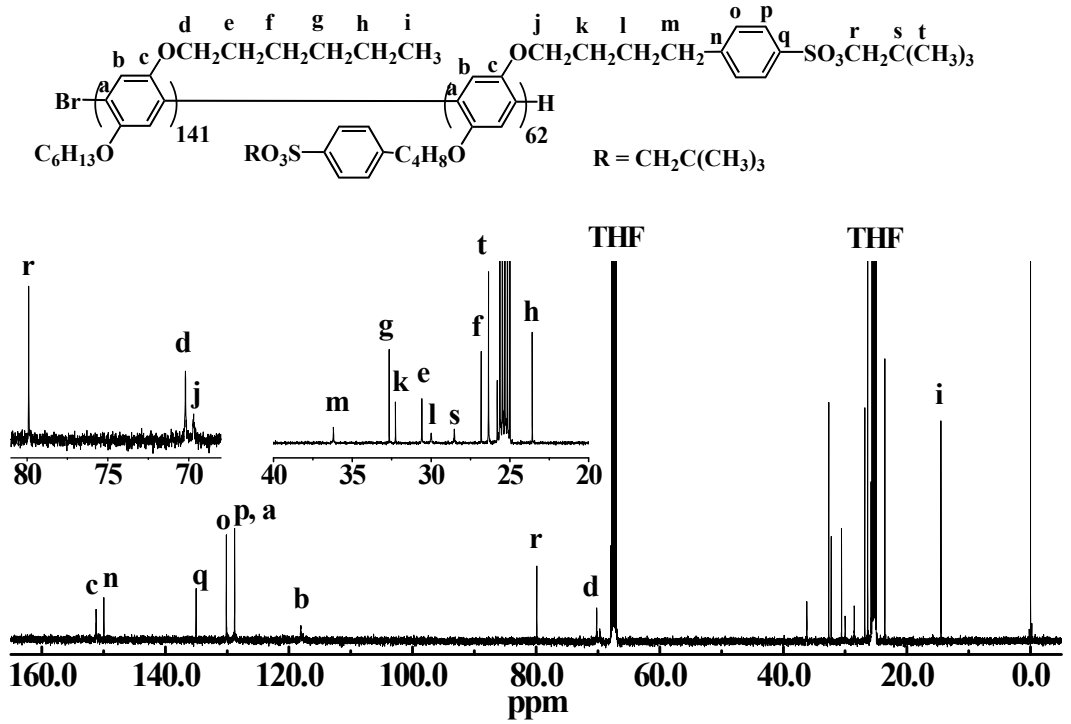


Figure S3. ^{13}C NMR spectrum of **P1-P2(62-141)** in THF-d_8.

