Supporting Information

Orthogonal electric and ionic conductivities in the thin film of thiophene–thiophene block copolymer

Sonoka Yamamoto,[a] Ryutaro Yamashita,[a] Chihiro Kubota,[a] Kentaro Okano,[a] Masatoshi Kitamura,[a] Masahiro Funahashi,[b] Syu-Cheng Ye,[c] Yung-Tin Pan,[c] Masaki Horie,[c] Takuji Shintani,[d] Hironori Murata,[a] Hideto Matsuyama,[ad] and Atsunori Mori[ad]

[a]*Graduate School of Engineering, Kobe University, 1-1 Rokkodai, Nada, Kobe 657-8501, Japan*
[b]*Department of Advanced Materials Science, Kagawa University, 2217-20 Hayashi-cho, Takamatsu, Kagawa 761-0396, Japan*
[c]*Department of Chemical Engineering, National Tsing Hua University, 101, Sec. 2, Kuang-Fu Road, Hsinchu 30013, Taiwan*
[d]*Research Center for Membrane and Film Technology, Kobe University, 1-1 Rokkodai, Nada 657-8501, Japan*

Contents

Concerning the possibility of gas bubble formation, additional AFM measurements are shown in Figure S1 and S2. Figure S1 shows phase mode AFM observation of block copolymer **5a** and resulting conversion to **6a** by thermal treatment suggesting less clear contrast before and after thermal treatment. The little change of the contrast in the phase mode of AMF supports that the formation of a gas bubble was not observed in the region of 2 μm x 2 μm.

The results on AFM analyses (height mode) of random copolymer **5a'** and alternating copolymer **5a''**, which are incapable of the formation of microphase separation along with thermal treatment to **6a'** and **6a''** are shown in Figure S2. Considering that the remarkable observation of dotted pattern was not shown in **6a'** and **6a''**, these results also support the dot found in **6a** (Figure 6b) is the microphase separation and the formation of a gas bubble is less likely.

(a) (b)

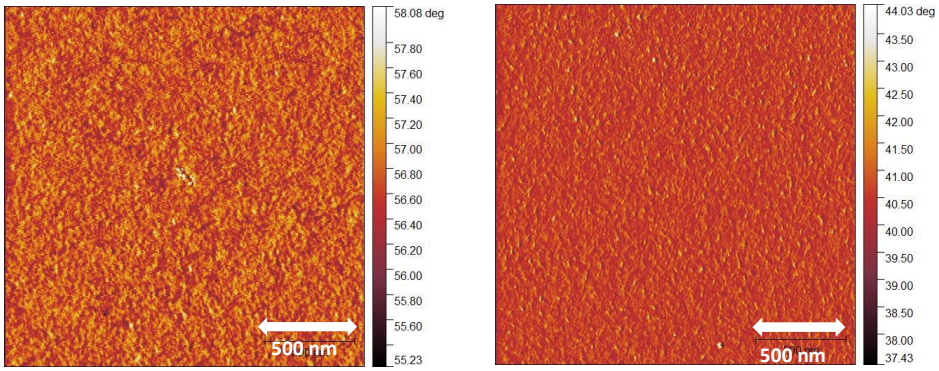


Figure S1. AFM image (phase mode) of the thin film of block copolymer (a) **5a**: before thermal treatment and (b) **6a**: (after thermal treatment)

