Supporting information

# Order–order transitions in poly(*N*-octadecyl acrylamide-co-hydroxyethyl acrylamide) statistical copolymer films

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**Contents**

## Experimental section

### Time-conversion study.

Different feed ratios of HEAm, ODA, and 1 mol% of AIBN relative to the total monomer amount were added to a pressure-resistant glass tube (ACE GLASS). To this glass tube, toluene and DMF at a volume ratio of 4:1 was added in a glove box filled with $N_2$ and sealed with a rubber septum. The total concentration was kept constant at 0.2 M. The polymerization was carried out at 60 °C. A small amount of solution was taken by a syringe under Ar flow in predetermined intervals, and the solution was cooled to -50℃ to terminate the progress of copolymerization. The actual monomer feed ratio was determined by $^1$H NMR before the reaction. The conversion of the vinyl group was determined by $^1$H NMR in $CDCl_3$ using the methylene group of ODA as an internal standard. The time-conversion study for the molecular feed ratio of ODA : HEAm = 9:1 could not be analyzed due to the overlap of $^1$H peaks of vinyl groups in this feed ratio.

### Evaluation of monomer reactivity ratios by Fineman-Ross plot

Monomer reactivity ratios, $r_1$ and $r_2$ ($M_1$ : HEAm and $M_2$ : ODA), were determined using a Fineman–Ross method[1], which used the following equation

$$F(f\text{-}1)/f = r_1 (F^2/f) - r_2$$

$F = [M_1]_0/[M_2]_0$ where $[M_1]_0$ and $[M_2]_0$ are initial HEAm and ODA concentrations and $f = P[M_1]/P[M_2]$, where $P[M_1]$ and $P[M_2]$ are the compositions of HEAm and ODA in the copolymer. Similar to the time-conversion study, HEAm, ODA and AIBN (1 mol% relative to the total monomer amount) were added to a pressure-resistant glass tube (ACE GLASS). To this glass tube, toluene and DMF at a volume ratio of 4:1 was added in a glove box filled with $N_2$ to give a total solute concentration of 0.2 M. The actual feed monomer ratios were $[M_1]_0$: $[M_2]_0$ = 3:7, 4:6, 5:5, 6:4, and 8:2, which were determined by $^1$H NMR of the solution before the polymerization. The polymerization was carried out at 60˚C and terminated at a total conversion of less than 6% except for the copolymerization with the monomer feed ratio of HEAm: ODA = 3: 7, which was 13%. The copolymer composition was calculated using the monomer conversion determined by $^1$H NMR using methylene groups of ODA as an internal standard. $F(f\text{-}1)/f$ was plotted against $F^2/f$. Then the data points are fitted to a straight line. The slope of the straight line gives $r_1$ and the intercept gives $r_2$.

### HEAm length calculation

The side chain length of HEAm was calculated by a molecular model created using Winmostar V11, which uses MOPAC to perform structure energy minimization.

### Powder XRD measurement.

p(ODA50/HEAm50) powder was placed in a glass sample tube. The glass tube was put into an oven at 115 ˚C for 24 h. Then the copolymer powder was placed in a glass sample holder to measure XRD. The measurement condition is the same for out-of-plane XRD measurement.

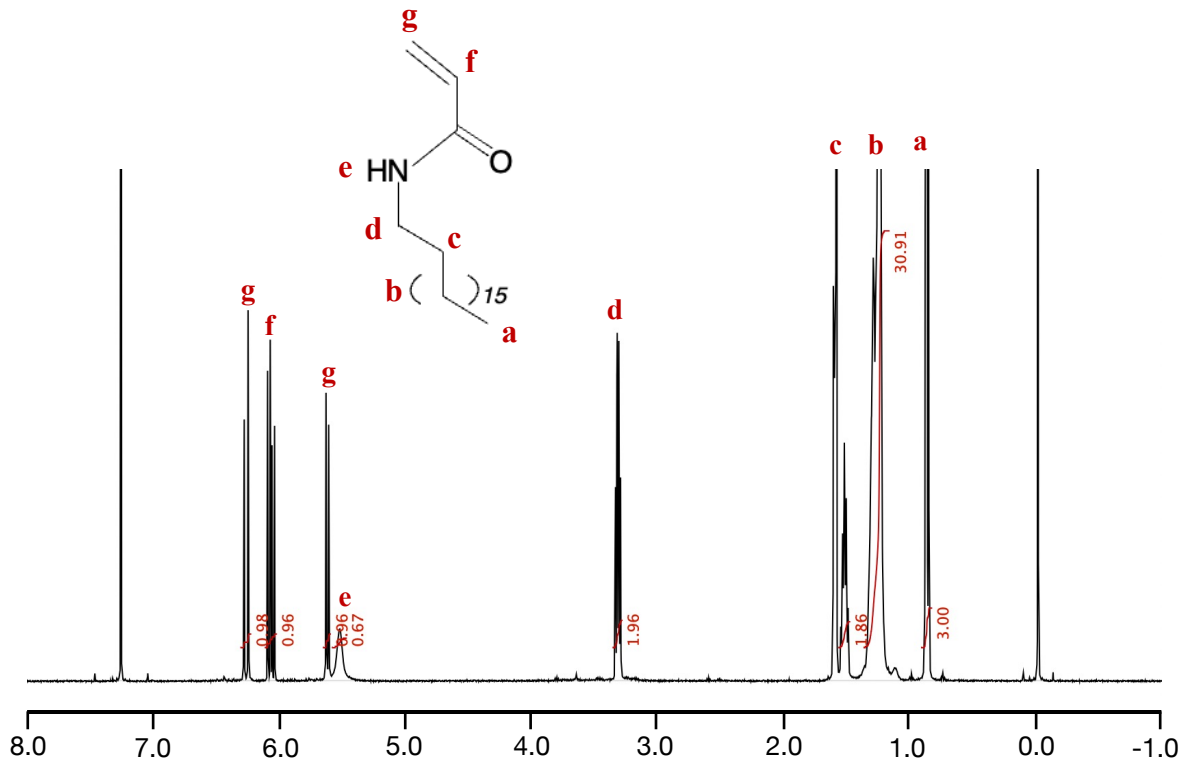
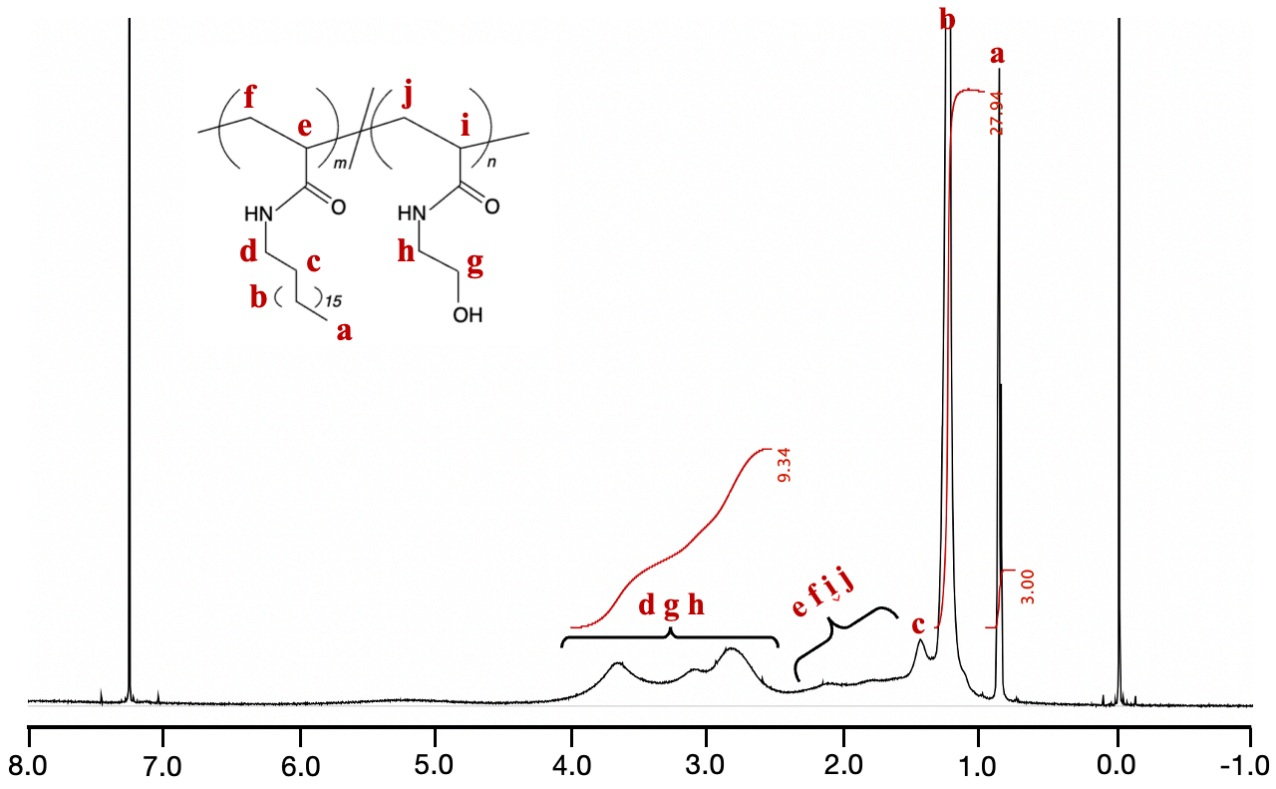


