Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Highly Efficient Flame Retardants of Polyacrylonitrile Copolymers Containing Bio-derived Caffeic Acid Derivatives by Controlling Thermal Oxidation Stabilization Process

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Experimental Section

1. Synthesis of Monomers

1.1 Synthesis of Methyl Caffeate (MCA)

10.0 g (55.5 mmol) of CA and 100 mL of MeOH was added into a 2-neck round-bottom flask. When CA was completely dissolved, 4.0 mL of sulfuric acid was added into the solution, and then the mixture was refluxed under 90 °C for 18 h. After finishing the reaction. the flask was cooled at room temperature. Saturated solution of Na_2CO_3 was added into the mixture diluted with EA. The organic layers were washed with saturated solution of Na_2CO_3 for removal of reactants and brine. And then the organic layers were dried over $MgSO_4$ and the solvent was evaporated using rotary evaporator under reduced pressure. After evaporation, the product was collected and dried using vacuum oven. White solid, 89 % yield. ^1H NMR (600 MHz, DMSO-d_6): δ 9.53–9.23 (d, 2H, –OH), 7.48–7.45 (d, 1H, Ph), 7.03 (s, 1H, Ph), 6.99–6.97 (d, 1H, Ph), 6.74–6.73 (d, 1H, –CH=), 6.28–6.24 (d, 1H, =CH–COO–), 3.66 (s, 3H, O–CH_3).

1.2 Synthesis of Acetonide-protected Methyl Caffeate (AMCA)

1.8 g (9 mmol) of MCA was added into the mixed solvent of dry acetone (30 mL) and chloroform (120 mL) on a 3-neck round-bottom flask and bubbled with argon gas for 30 min. 150 mg of PTSA was added as a catalyst into the reaction mixture and the mixture was refluxed for 2 h through Dean–Stark apparatus. Then, 3.96 mL (29.16 mmol) of 2,2-dimethoxypropane was injected into the mixture using syringe. After installation of a Soxhlet's extractor filled with 20 g of molecular sieve (4 Å) 30 g of $CaCl_2$, the reaction was then stirred in a dark room under reflux for 12 h. The mixture was diluted with MC, and the diluted solution washed with distilled Saturated solution of Na_2CO_3, brine and water, then dried over $MgSO_4$. The product was collected by evaporation of MC, and dried under vacuum oven for 24 h. Brown liquid, 73% yield. ^{1}H NMR (600 MHz, DMSO-d_6): δ 7.55–7.53 (d, 1H, Ph), 7.31 (s, 1H, Ph), 7.14–7.13 (d, 1H, Ph), 6.85–6.84 (d, 1H, –CH=), 6.49–6.45 (d, 1H, =CH–COO–), 3.67 (s, 3H, O–CH_3), 1.63 (s, 6H, $(CH_3)_2$–C–).

1.3 Synthesis of Acetonide-protected Caffeic Acid (ACA)

3 g (12.9 mmol) of AMCA was dissolved in a mixed solvent of MeOH and milli-Q water (18.2 MΩ.cm, Millipore). 4.5 g of KOH was added into the mixture, and then the reaction mixture was stirred at room temperature for 24 h. Then, MeOH was evaporated in vacuo, and the pH value of aqueous phase was adjusted to 4~5 using a saturated citric acid aqueous solution, for precipitation of the product. The precipitated solid was washed with water and hexane several time. the product was collected and dried by vacuum oven at 60 °C for 12 h. Yellow solid, 85% yield. ^{1}H NMR (600 MHz, DMSO-d_6): δ 12.22 (s, 1H, -COOH), 7.48–7.45 (d, 1H, Ph), 7.26 (s, 1H, Ph), 7.10–7.08 (d, 1H, Ph), 6.85–6.83 (d, 1H, –CH=), 6.36–6.33 (d, 1H, =CH–COO–), 1.63 (s, 6H, $(CH_3)_2$–C–).

1.4 Synthesis of 3,4-Dihydroxystryene (DHS)

10 g (111.0 mmol) of CA was dissolved in 200 mL of DMF. 2 g of NaOEt as a catalyst was added into the CA solution on 3-neck round flask, and then the reaction mixture was stirred at at 110 °C for 1 h. After cooling to room temperature, the product was extracted with n-hexane and the organic layer was washed with brine and water. The solvent was evaporated by rotary evaporator, and the product was stored at −20 °C before further experiments for acetonide protection.

1.5 Synthesis of Acetonide-protected 3,4-Dihydroxystryene (ADHS)

1.8 g (13.2 mmol) of DHS was added into the mixed solvent of dry acetone (30 mL) and chloroform (120 mL) on a 3-neck round-bottom flask and bubbled with argon gas for 30 min.

150 mg of PTSA was added as a catalyst into the reaction mixture and the mixture was refluxed for 2 h through Dean–Stark apparatus. Then, 3.96 mL (29.16 mmol) of 2,2-dimethoxypropane was injected into the mixture using syringe. After installation of a Soxhlet's extractor filled with 20 g of molecular sieve (4 Å) 30 g of $CaCl_2$, the reaction was then stirred in a dark room under reflux for 12 h. The mixture was diluted with MC, and the diluted solution washed with distilled Saturated solution of Na_2CO_3, brine and water, then dried over $MgSO_4$. The product was collected by evaporation of MC, and dried under vacuum oven for 24 h. Brown liquid, 73% yield. White solid, 85% yield. ^1H NMR (600 MHz, DMSO-d_6): δ 6.47 (br, 1H, Ar-H), 6.36 (m, 1H, Ar-H), 6.10 (d, 1H, Ar-H), 5.50 (d, 1H, –CH=), 5.30 (d, 2H, $=CH_2$), 1.54 (s, 6H, $(CH_3)_2$–C–).

2. Comonomer Composition and ^1H NMR data of PAN Copolymers

2.1 Acrylonitrile-3,4-Dimethoxystyrene Copolymer, P(AN-co-DMS$_1$)

The molar feed-ratio of AN and DMS was 99:1. The ratio of AN unit and DMS unit after polymerization was determined to be 98.3:1.7 by ^1H NMR spectrum. ^1H NMR (600 MHz, DMSO-d_6): δ 7.0–6.72 (m, 3H, Ar-H), 3.75 (d, 6H, CH_3–O–), 3.17–3.12 (br, 2H, –CH–), 2.16–2.03 (br, 4H, $–CH_2–$).

2.2 Acrylonitrile-3,4-Dimethoxycinnamic acid Copolymer, P(AN-co-DCA$_1$)

The molar feed-ratio of AN and DCA was 99:1. The ratio of AN unit and DCA unit after polymerization was determined to be 98.9:1.1 by ^1H NMR spectrum. ^1H NMR (600 MHz, DMSO-d_6): δ 13.31 (s, 1H, –COOH), 7.20–6.65 (m, 3H, Ar-H), 3.77–3.73 (d, 6H, CH_3–O–), 3.15–3.11 (br, 1H, –CH–), 2.14–2.01 (br, 2H for $–CH_2–$ of AN and 1H for –CH– of ACA).

2.3 Acrylonitrile-Acetonide-protected Dihydroxystyrene (1 mol%) Copolymer, P(AN-co-ADHS$_1$)

The molar feed-ratio of AN and ADHS was 99:1. The ratio of AN unit and ADHS unit after polymerization was determined to be 98:2 by ^{1}H NMR spectrum. ^{1}H NMR (600 MHz, DMSO-d_6): δ 6.53–6.16 (m, 3H, Ar-H), 3.18–3.10 (br, 2H, –CH–), 2.14–2.01 (br, 4H, $–CH_2–$), 1.55 (s, 6H, $–(OCH_3)_2$).

2.4 Acrylonitrile-Acetonide-protected Dihydroxystyrene (3 mol%) Copolymer, P(AN-co-ADHS$_3$)

The molar feed-ratio of AN and ADHS was 97:3. The ratio of AN unit and ADHS unit after polymerization was determined to be 97:3 by ^{1}H NMR spectrum. ^{1}H NMR (600 MHz, DMSO-d_6): δ 6.53–6.16 (m, 3H, Ar-H), 3.18–3.10 (br, 2H, –CH–), 2.16–2.03 (br, 4H, $–CH_2–$), 1.55 (s, 6H, $–(OCH_3)_2$).

2.5 Acrylonitrile-Acetonide-protected Caffeic acid (1 mol%) Copolymer, P(AN-co-ACA$_1$)

The molar feed-ratio of AN and ACA was 99:1. The ratio of AN unit and ACA unit after polymerization was determined to be 98.8:1.2 by ^{1}H NMR spectrum. ^{1}H NMR (600 MHz, DMSO-d_6): δ 13.31 (s, 1H, –COOH), 7.20–6.65 (m, 3H, Ar-H), 3.77–3.73 (d, 6H, $CH_3–O–$), 3.15–3.11 (br, 1H, –CH–), 2.14–2.01 (br, 2H for $–CH_2–$ of AN and 1H for –CH– of ACA), 1.55 (s, 6H, $–(OCH_3)_2$).

2.6 Acrylonitrile-Acetonide-protected Caffeic acid (3 mol%) Copolymer, P(AN-co-ACA$_3$)

The molar feed-ratio of AN and ACA was 97:3. The ratio of AN unit and ACA unit after polymerization was determined to be 97.5:2.5 by ^{1}H NMR spectrum. ^{1}H NMR (600 MHz, DMSO-d_6): δ 13.27 (s, 1H, –COOH), 7.18–6.64(m, 3H, Ar-H), 3.15–3.11 (br, 1H, –CH–), 2.14–2.01 (br, 2H for $–CH_2–$ of AN and 1H for –CH– of ACA), 1.55 (s, 6H, $–(OCH_3)_2$).