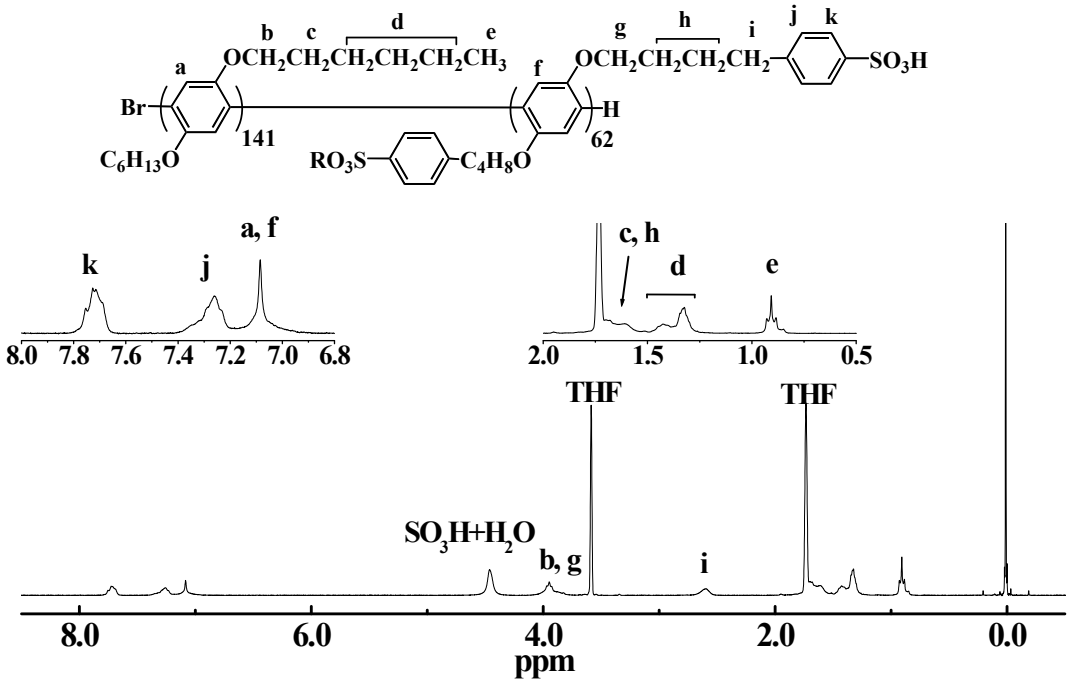


Figure S4. ^{1}H NMR spectrum of **SP1-P2(62-141)** in THF-d_8.

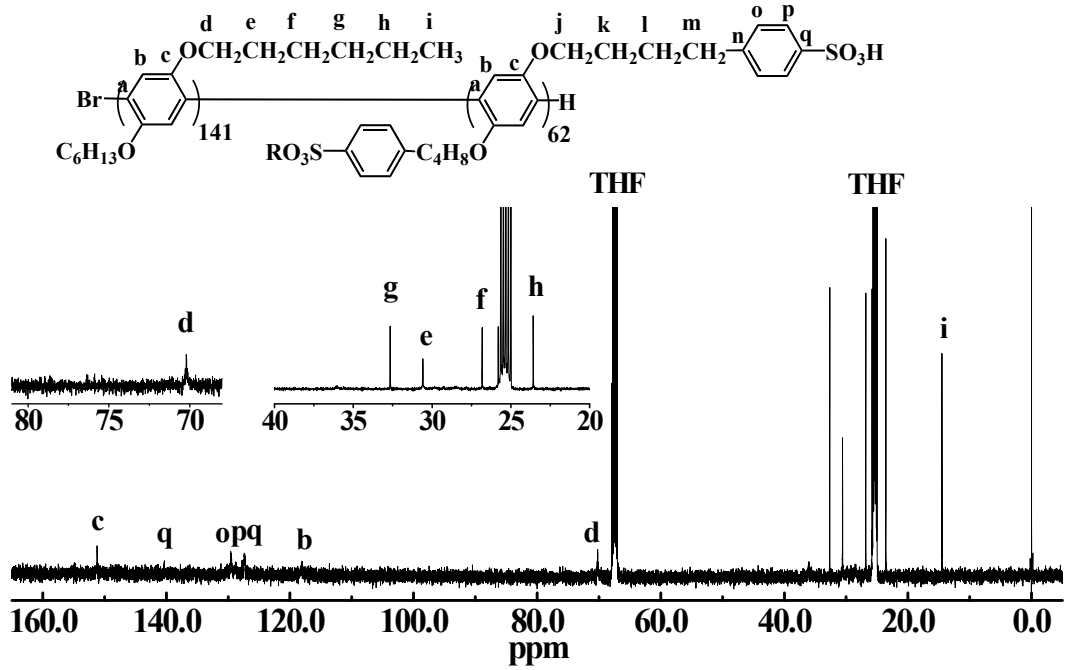


Figure S5. ^{13}C NMR spectrum of **SP1-SP2(62-141)** in THF-d_8.