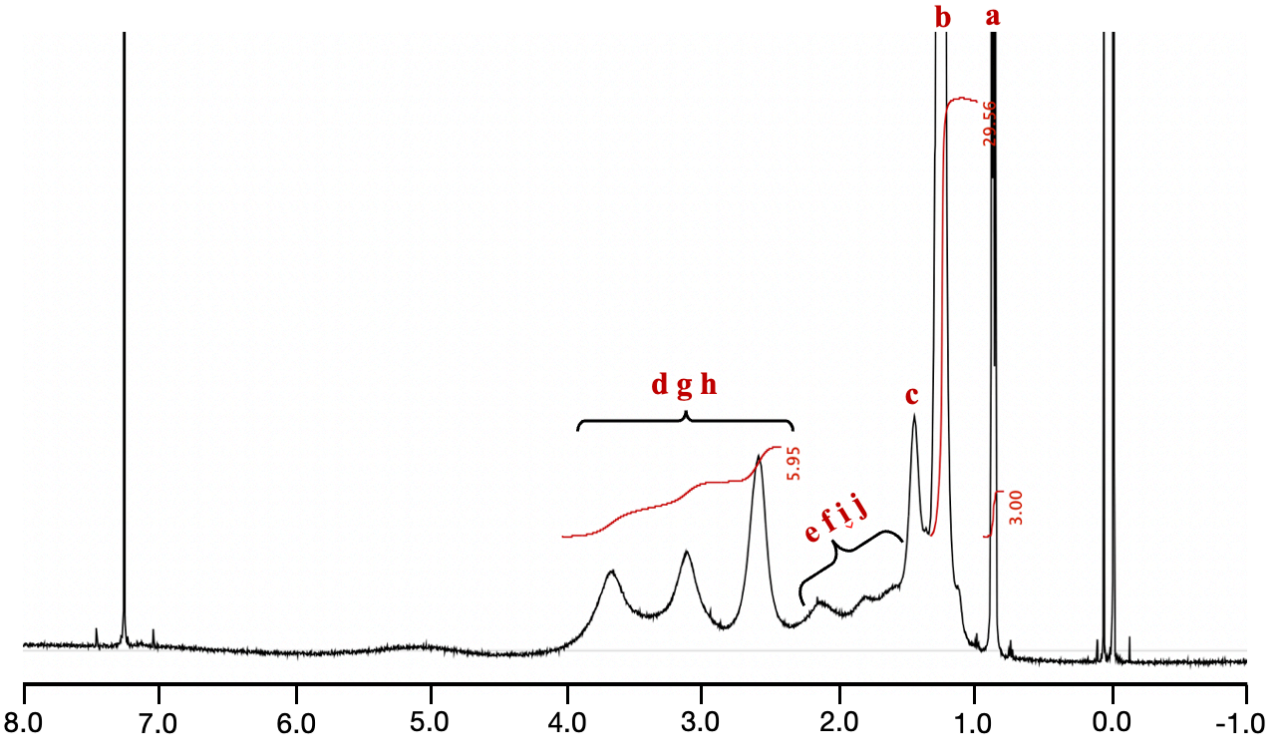

**Figure S1** $^{1}$H-NMR spectrum of ODA

(a)