2.7 Acrylonitrile-Acetonide-protected Methyl Caffeate (3 mol%) Copolymer, P(AN-co-AMCA$_3$)

The molar feed-ratio of AN and AMCA was 97:3. The ratio of AN unit and AMCA unit after polymerization was determined to be 97.5:2.5 by ^{1}H NMR spectrum. ^{1}H NMR (600 MHz, DMSO-*d$_6$*): δ 7.18–6.64 (m, 3H, Ar-H), 3.74 (d, 3H, –COOCH$_3$), 3.15–3.10 (br, 1H, –CH–), 2.14–2.01 (br, 2H for –CH$_2$– of AN and 1H for –CH– of ACA), 1.59 (s, 6H, –(OCH$_3$)$_2$).

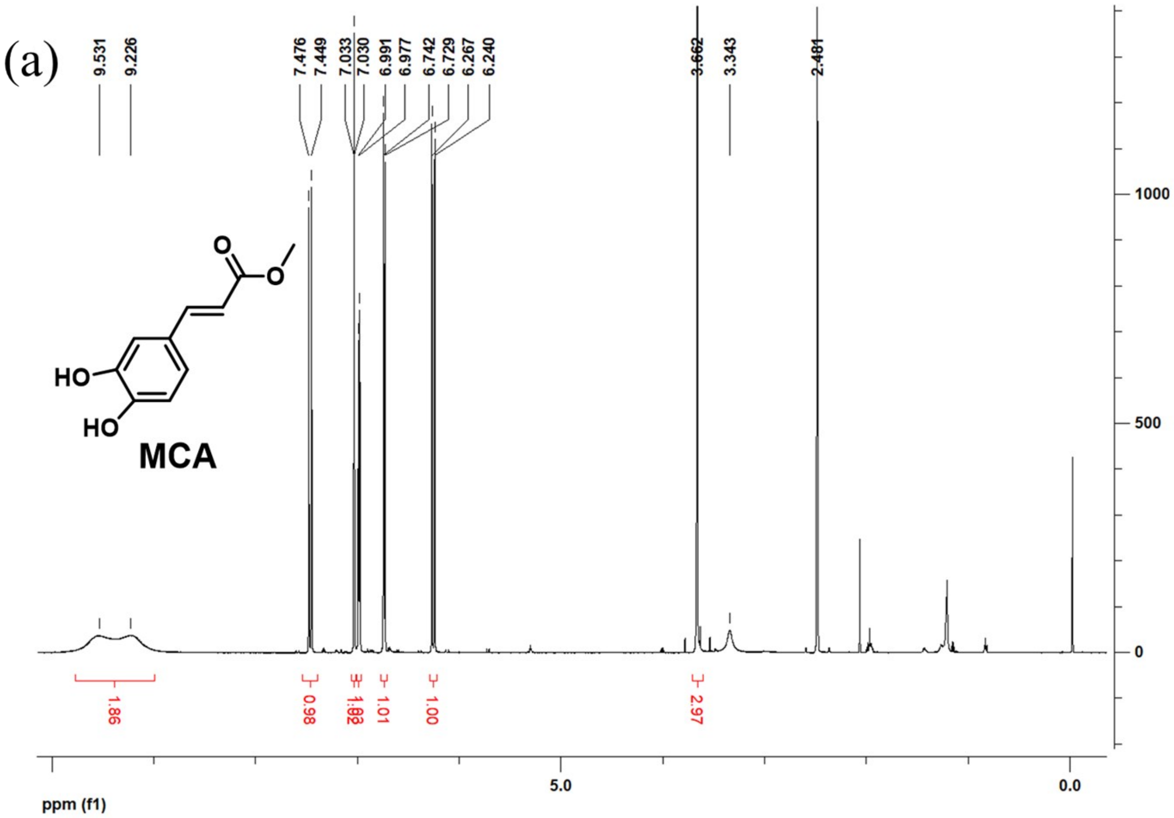
2.8 Acrylonitrile-Itaconic acid (1 mol%) Copolymer, P(AN-co-IA$_1$)

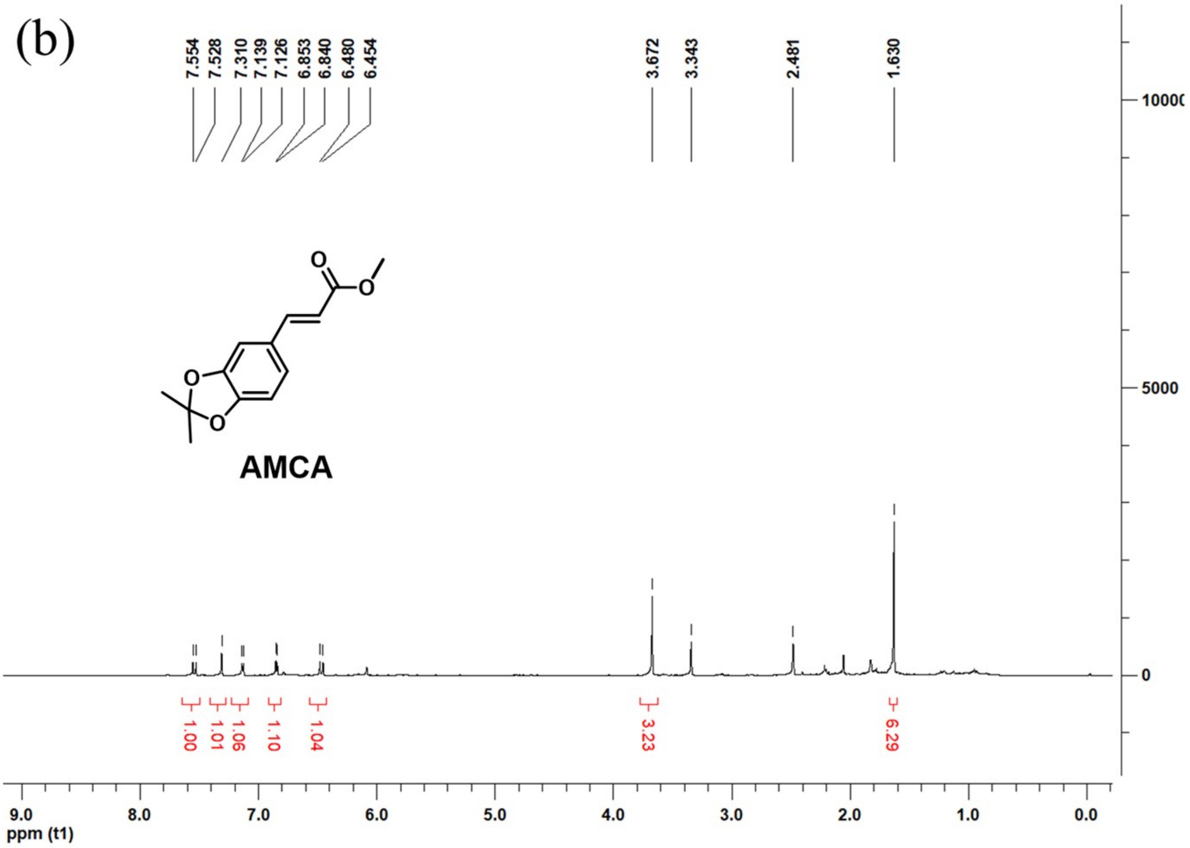
The molar feed-ratio of AN and IA (purified by re-crystalizaiton) was 99:1. The ratio of AN unit and AMCA unit after polymerization was determined to be 98.7:1.3 by ^{1}H NMR spectrum. ^{1}H NMR (600 MHz, DMSO-*d$_6$*): δ 10.23 (s, 2H, –COOH), 3.24–3.02 (s, 1H, –CH), 2.32–1.81 (d, 6H, –CH$_2$–, –CCH2COO– of IA),

Table S1. Feed-ratio for polymerization, content of comonomers after polymerization, and acetonide-deprotection ratio of polymers.

Sample codes	Acetonide-deprotection ratio[a] (%)
P(AN-*co*-DHS_1)	88
P(AN-*co*-DHS_3)	60
P(AN-*co*-CA_1)	57
P(AN-*co*-CA_3)	53
P(AN-*co*-MCA_3)	57

[a] Calculated from ^{1}H-NMR sptectra of the polymers


(a)
9.531
9.226
7.476
7.449
7.033
7.030
6.991
6.977
6.742
6.729
6.267
6.240
3.662
3.343
2.481
1000
500
0
O
O
HO
HO
MCA
1.86
0.98
1.02
1.01
1.00
2.97
5.0
0.0
ppm (f1)


(b)
7.554
7.528
7.310
7.139
7.126
6.853
6.840
6.480
6.454
3.672
3.343
2.481
1.630
10000
5000
0
O
O
O
O
AMCA
1.00
1.01
1.06
1.10
1.04
3.23
6.29
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