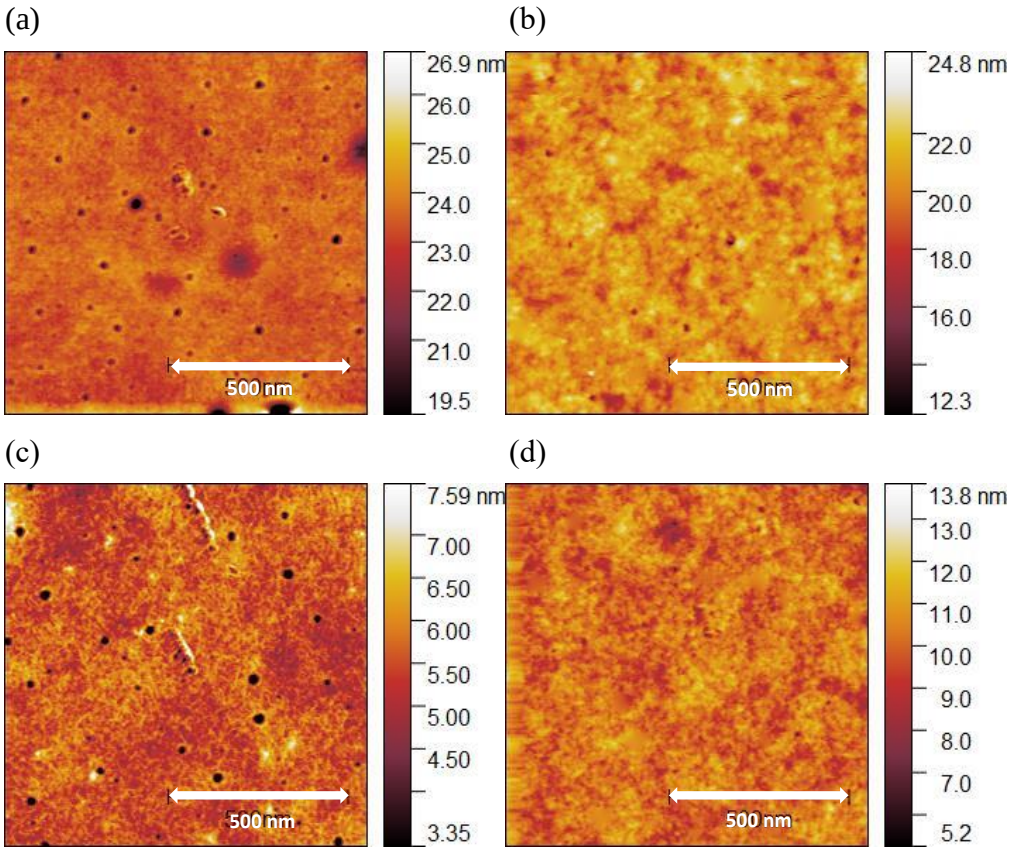


Figure S2. AFM topographic image of (a) random copolymer **5a'** , (b) the related **6a'** after thermal treatment, (c) alternating copolymer **5a''**, and (d) the related **6a''** after thermal treatment.

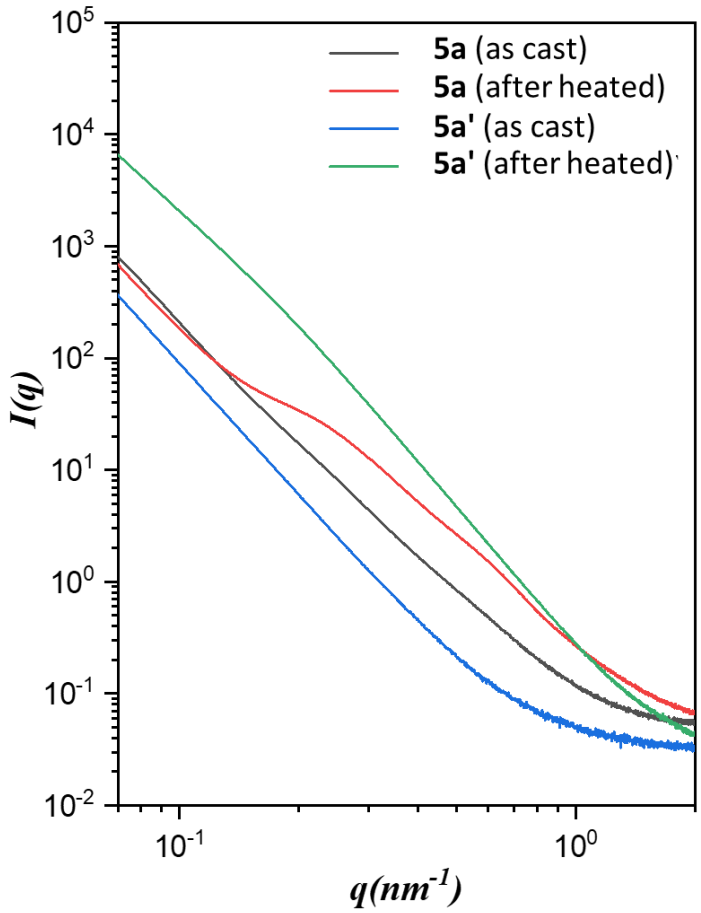


Figure S3. Measurements of SAXS for polythiophene block copolymer **5a** and the related random copolymer **5a'** before and after thermal treatment at 200 °C for 20 min. Black: **5a** before thermal treatment, red: **5a** after thermal treatement, blue: **5a'** before thermal treatment, and green: **5a'** after thermal treatment.

Details on electronic conductivity of polythiophene block copolymers **5** on a glass substrate, where electrodes and polymer films were set as depicted in Figure 4(a)–(c).