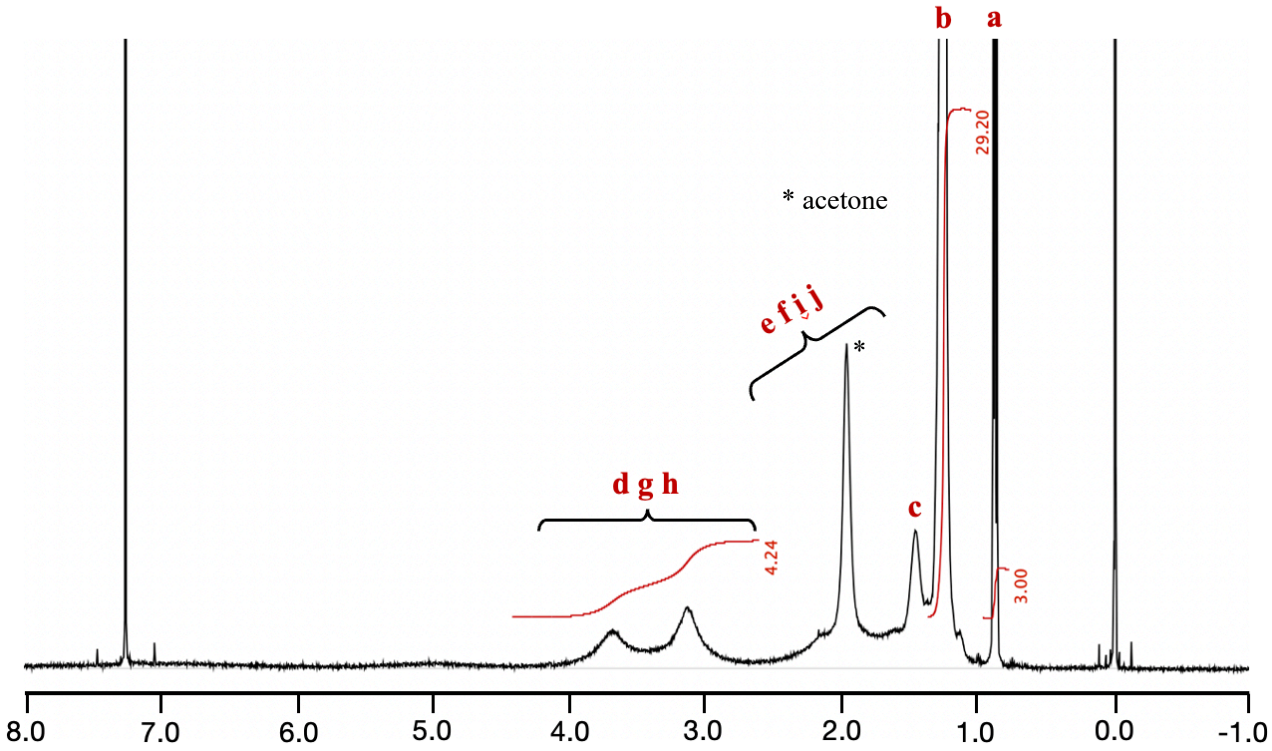

Chemical Shift / ppm

(b)

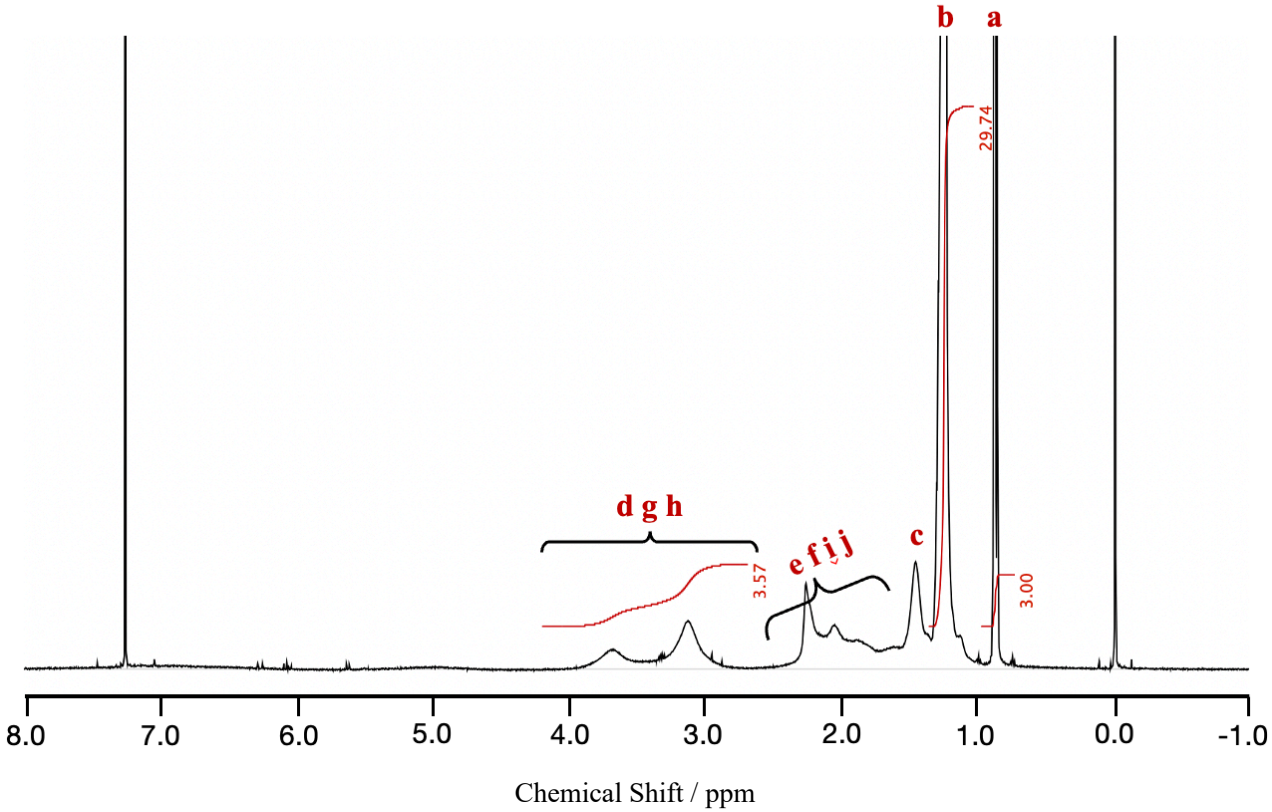



Chemical Shift / ppm

(c)


b
a
29.20
* acetone
e f i j
*
d g h
c
4.24
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
Chemical Shift / ppm

(d)


b
a
29.74
d g h
e f i j
c
3.57
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
Chemical Shift / ppm

(e)