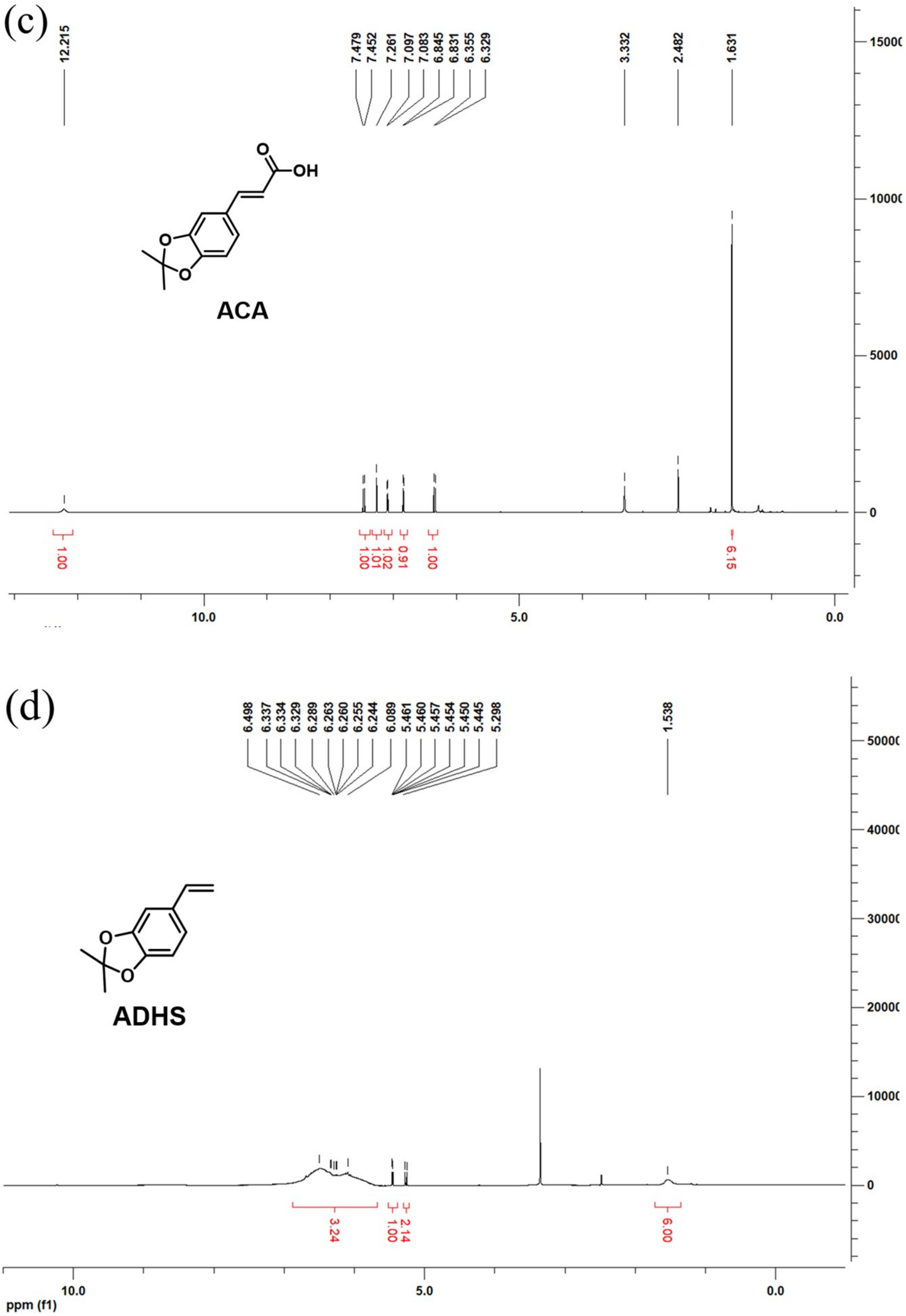


Fig. S1 ^{1}H NMR spectra of (a) MCA, (b) AMCA, (c) ACA, and (b) ADHS.

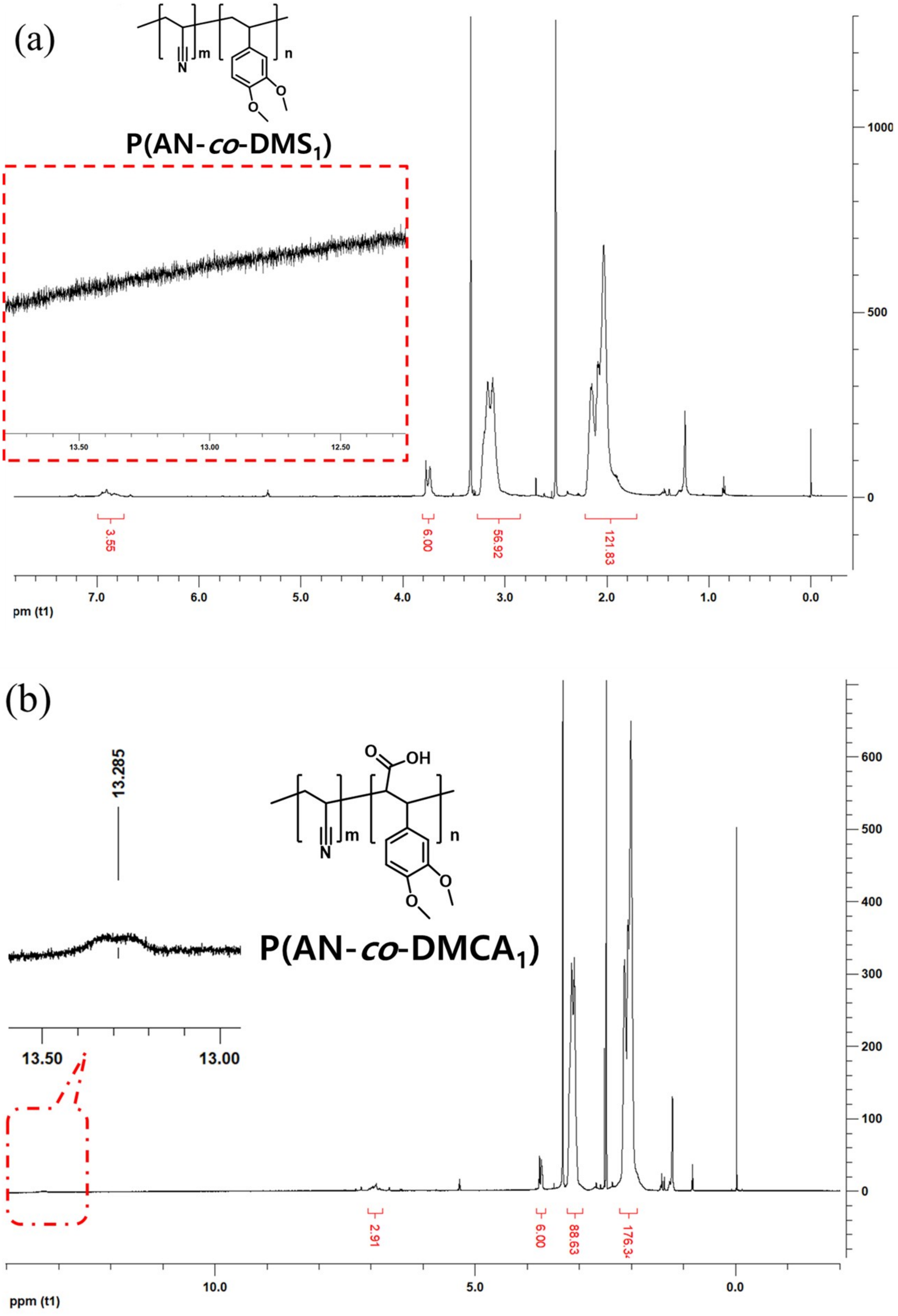
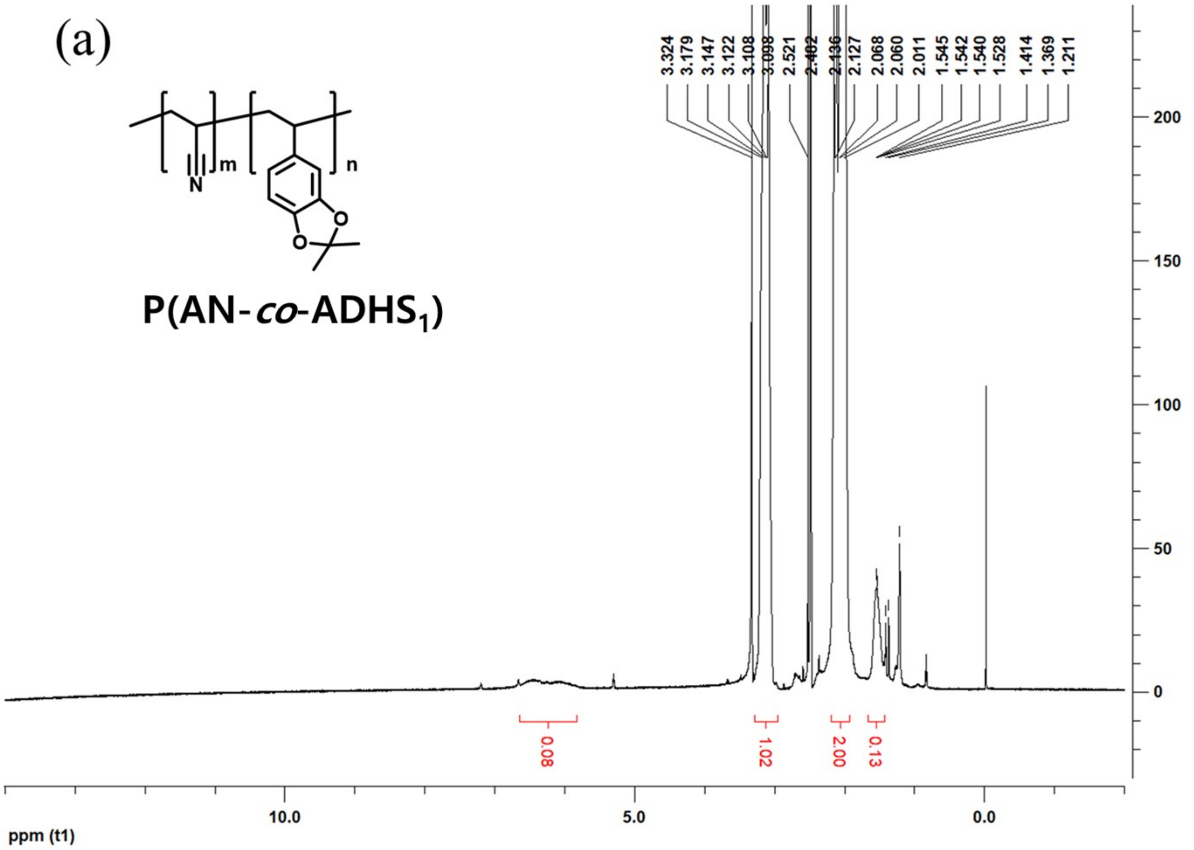
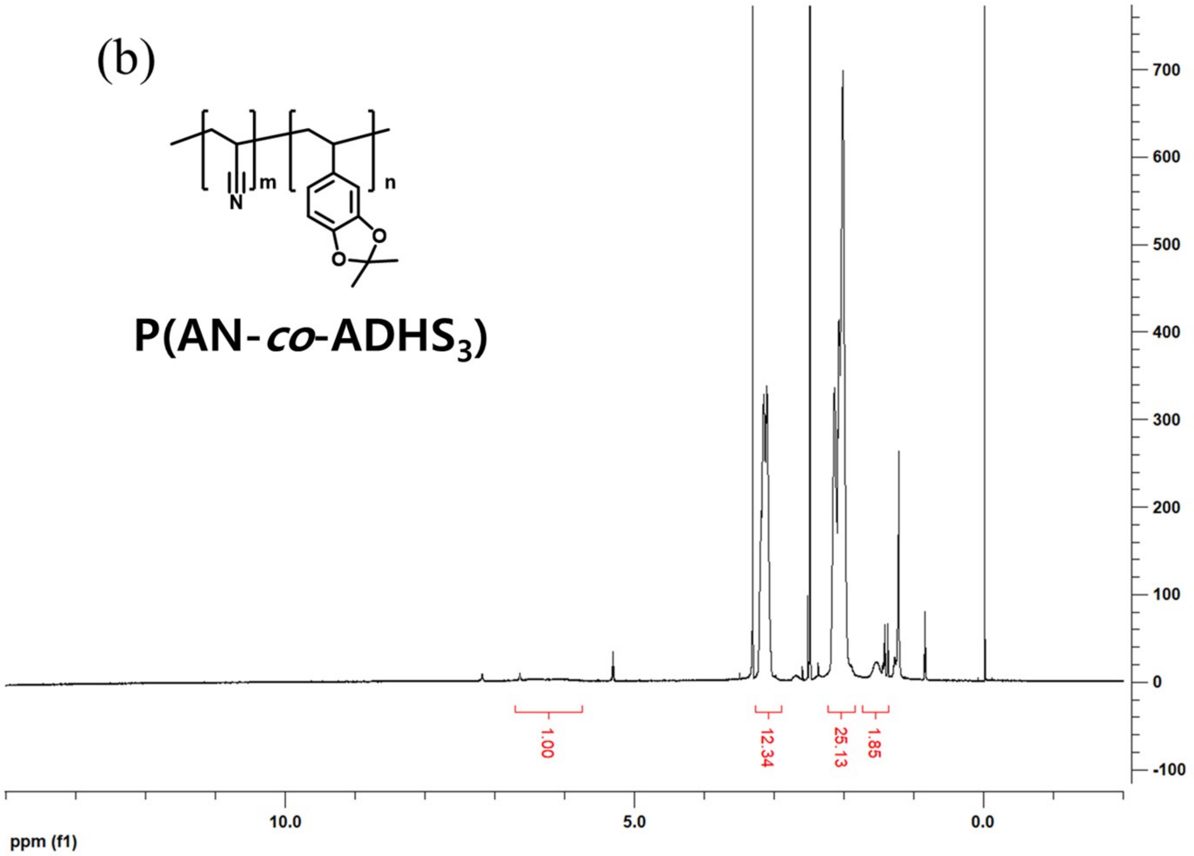
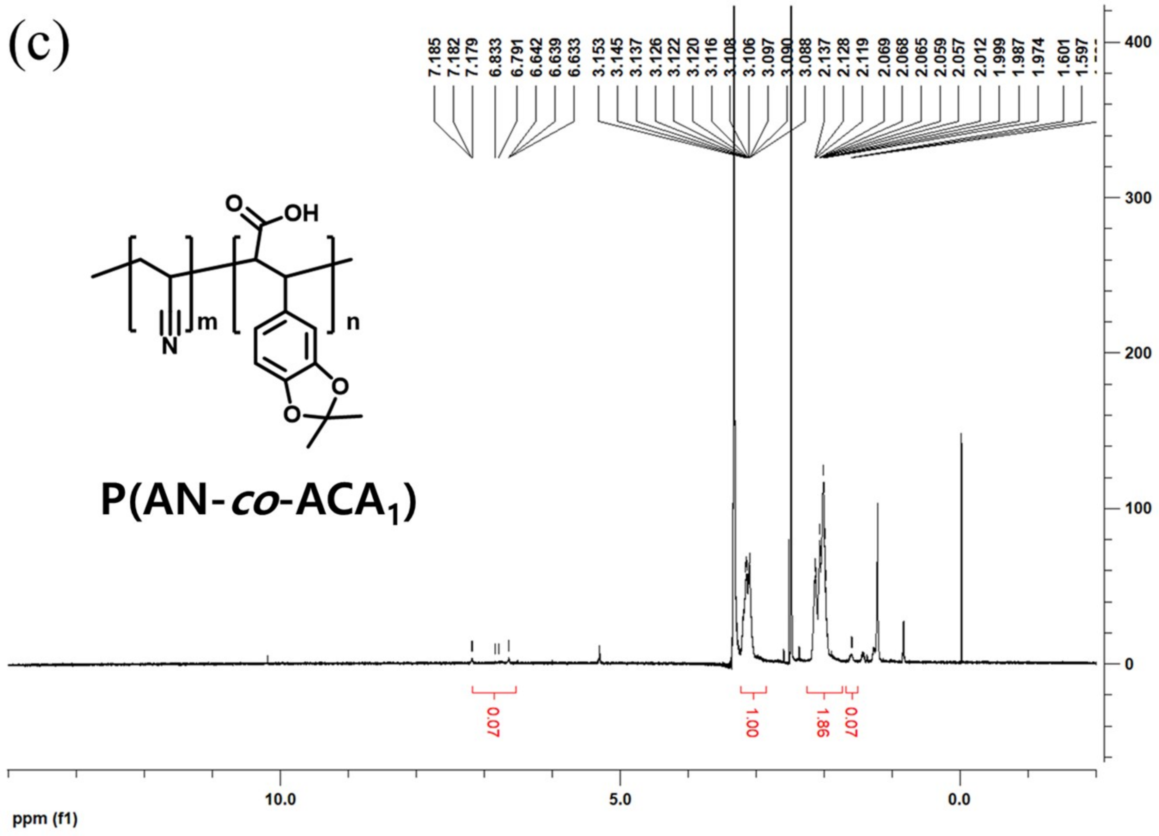