Table S1. Electric conductivity of block copolymer **5a** before/after thermal treatment over the range of applied voltage 0–100 V (See: Figure 4a)

Applied Voltage (V)	Current of **5a** before thermal treatment (A)	Conductivity of **5a** before thermal treatment (S/cm)	Current of **5a** after thermal treatment (A)	Conductivity of **5a** after thermal treatment (S/cm)
0	0	0	0	0
10	3.63×10^{-7}	8.82×10^{-5}	2.00×10^{-6}	4.86×10^{-4}
20	7.29×10^{-7}	8.85×10^{-5}	5.00×10^{-6}	6.07×10^{-4}
30	1.10×10^{-6}	8.87×10^{-5}	1.00×10^{-5}	8.09×10^{-4}
40	1.46×10^{-6}	8.88×10^{-5}	3.20×10^{-5}	1.94×10^{-3}
50	1.83×10^{-6}	8.90×10^{-5}	5.80×10^{-4}	2.82×10^{-3}
60	2.20×10^{-6}	8.90×10^{-5}	1.00×10^{-4}	4.05×10^{-3}
70	2.57×10^{-6}	8.91×10^{-5}	1.54×10^{-4}	5.34×10^{-3}
80	2.94×10^{-6}	8.91×10^{-5}	2.12×10^{-4}	6.44×10^{-3}
90	3.31×10^{-6}	8.92×10^{-5}	2.82×10^{-4}	7.61×10^{-3}
100	3.68×10^{-6}	8.92×10^{-5}	3.86×10^{-4}	9.37×10^{-3}

Table S2. Electric conductivity of block copolymer **5a** before/after thermal treatment over the range of applied voltage 0–10 V (See: Figure 4b)

Applied Voltage (V)	Current of **5a** before thermal treatment (A)	Conductivity of **5a** before thermal treatment (S/cm)	Current of **5a** after thermal treatment (A)	Conductivity of **5a** after thermal treatment (S/cm)
0	0	0	0	0
0.5	1.48×10^{-9}	1.54×10^{-5}	8.97×10^{-8}	9.35×10^{-4}
1	9.47×10^{-9}	4.94×10^{-5}	2.08×10^{-7}	1.08×10^{-3}
1.5	2.23×10^{-8}	7.74×10^{-5}	3.49×10^{-7}	1.18×10^{-3}
2	3.78×10^{-8}	9.86×10^{-5}	4.80×10^{-7}	1.25×10^{-3}
2.5	5.43×10^{-8}	5.82×10^{-4}	6.25×10^{-7}	1.30×10^{-3}
3	7.20×10^{-8}	1.25×10^{-4}	7.74×10^{-7}	1.34×10^{-3}
3.5	9.00×10^{-8}	1.34×10^{-4}	9.25×10^{-7}	1.38×10^{-3}
4	1.08×10^{-7}	1.41×10^{-4}	1.08×10^{-6}	1.41×10^{-3}
4.5	1.26×10^{-7}	1.46×10^{-4}	1.23×10^{-6}	1.43×10^{-3}
5	1.45×10^{-7}	1.51×10^{-4}	1.39×10^{-6}	1.45×10^{-3}
5.5	1.63×10^{-7}	1.55×10^{-4}	1.55×10^{-6}	1.47×10^{-3}
6	1.83×10^{-7}	1.59×10^{-4}	1.71×10^{-6}	1.48×10^{-3}
6.5	2.02×10^{-7}	1.62×10^{-4}	1.87×10^{-6}	1.50×10^{-3}
7	2.20×10^{-7}	1.64×10^{-4}	2.03×10^{-6}	1.51×10^{-3}
7.5	2.39×10^{-7}	1.66×10^{-4}	2.19×10^{-6}	1.52×10^{-3}
8	2.59×10^{-7}	1.69×10^{-4}	1.36×10^{-6}	1.54×10^{-3}
8.5	2.78×10^{-7}	1.70×10^{-4}	2.52×10^{-6}	1.55×10^{-3}
9	2.97×10^{-7}	1.72×10^{-4}	2.69×10^{-6}	1.56×10^{-3}
9.5	3.17×10^{-7}	1.74×10^{-4}	2.85×10^{-6}	1.57×10^{-3}
10	3.36×10^{-7}	1.75×10^{-4}	3.02×10^{-6}	1.58×10^{-3}

Table S3. Electric conductivity of block copolymer **5a** perpendicular to the substrate before/after thermal treatment over the range of applied voltage 0–10 V
(See: Figure 4c)