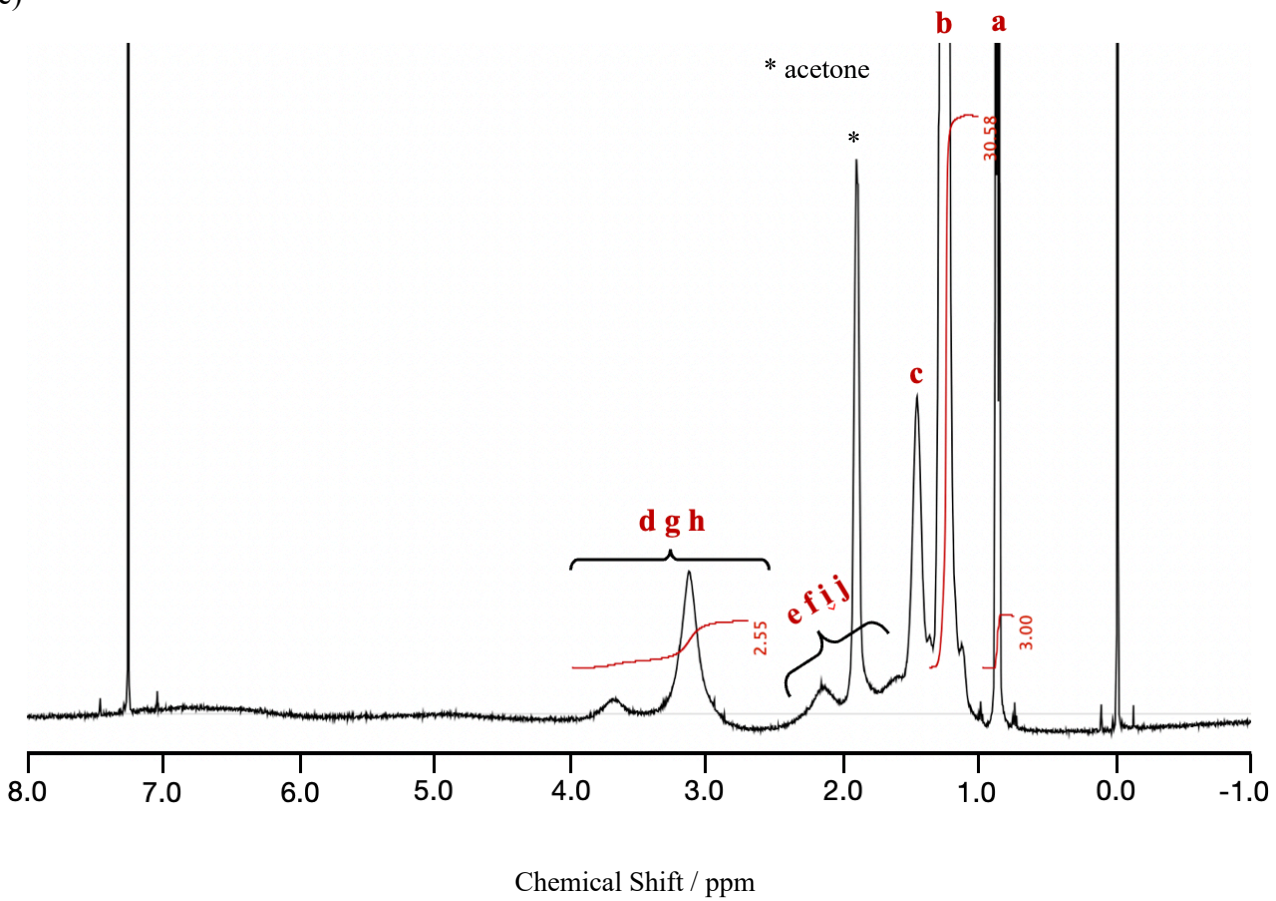
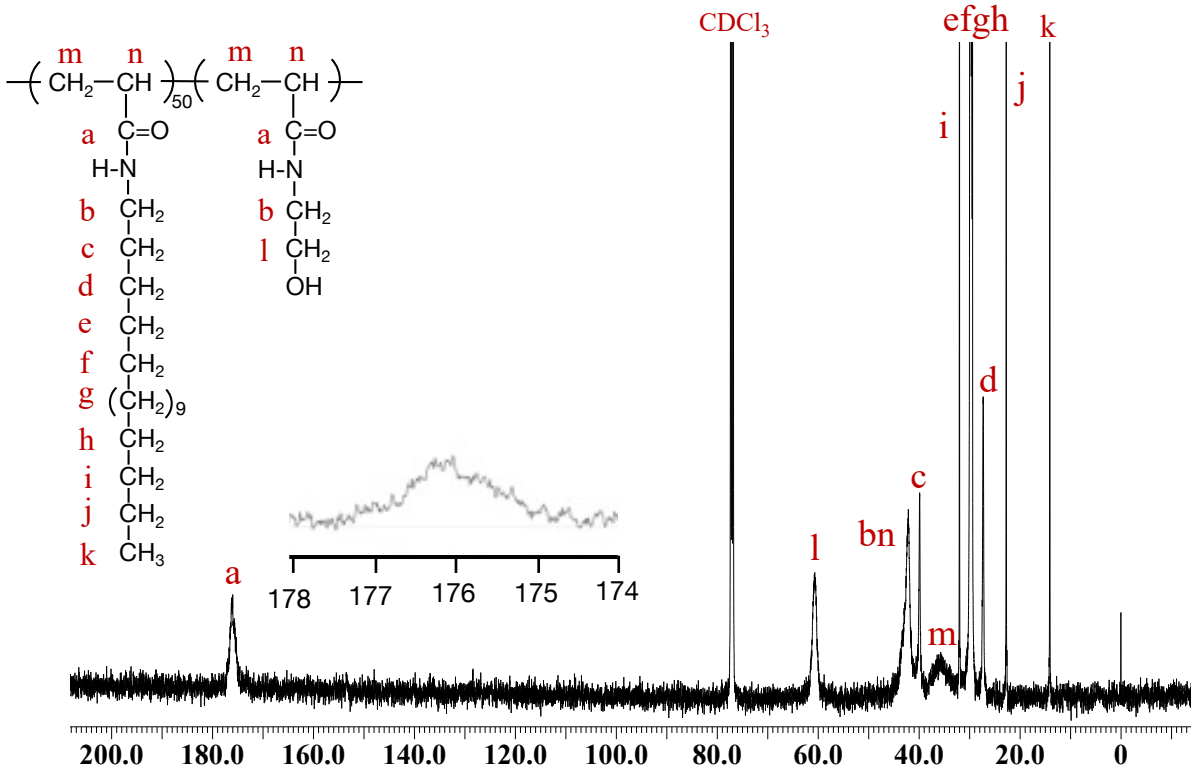
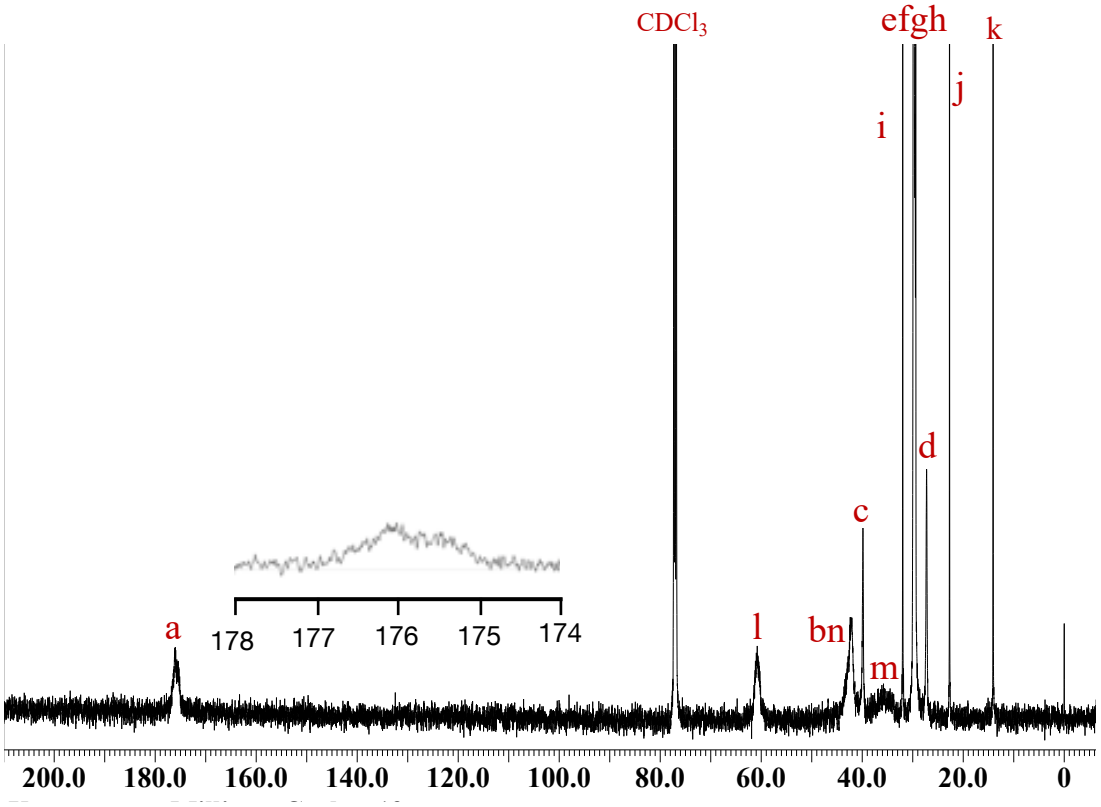