Fig. S2 ^{1}H NMR spectra of dimethoxylated catechol contained PAN copolymers, (a) P(AN-*co*-DMS$_1$) and (b) P(AN-*co*-DCA$_1$).


(a)
m
n
N
O
O
P(AN-co-ADHS1)
3.324
3.179
3.147
3.122
3.108
3.098
2.521
2.492
2.136
2.127
2.068
2.060
2.011
1.545
1.542
1.540
1.528
1.414
1.369
1.211
200
150
100
50
0
0.08
1.02
2.00
0.13
10.0
5.0
0.0
ppm (t1)


(b)
m
n
N
O
O
P(AN-co-ADHS3)
700
600
500
400
300
200
100
0
-100
1.00
12.34
25.13
1.85
10.0
5.0
0.0
ppm (f1)


(c)
7.185
7.182
7.179
6.833
6.791
6.642
6.639
6.633
3.153
3.145
3.137
3.126
3.122
3.120
3.116
3.108
3.106
3.097
3.090
3.088
2.137
2.128
2.119
2.069
2.068
2.065
2.059
2.057
2.012
1.999
1.987
1.974
1.601
1.597
OH
O
N
m
n
O
O
P(AN-co-ACA1)
0.07
1.00
1.86
0.07
400
300
200
100
0
10.0
5.0
0.0
ppm (f1)