Applied Voltage (V)	Current of **5a** before thermal treatment (A)	Conductivity of **5a** before thermal treatment (S/cm)	Current of **5a** after thermal treatment (A)	Conductivity of **5a** after thermal treatment (S/cm)
0	0	0	0	0
0.5	1.72×10^{-9}	3.34×10^{-11}	2.83×10^{-8}	5.49×10^{-10}
1	4.57×10^{-9}	4.44×10^{-11}	5.68×10^{-8}	5.52×10^{-10}
1.5	7.99×10^{-9}	5.17×10^{-11}	8.59×10^{-8}	5.56×10^{-10}
2	1.18×10^{-8}	5.71×10^{-11}	1.15×10^{-7}	5.60×10^{-10}
2.5	1.57×10^{-8}	6.09×10^{-11}	1.45×10^{-7}	5.63×10^{-10}
3	1.98×10^{-8}	6.40×10^{-11}	1.75×10^{-7}	5.67×10^{-10}
3.5	2.40×10^{-8}	6.64×10^{-11}	2.06×10^{-7}	5.70×10^{-10}
4	2.82×10^{-8}	6.85×10^{-11}	2.36×10^{-7}	5.74×10^{-10}
4.5	3.26×10^{-8}	7.02×10^{-11}	2.67×10^{-7}	5.77×10^{-10}
5	3.70×10^{-8}	7.18×10^{-11}	2.99×10^{-7}	5.80×10^{-10}
5.5	4.14×10^{-8}	7.31×10^{-11}	3.30×10^{-7}	5.82×10^{-10}
6	4.59×10^{-8}	7.43×10^{-11}	3.62×10^{-7}	5.85×10^{-10}
6.5	5.04×10^{-8}	7.53×10^{-11}	3.94×10^{-7}	5.88×10^{-10}
7	5.50×10^{-8}	7.63×10^{-11}	4.26×10^{-7}	5.91×10^{-10}
7.5	5.97×10^{-8}	7.72×10^{-11}	4.59×10^{-7}	5.93×10^{-10}
8	6.43×10^{-8}	7.80×10^{-11}	4.91×10^{-7}	5.96×10^{-10}
8.5	6.90×10^{-8}	7.88×10^{-11}	5.24×10^{-7}	5.98×10^{-10}
9	7.37×10^{-8}	7.94×10^{-11}	5.57×10^{-7}	6.01×10^{-10}
9.5	7.84×10^{-8}	8.01×10^{-11}	5.91×10^{-7}	6.03×10^{-10}
10	8.31×10^{-8}	8.07×10^{-11}	6.24×10^{-7}	6.06×10^{-10}

Table S4. Electric conductivity of block copolymer **5b** before/after thermal treatment over the range of applied voltage 0–100 V (See: Figure 4a)

Applied Voltage (V)	Current of **5b** before thermal treatment (A)	Conductivity of **5b** before thermal treatment (S/cm)	Current of **5b** after thermal treatment (A)	Conductivity of **5b** after thermal treatment (S/cm)
0	0	0	0	0
10	1.38×10^{-6}	1.05×10^{-3}	3.00×10^{-7}	2.29×10^{-4}
20	2.76×10^{-6}	1.05×10^{-3}	1.00×10^{-6}	3.81×10^{-4}
30	4.14×10^{-6}	1.05×10^{-3}	1.30×10^{-6}	3.30×10^{-4}
40	5.54×10^{-6}	1.05×10^{-3}	1.60×10^{-6}	3.05×10^{-4}
50	6.96×10^{-6}	1.06×10^{-3}	2.00×10^{-6}	3.05×10^{-4}
60	8.39×10^{-6}	1.07×10^{-3}	2.00×10^{-6}	2.54×10^{-4}
70	9.85×10^{-6}	1.07×10^{-3}	2.30×10^{-6}	2.50×10^{-4}
80	1.14×10^{-5}	1.08×10^{-3}	2.60×10^{-6}	2.48×10^{-4}
90	1.29×10^{-5}	1.09×10^{-3}	3.00×10^{-6}	2.54×10^{-4}
100	1.45×10^{-5}	1.10×10^{-3}	3.30×10^{-6}	2.51×10^{-4}

Table S5. Electric conductivity of block copolymer **5g** after thermal treatment over the range of applied voltage 0–100 V (See: Figure 4a)

Applied Voltage (V)	Current of **5g** before thermal treatment (A)	Conductivity of **5g** before thermal treatment (S/cm)	Current of **5g** after thermal treatment (A)	Conductivity of **5g** after thermal treatment (S/cm)
0	–	–	0	0
10	–	–	1.30×10^{-6}	9.90×10^{-4}
20	–	–	4.60×10^{-6}	1.75×10^{-3}
30	–	–	2.21×10^{-5}	5.61×10^{-3}
40	–	–	8.40×10^{-5}	1.60×10^{-2}
50	–	–	2.26×10^{-4}	3.44×10^{-2}
60	–	–	4.45×10^{-4}	5.65×10^{-2}
70	–	–	6.06×10^{-4}	6.59×10^{-2}
80	–	–	7.97×10^{-4}	7.59×10^{-2}
90	–	–	9.49×10^{-4}	8.03×10^{-2}
100	–	–	1.07×10^{-3}	8.12×10^{-2}