**Figure S2** $^{1}$H spectrum for p(ODA/HEAm). (a) p(ODA40/HEAm60), (b) p(ODA50/HEAm50), (c) p(ODA60/HEAm40), (d) p(ODA70/HEAm30), (e) p(ODA90/HEAm10).

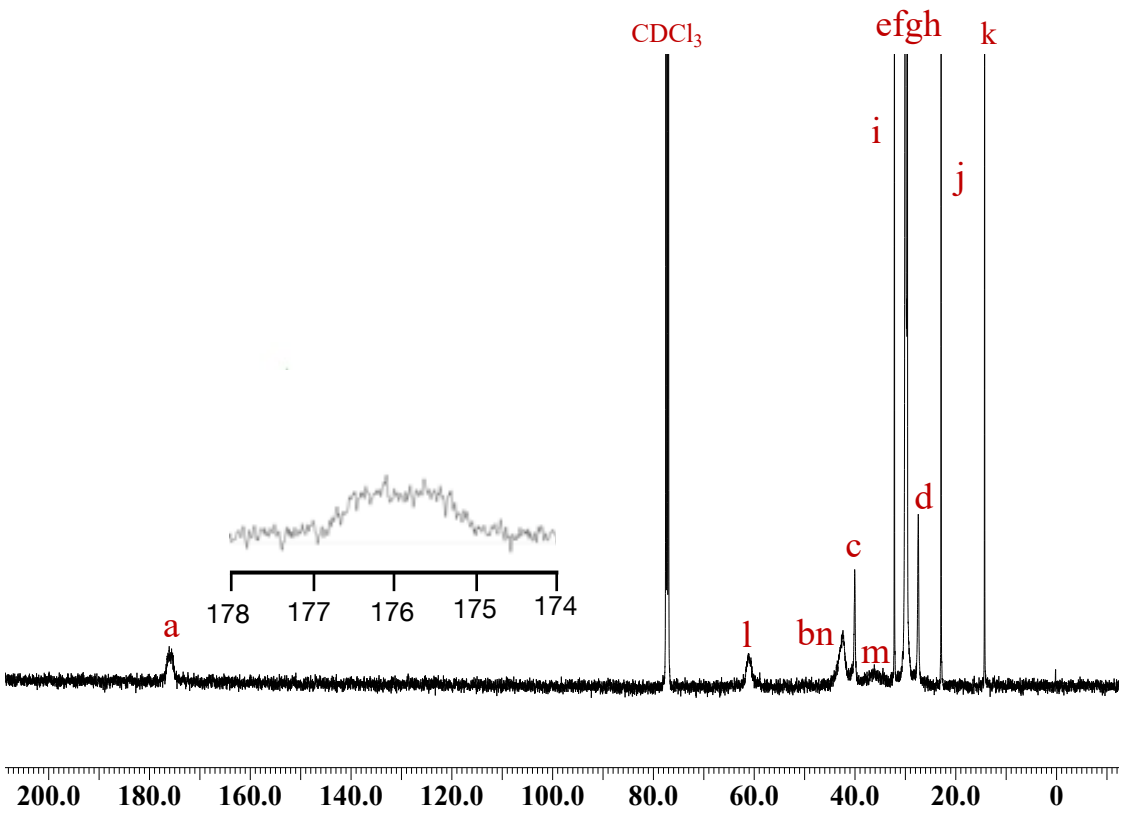
(a)


m
n
50
a
C=O
H-N
b
CH2
c
CH2
d
CH2
e
CH2
f
CH2
g
(CH2)9
h
CH2
i
CH2
j
CH2
k
CH3
l
CH2
OH
CDCl3
efgh
k
j
i
d
c
bn
l
m
a
178
177
176
175
174
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0
Chemical Shift / ppm

(b)