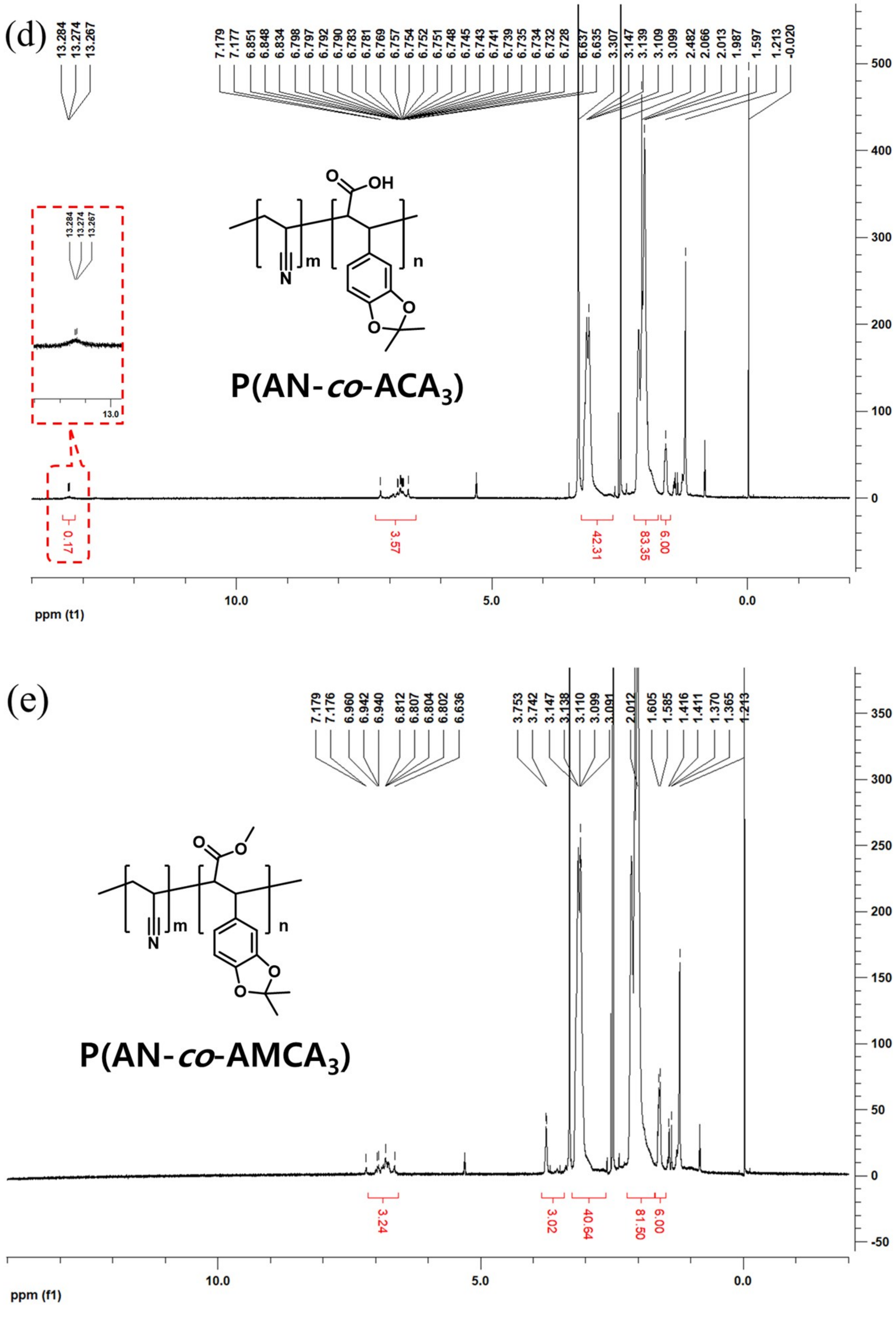
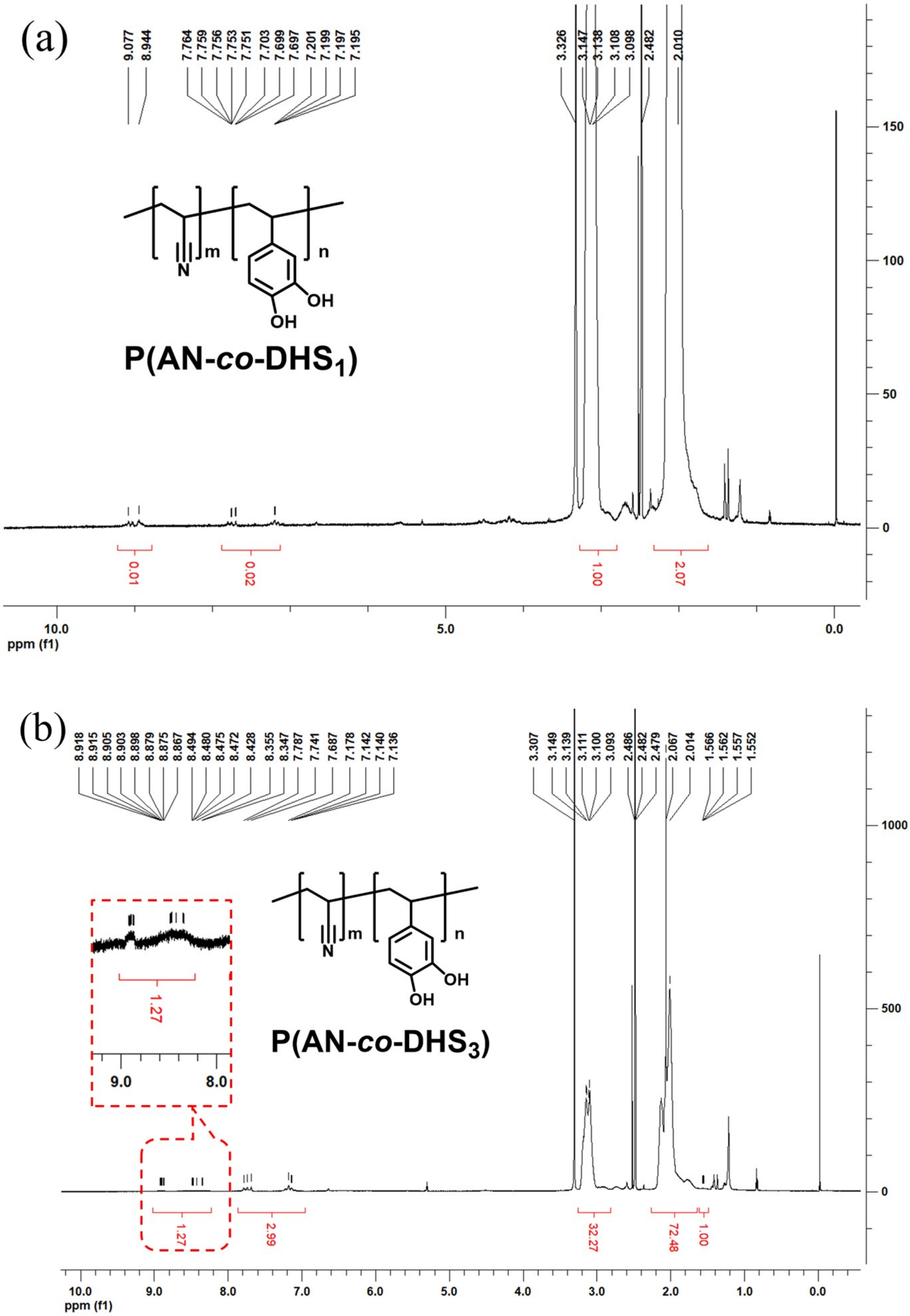
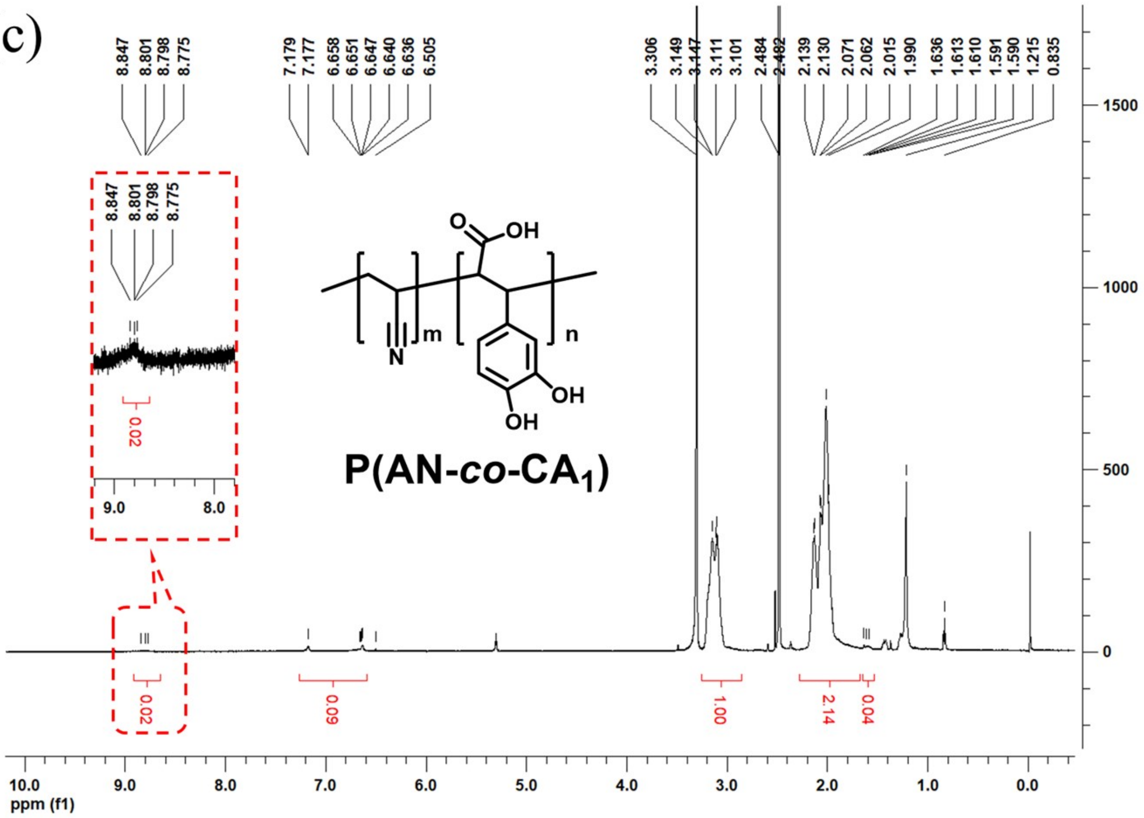


Fig. S3 ^{1}H NMR spectra of acetonide-protected PAN copolymers, (a) P(AN-*co*-ADHS$_1$), (b)