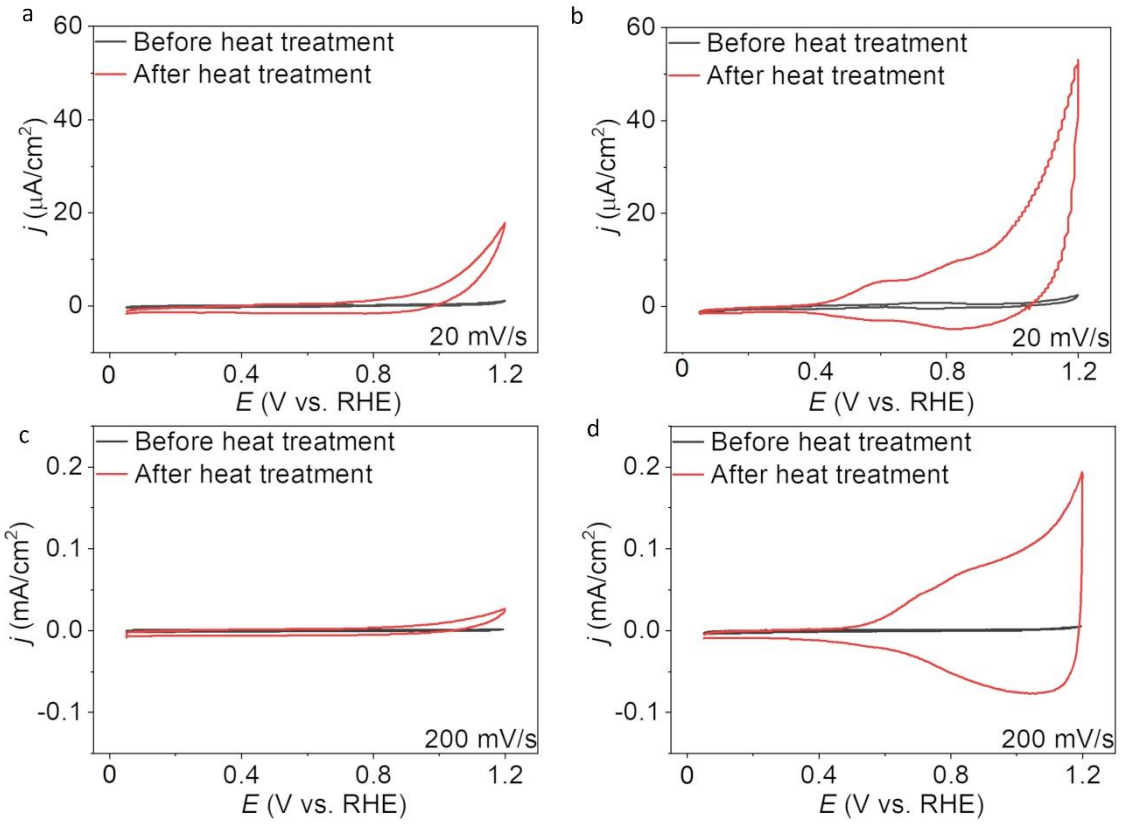
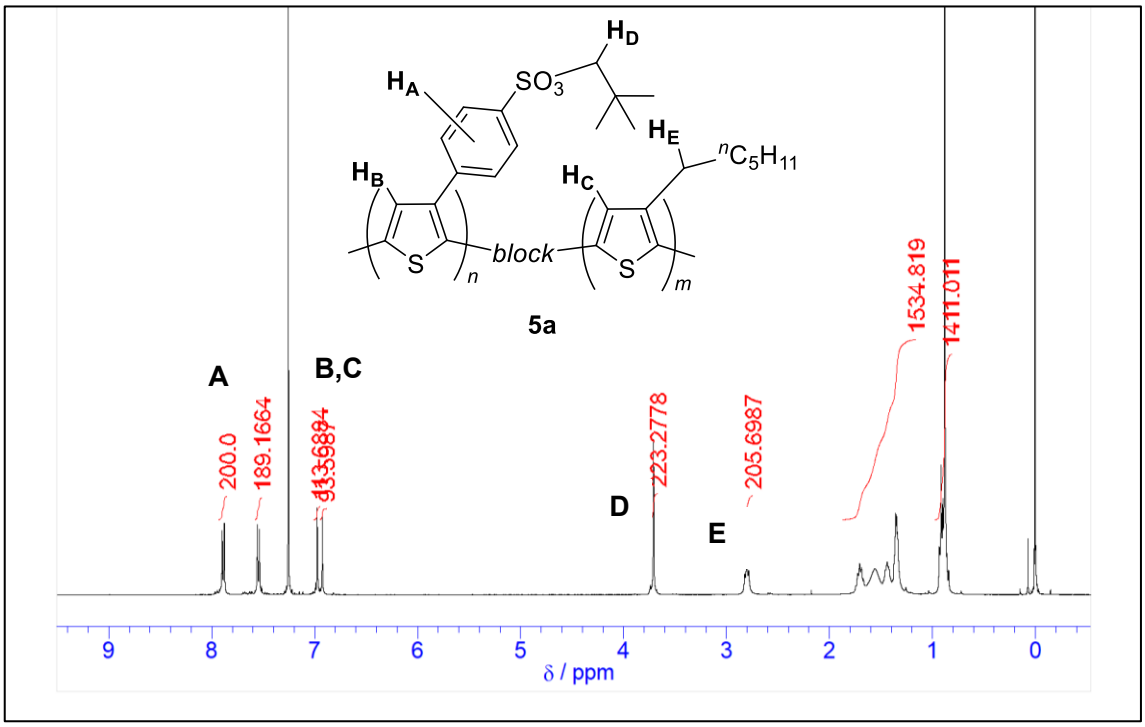