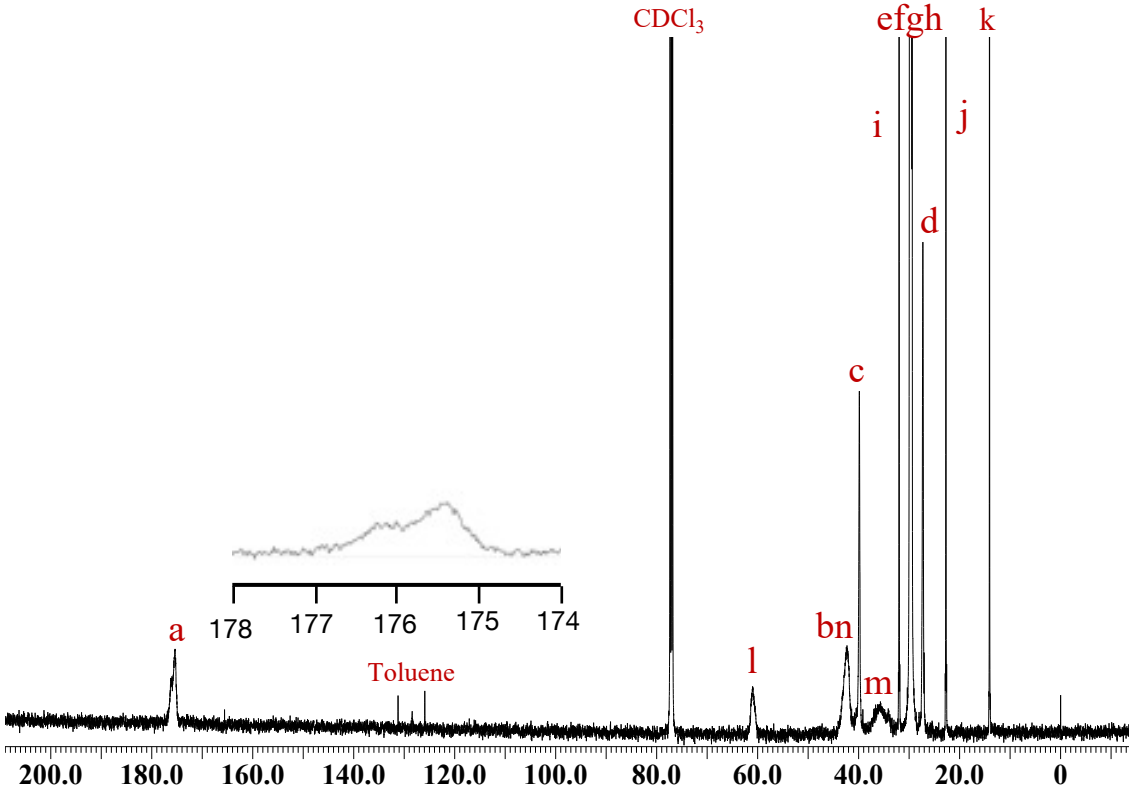

CDCl3
efgh
k
j
i
d
c
bn
l
m
a
178
177
176
175
174
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0
Chemical Shift / ppm

(c)




Chemical Shift / ppm

(d)




Chemical Shift / ppm

(e)

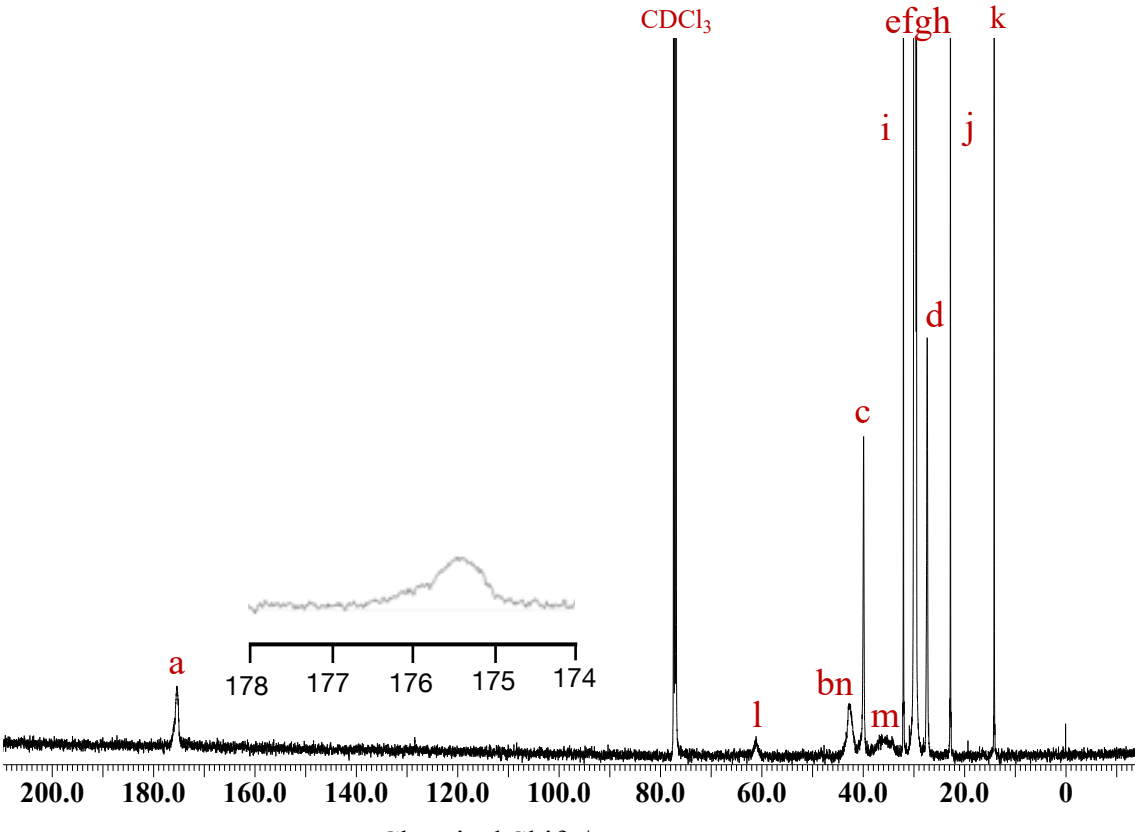



**Figure S3** $^{13}$C-NMR spectrum for p(ODA/HEAm). (a) p(ODA40/HEAm60), (b) p(ODA50/HEAm50), (c) p(ODA60/HEAm40), (d) p(ODA70/HEAm30), and (e) p(ODA90/HEAm10).