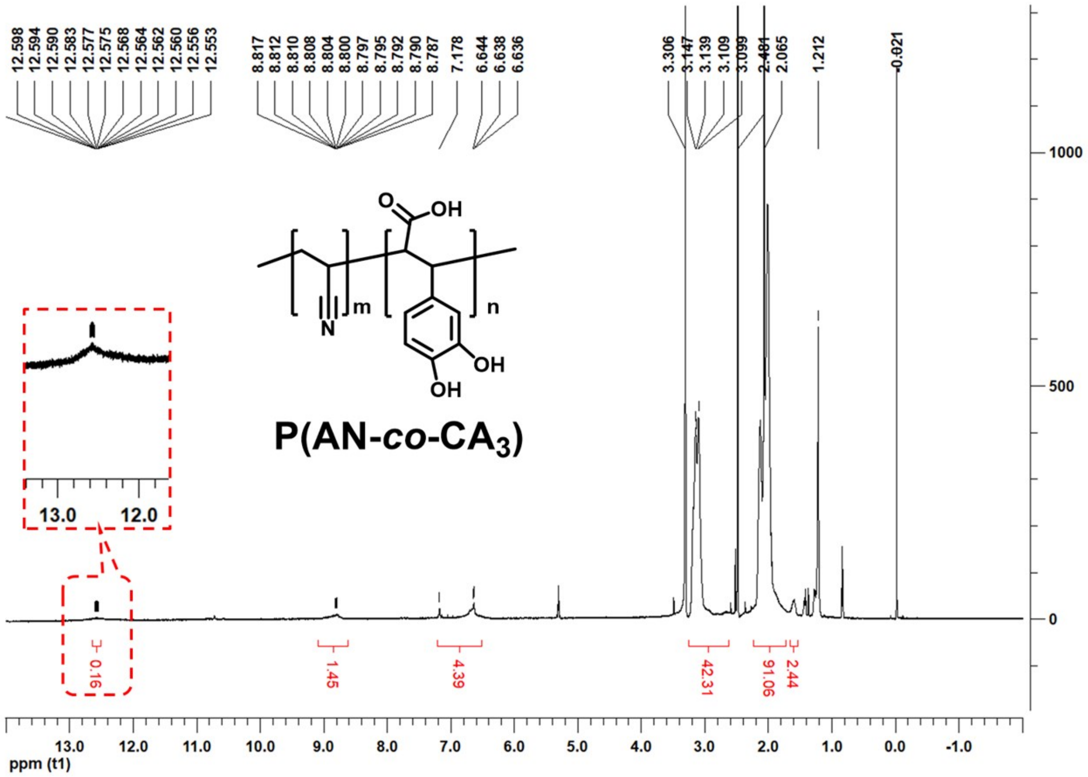
P(AN-*co*-ADHS$_3$), (c) P(AN-*co*-ACA$_1$), (d) P(AN-*co*-ACA$_3$), and (d) P(AN-*co*-AMCA$_3$).


(a)
9.077
8.944
7.764
7.759
7.756
7.753
7.751
7.703
7.699
7.697
7.201
7.199
7.197
7.195
3.326
3.147
3.138
3.108
3.098
2.482
2.010
m
n
N
OH
OH
P(AN-co-DHS1)
150
100
50
0
0.01
0.02
1.00
2.07
10.0
5.0
0.0
ppm (f1)
(b)
8.918
8.915
8.905
8.903
8.898
8.879
8.875
8.867
8.494
8.480
8.475
8.472
8.428
8.355
8.347
7.787
7.741
7.687
7.178
7.142
7.140
7.136
3.307
3.149
3.139
3.111
3.100
3.093
2.486
2.482
2.479
2.067
2.014
1.566
1.562
1.557
1.552
1000
500
0
1.27
9.0
8.0
m
n
N
OH
OH
P(AN-co-DHS3)
1.27
2.99
32.27
72.48
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

(c)


8.847
8.801
8.798
8.775
7.179
7.177
6.658
6.651
6.647
6.640
6.636
6.505
3.306
3.149
3.147
3.111
3.101
2.484
2.482
2.139
2.130
2.071
2.062
2.015
1.990
1.636
1.613
1.610
1.591
1.590
1.215
0.835
0.02
9.0
8.0
O
OH
N
m
n
OH
OH
P(AN-co-CA$_1$)
1500
1000
500
0
0.02
0.09
1.00
2.14
0.04
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

(d)


12.598
12.594
12.590
12.583
12.577
12.575
12.568
12.564
12.562
12.560
12.556
12.553
8.817
8.812
8.810
8.808
8.804
8.800
8.797
8.795
8.792
8.790
8.787
7.178
6.644
6.638
6.636
3.306
3.147
3.139
3.109
3.099
2.481
2.065
1.212
-0.021
O
OH
N
m
n
OH
OH
P(AN-co-CA$_3$)
13.0
12.0
1000
500
0
0.16
1.45
4.39
42.31
91.06
2.44
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
ppm (t1)

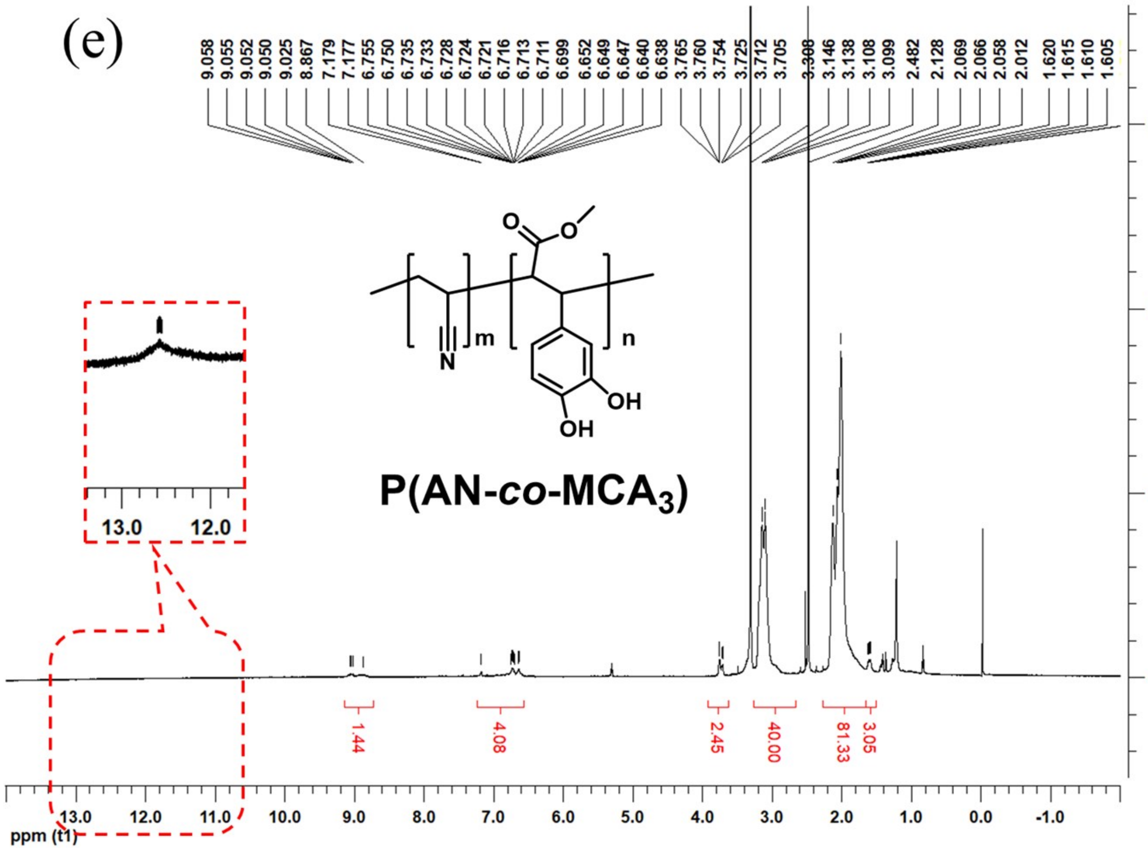
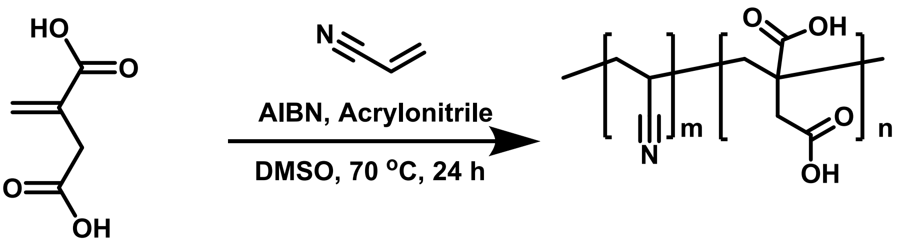


Fig. S4 ^{1}H NMR spectra of acetonide-deprotected PAN copolymers, (a) P(AN-*co*-DHS$_1$), (b) P(AN-*co*-DHS$_3$), (c) P(AN-*co*-CA$_1$), (d) P(AN-*co*-CA$_3$), and (d) P(AN-*co*-MCA$_3$).



Itaconic acid (IA) **P(AN-co-IA1)**

Scheme S1 Polymerization of itaconic acid (IA) contained PAN copolymer

Table S2 Feed-ratio for polymerization, content of comonomers after polymerization.

Sample code	Feed-ratio		Content of comonomers in polymer[a] (mol%)	Mn[b] ($\times 10^3$)	Polydispersity index[b]
	IA	AN			
P(AN-*co*-IA$_1$)	1	99	1.3	68.5	2.1

[a] Calculated from 1H-NMR spectra of the polymers.