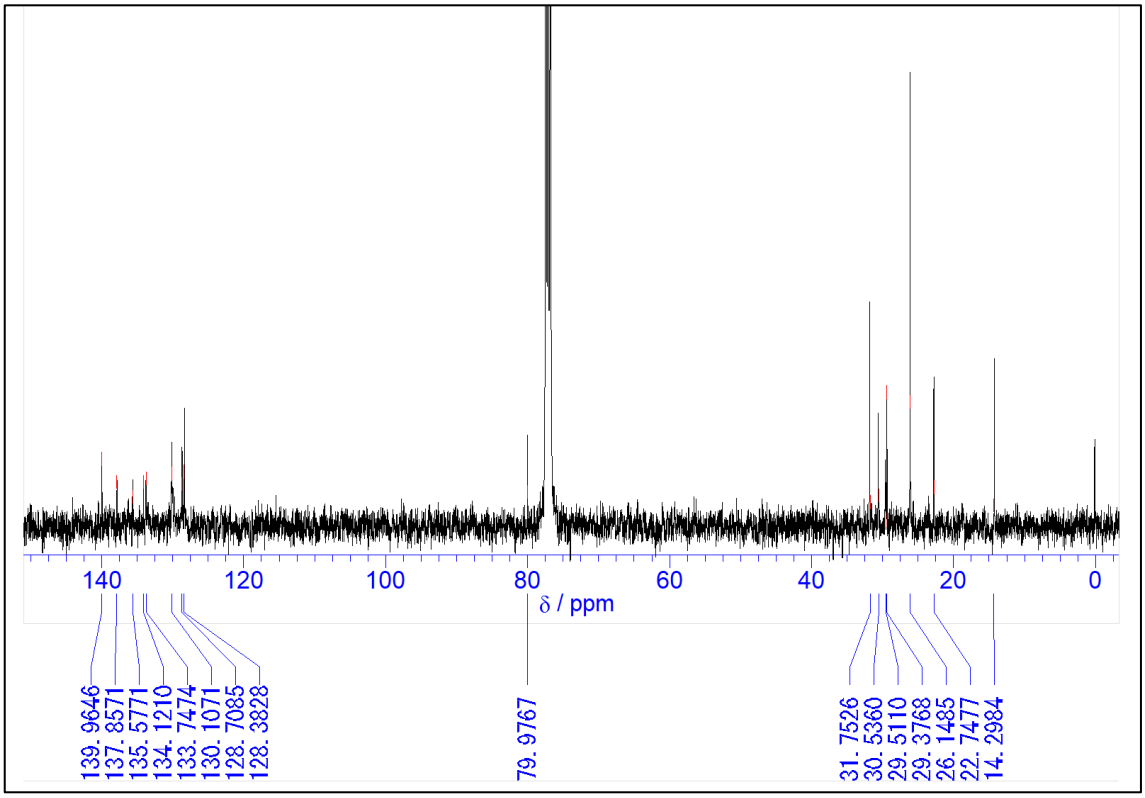