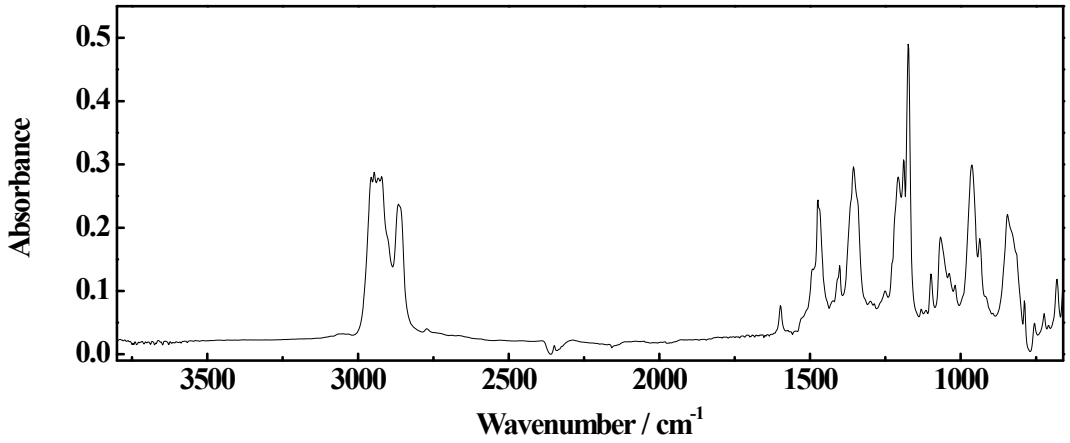


Figure S6. FT-IR spectrum of **P1-P2(141-62)**.

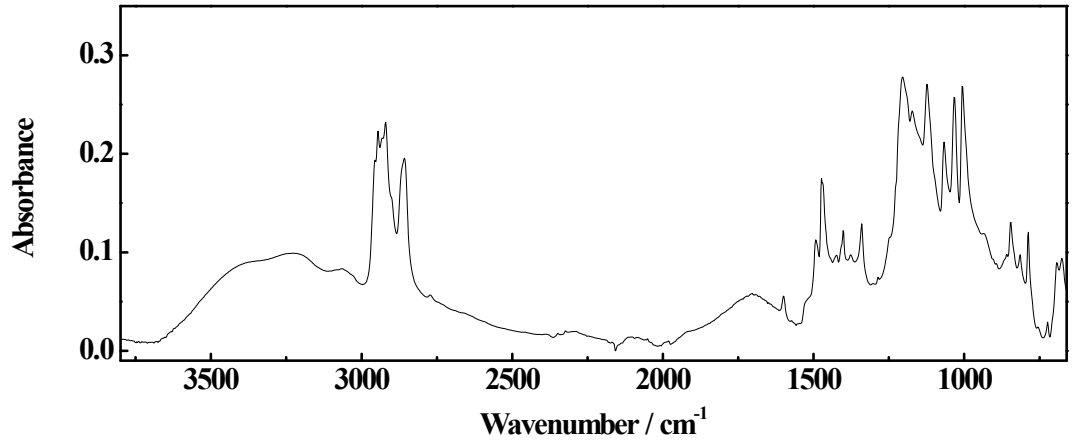


Figure S7. FT-IR spectrum of **SP1-P2(141-62).**

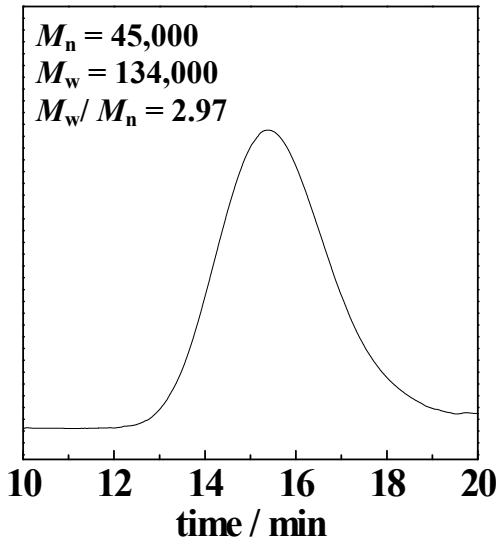


Figure S8. GPC profile of S-PPBP.