[b] Determined by GPC using DMF at 80 °C with PMMA as a standard material

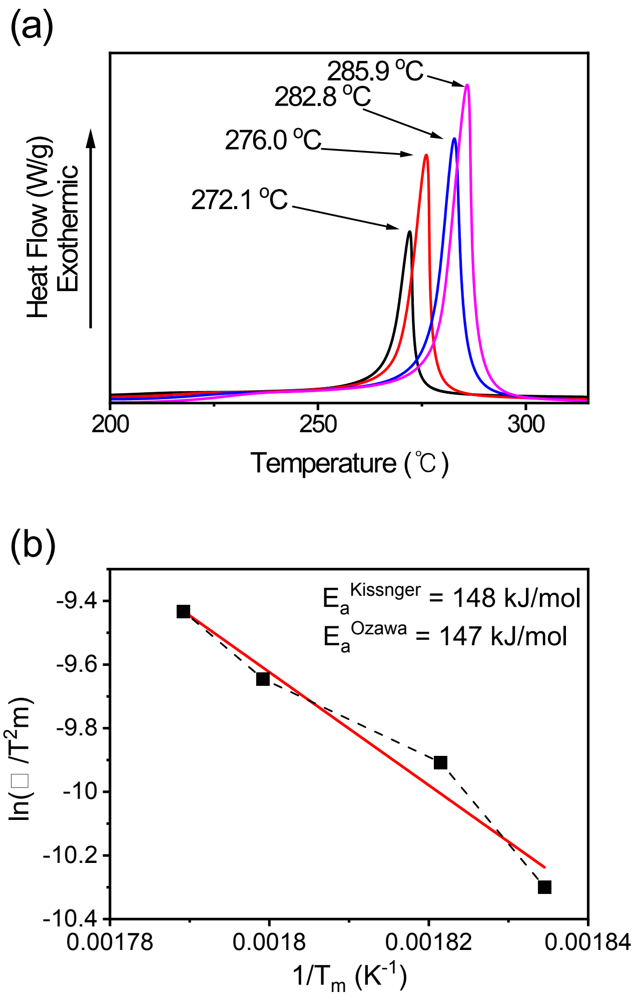


Fig. S5 (a) DSC thermograms and (b) Plots of $\ln\left(\varphi/T_m^2\right)$ *versus* $1/T_\mathrm{m}$(K^{-1}) according to the Kissinger method for P(AN-*co*-IA$_1$)

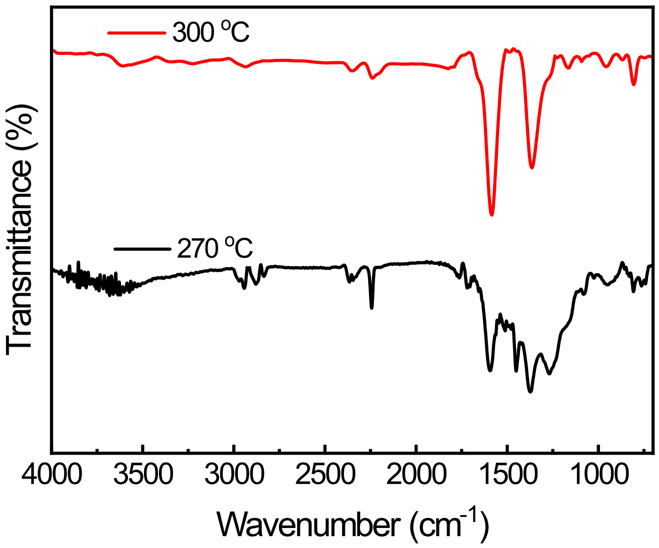


Fig. S6 FT-IR spectra of P(AN-*co*-IA$_1$) films after stabilization at 270 °C (black line) and 300 °C (red line) under air atmosphere.

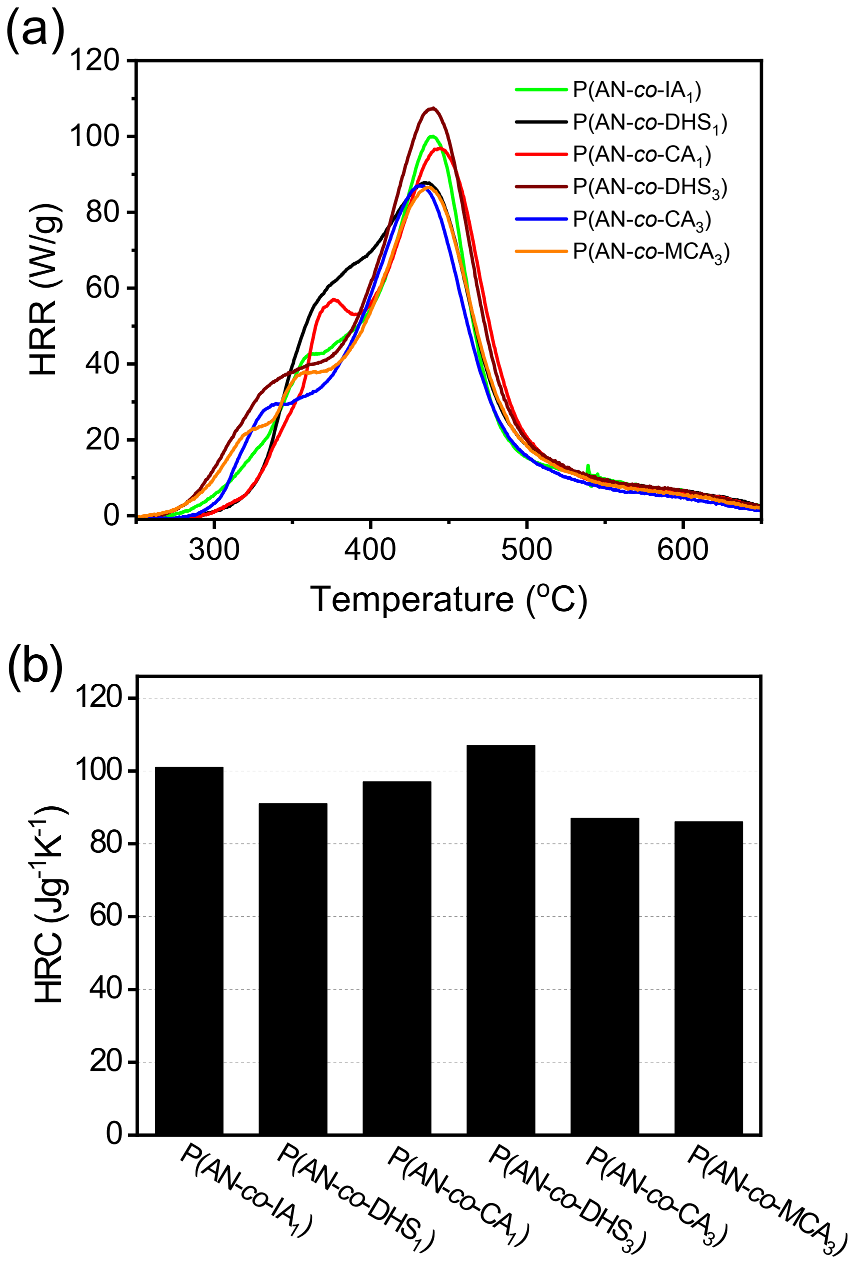


Fig. S7 (a) HRR *versus* temperature and (b) HRC of PAN copolymers oxidized at 270 °C.

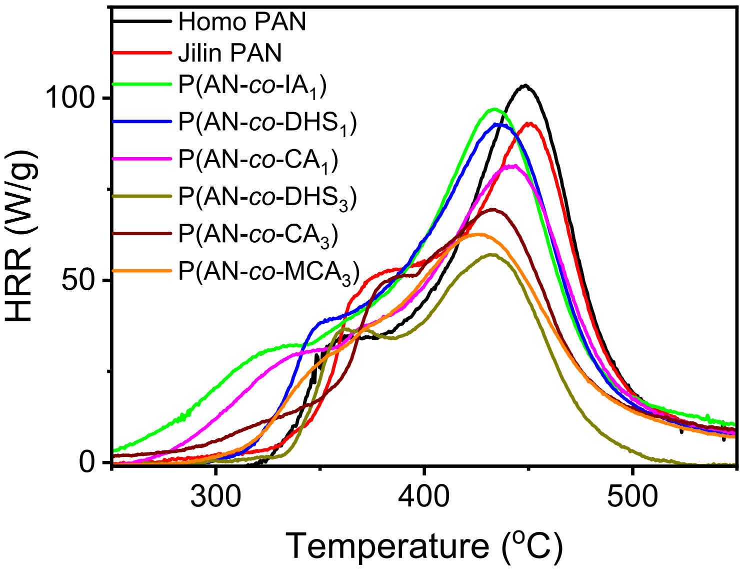


Fig. S8 HRR *versus* temperature of Homo PAN, Jilin PAN and PAN copolymer films stabilized at 300 ˚C under air atmosphere.