Figure S4. CVs acquired in 0.5 M $Li_2SO_{4(aq)}$ at 20 mV/s for before and after thermal treatment for (a) random **5a'** and (b) block copolymer **5a** thin film electrodes. (c, d) CVs acquired at 200 mV/s for the aforementioned electrodes.


H_D
H_A
SO3
H_E
nC5H11
H_B
H_C
S
n
block
S
m
5a
A
B,C
D
E
200.0
189.1664
223.2778
205.6987
1534.819
1411.011
9
8
7
6
5
4
3
2
1
0
δ / ppm


140
120
100
80
60
40
20
0
δ / ppm
139.9646
137.8571
135.5771
134.1210
133.7474
130.1071
128.7085
128.3828
79.9767
31.7526
30.5360
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29.3768
26.1485
22.7477
14.2984

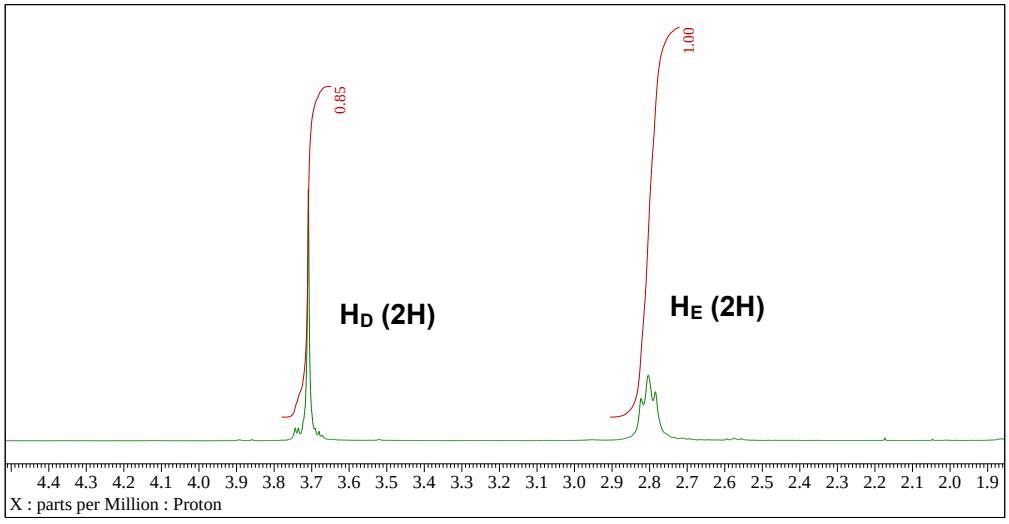

Figure S5. (a) ^{1}H NMR and (b) ^{13}C{^{1}H} NMR spectrum of block copolymer **5a**. (c) detamination of the ratio of *m*:*n* in **5a**.