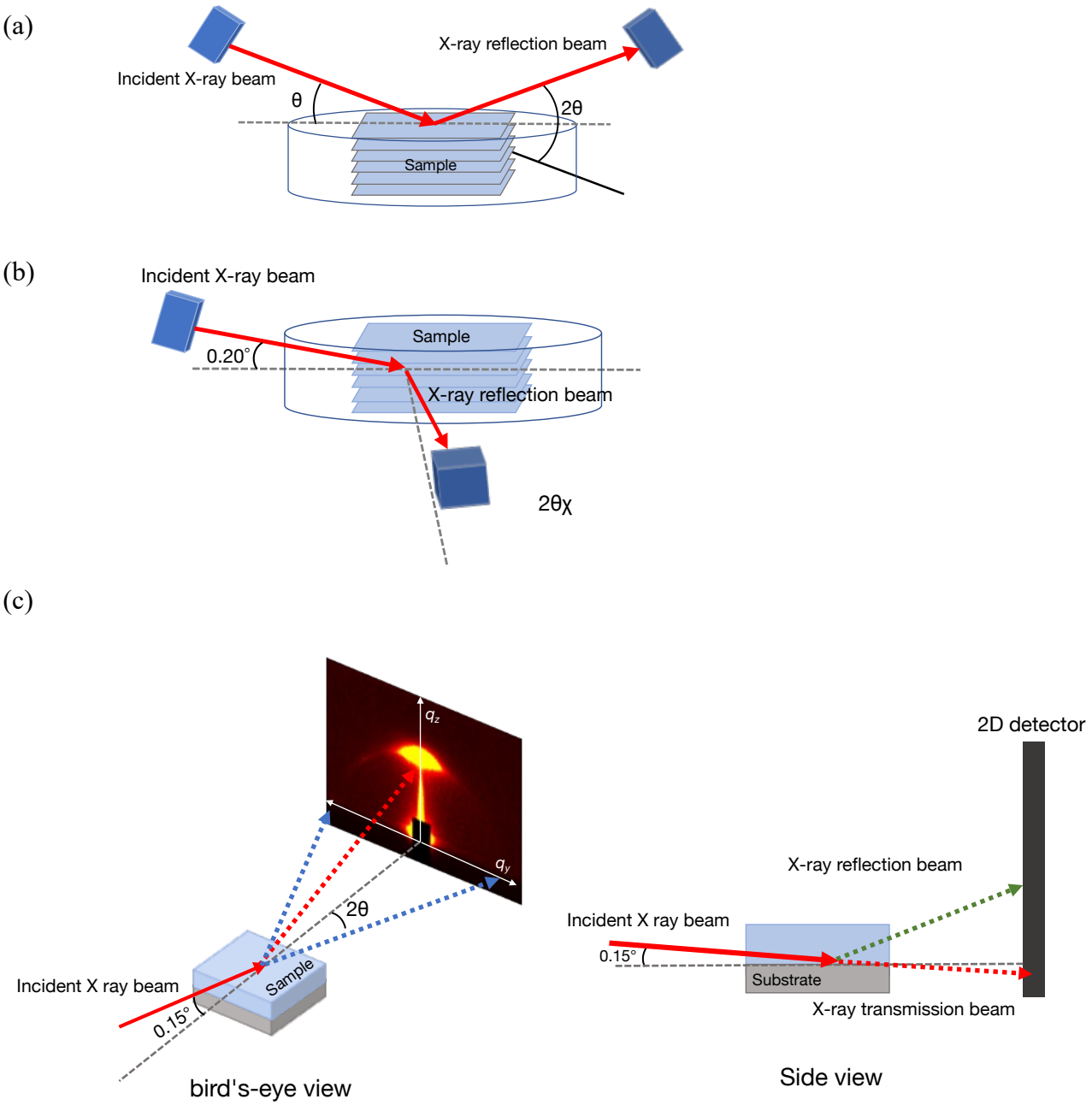



**Figure S4** Experimental geometry for (a) out-of-plane XRD, (b) in-plane XRD and (c) 2D GI-XRD.[2]

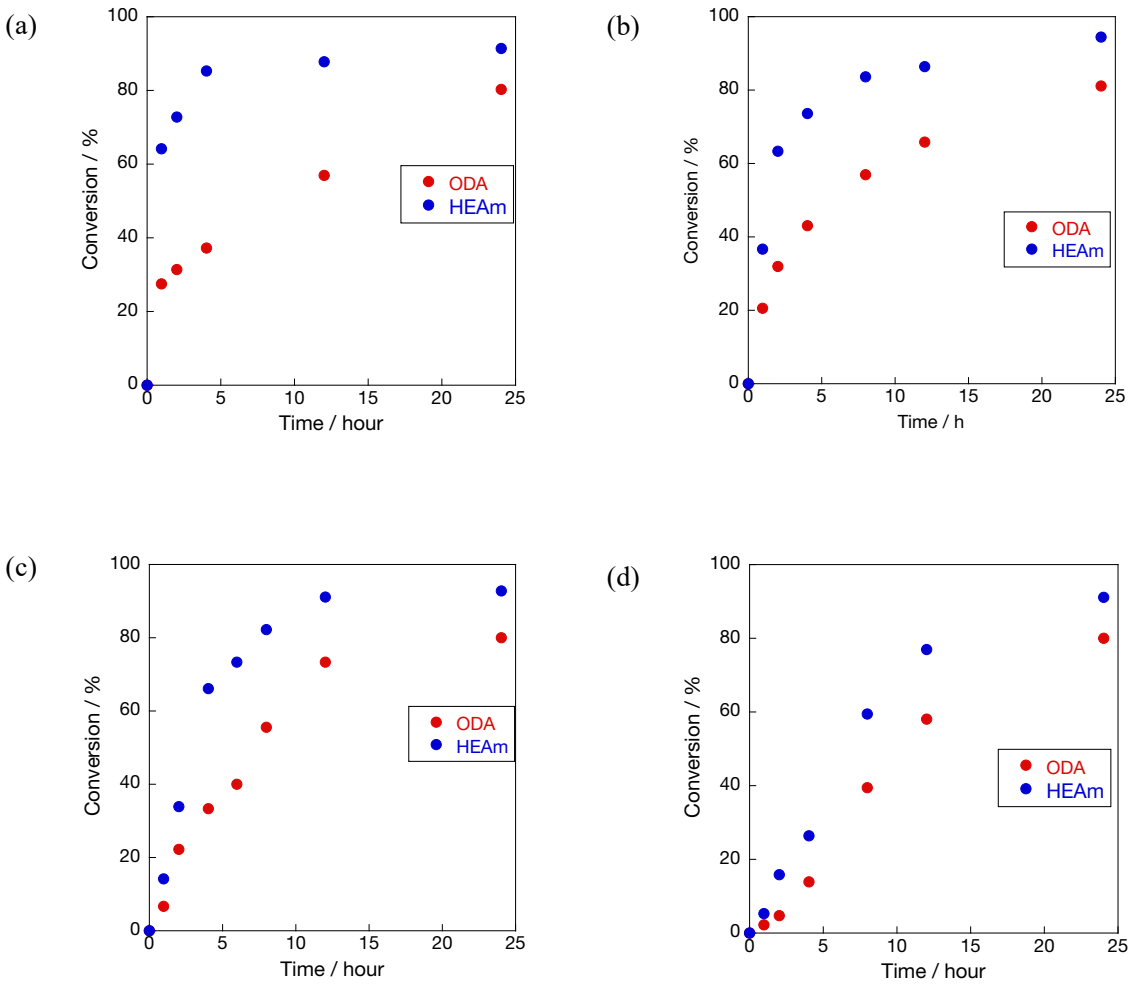



**Figure S5** Time-conversion curves for the free radical copolymerization of ODA and HEAm with the molar feed ratio of ODA : HEAm to (a) 4:6, (b) 5:5, (c) 6:4, and (d) 7:3.