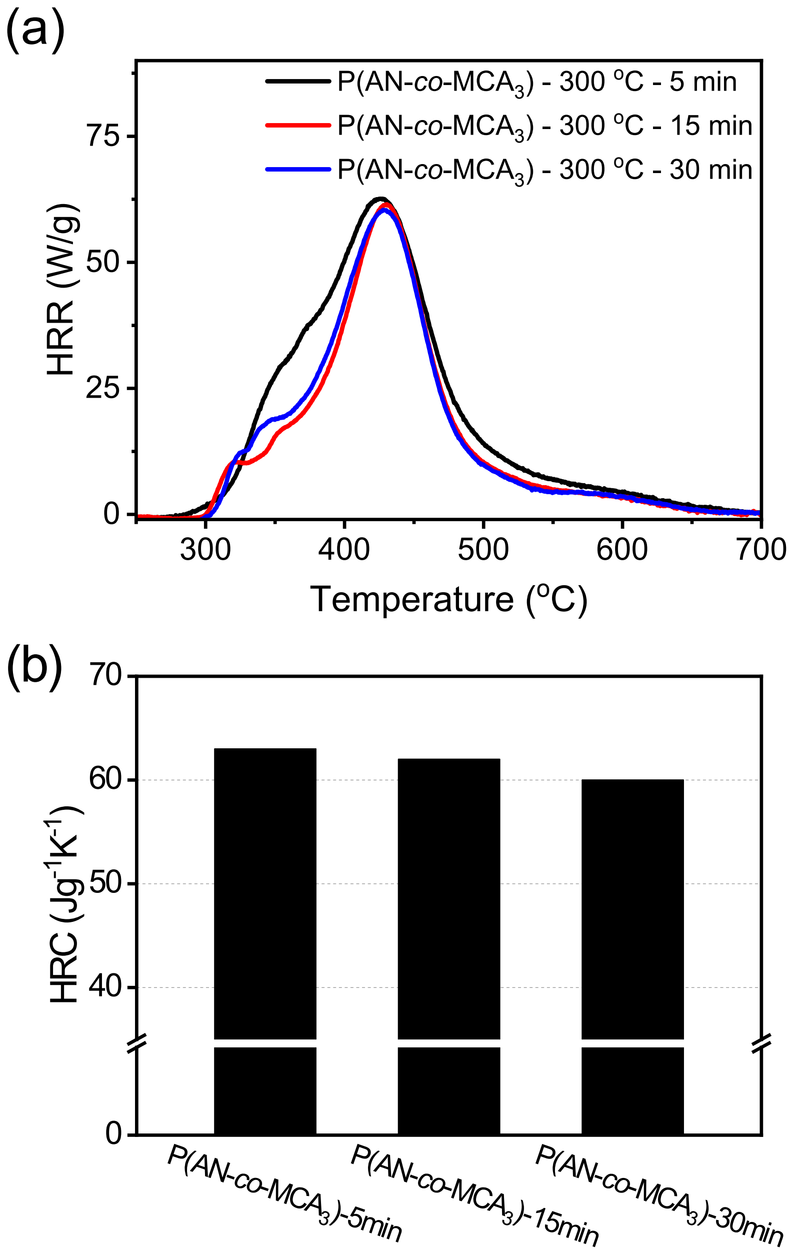


Fig. S9 (a) HRR *versus* temperature and (b) HRC of PAN homopolymer, and copolymers according to different residence time for oxidized at 300 °C under air atmosphere.

Table S3 MCC and LOI results of the PAN copolymers stabilized at 270 °C.

Sample code	PHRR (W/g)	THR (kJ/g)	TPHRR (°C)	HRC (J/g K)	Char fraction (%)[b]	LOI (%)[c]	Density (g/cm^3)[d]
P(AN-*co*-IA_1)[a]	100.0 ± 3.6	10.4 ± 0.3	438.5 ± 0.8	101 ± 1.3	40.5	34.7 ± 0.8	1.32
P(AN-*co*-DHS_1)[a]	91.0 ± 3.3	10.7 ± 0.2	444.8 ± 0.5	91 ± 1.1	41.5	34.1 ± 0.8	1.32
P(AN-*co*-CA_1)[a]	96.6 ± 0.7	10.9 ± 0.1	440.8 ± 3.2	97 ± 4.1	41.2	34.0 ± 0.9	1.34
P(AN-*co*-DHS_3)[a]	106.4 ± 4.1	12.1 ± 0.2	435.0 ± 1.1	107 ± 5.5	40.2	33.6 ± 0.7	1.34
P(AN-*co*-CA_3)[a]	86.7 ± 2.8	9.5 ± 0.3	430.4 ± 1.6	87 ± 0.4	45.4	35.7 ± 0.4	1.33
P(AN-*co*-MCA_3)[a]	86.5 ± 3.6	10.3 ± 0.2	436.5 ± 0.7	86 ± 0.3	46.7	36.2 ± 0.7	1.33

a: heating rate was 20 °C/min and then samples were held for 5 min at 270 °C
b: means the char fraction at 850 ˚C after MCC analysis
c: calculated by 'LOI = 17.5 + 0.4 × (char fraction)' [Eq. 4]
d: determined by density gradient column

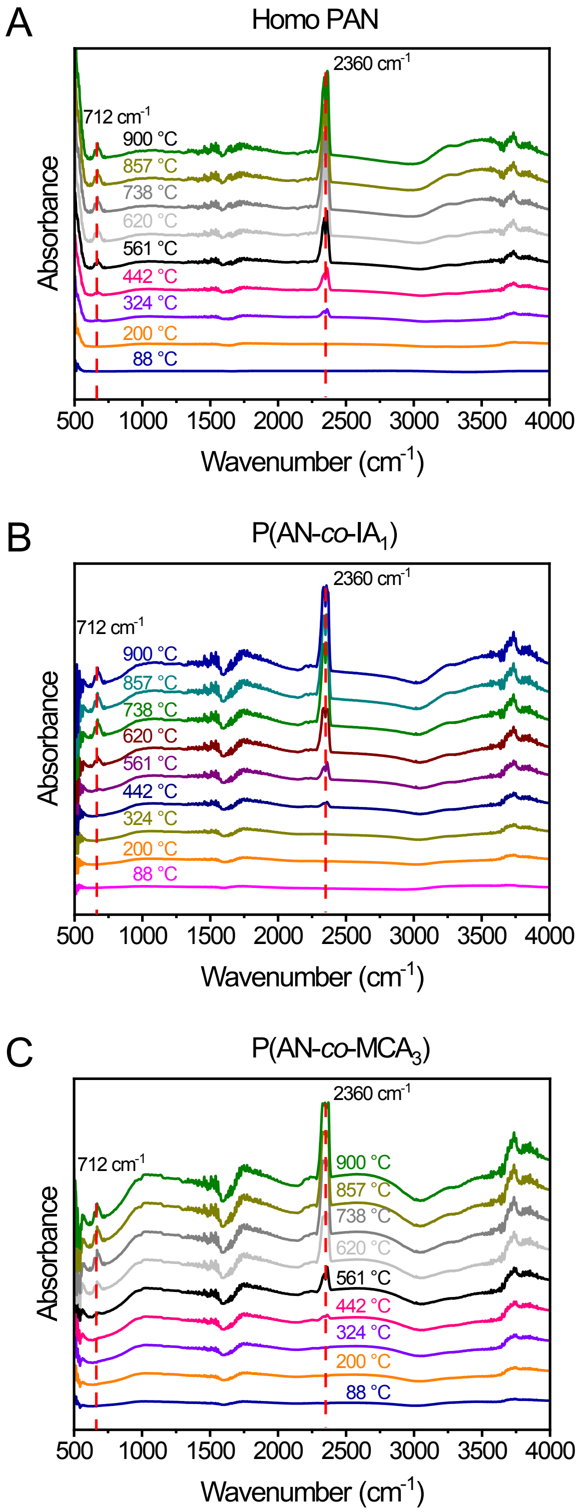


Fig. S10 TG-IR spectra of (a) Homo PAN, (b) P(AN-*co*-IA$_1$) and (c) P(AN-*co*-MCA$_3$) films at various temperature (200 - 900 °C).

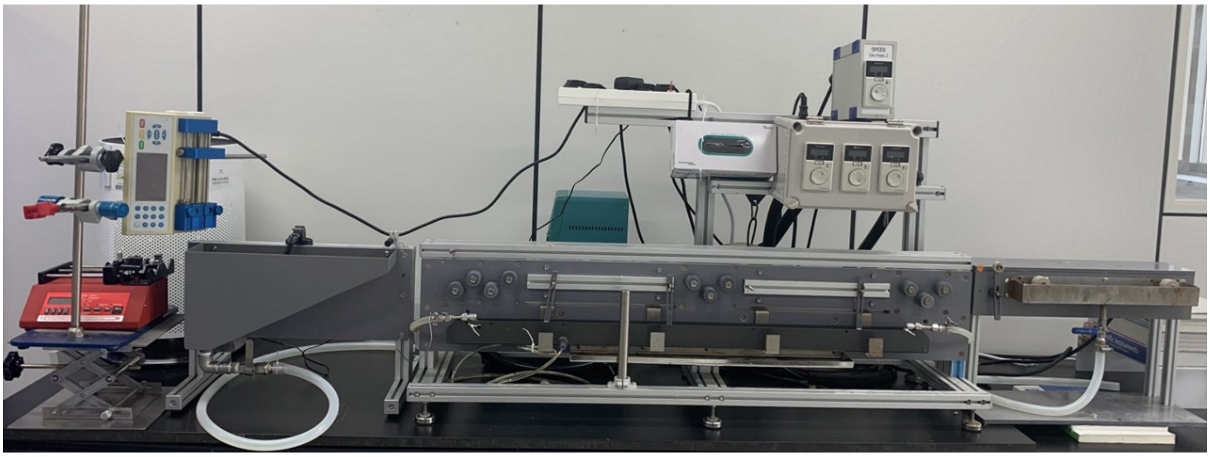


Fig. S11 Photograph image of single nozzle wet-spinning system for fabrication of PAN homo- or co-polymer fibers.

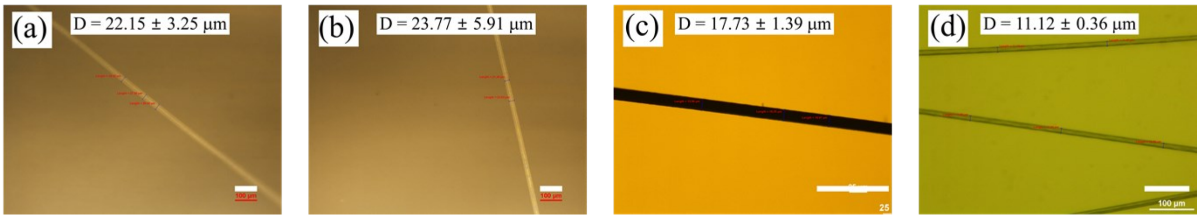


Fig. S12 Optical microscopy images of (a) Homo PAN, (b) P(AN-*co*-IA_1), (c) P(AN-*co*-MCA_3) and (d) commercial Jilin PAN fiber before stabilization. scale bar: 100 μm