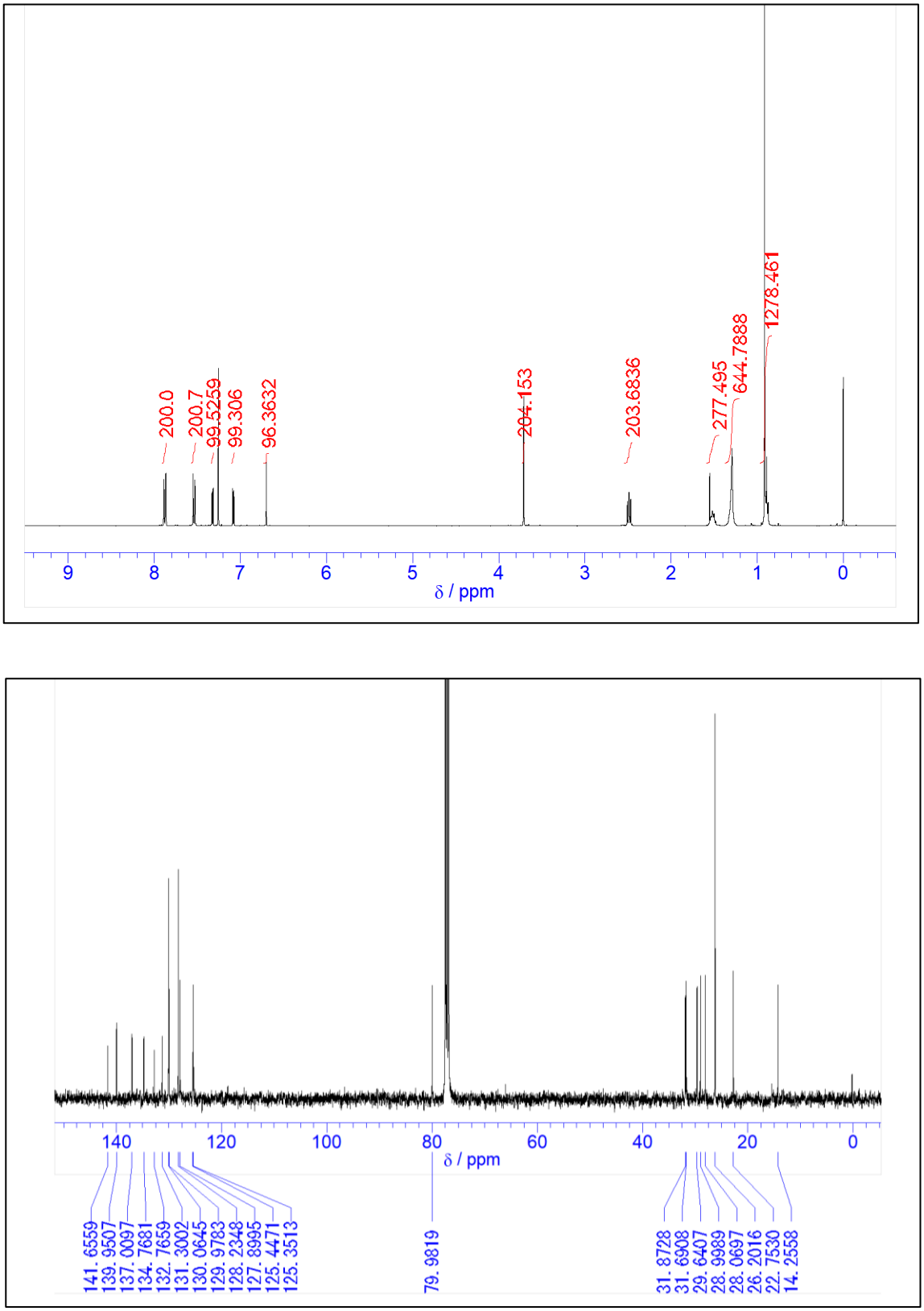

Figure S6. (a) ^{1}H NMR and (b) $^{13}C\{^{1}H\}$ NMR spectrum of bithiophene **6**

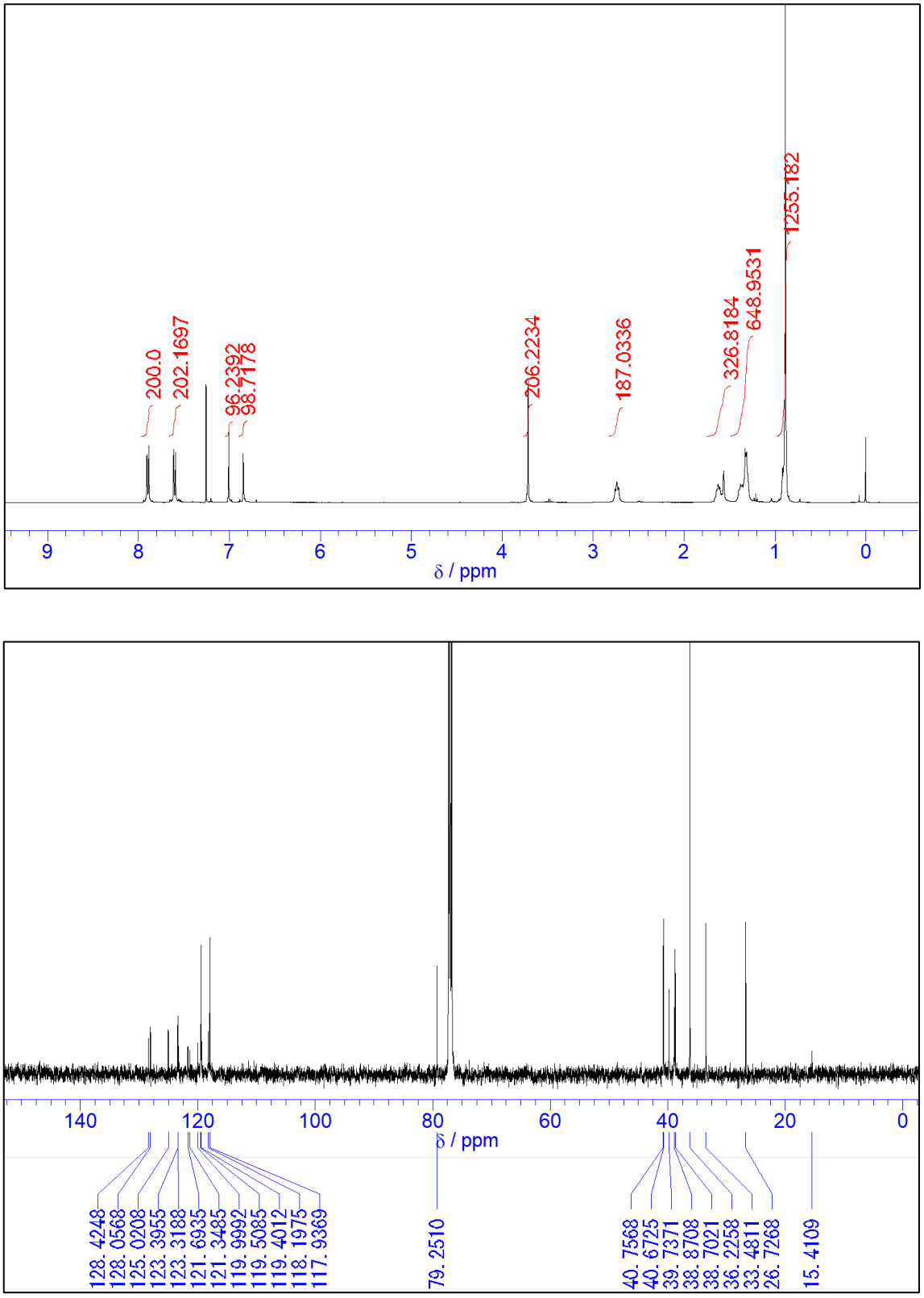

Figure S7. (a) ^{1}H NMR and (b) $^{13}C\{^{1}H\}$ NMR spectrum of alternating copolymer **5a''**