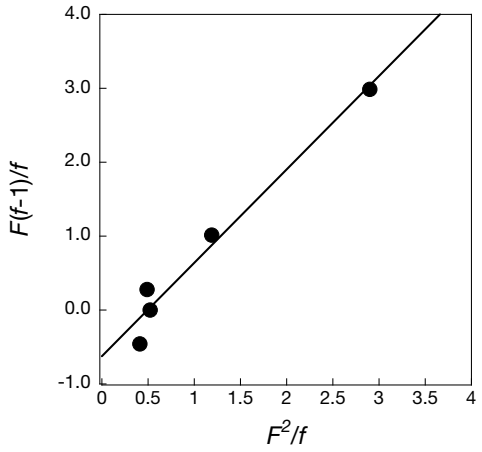



**Figure S6** Fineman-Ross plot for HEAm : ODA copolymerization. The straight line indicates linear fit with correlation coefficient $R^2 = 0.968$

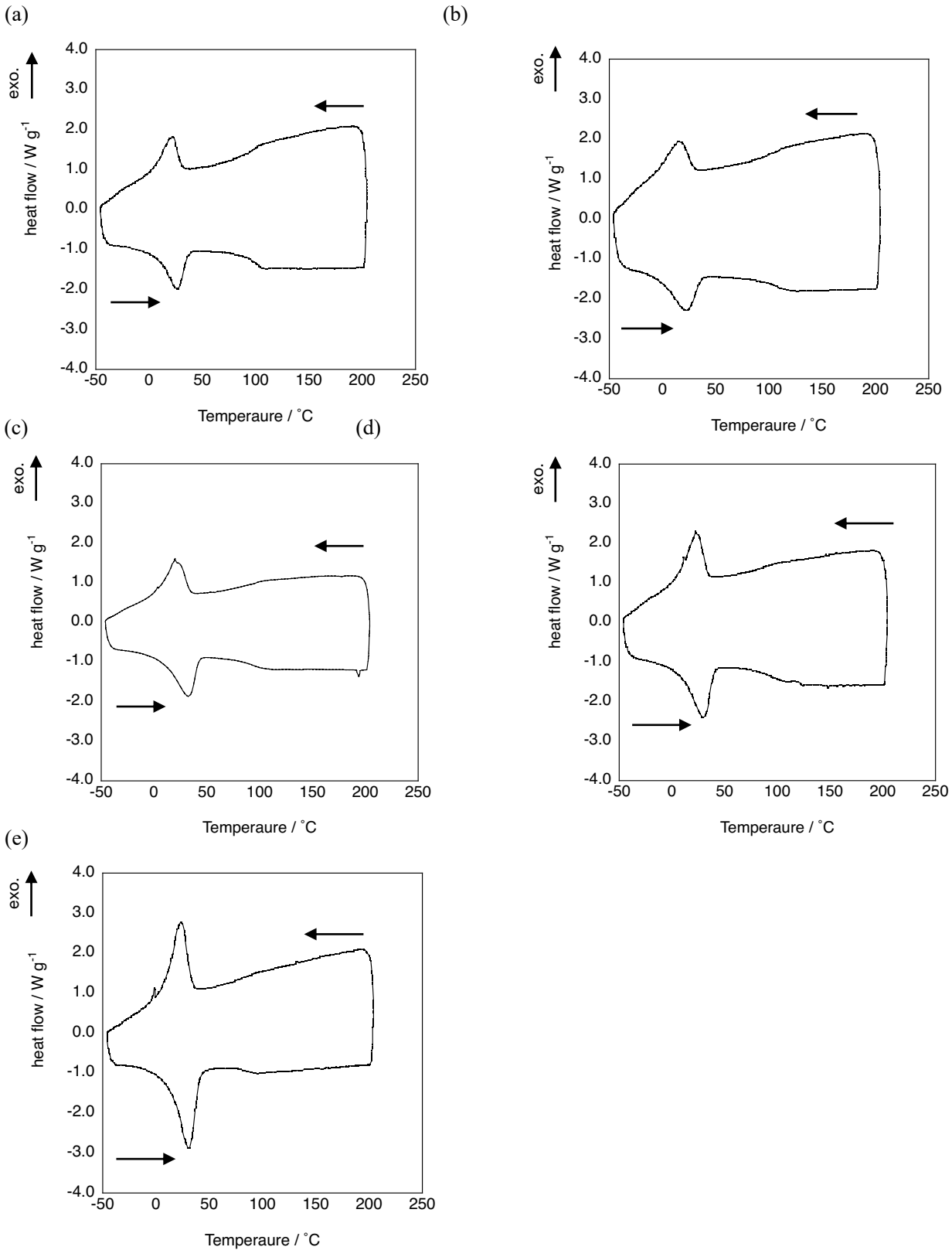
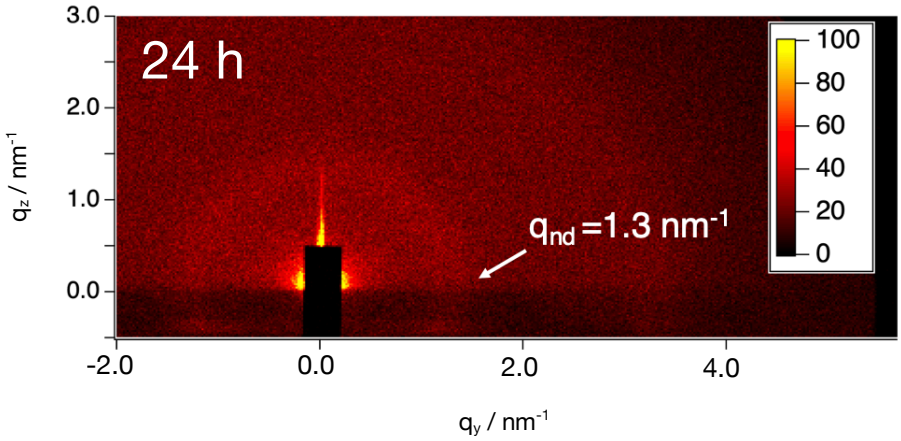



**Figure S7** DSC curve for the third heating and cooling curve for (a) p(ODA40/HEAm60), (b) p(ODA50/HEAm50), (c) p(ODA60/HEAm40), (d) p(ODA70/HEAm30), and (e) p(ODA90/HEAm10).

(a)




(b)

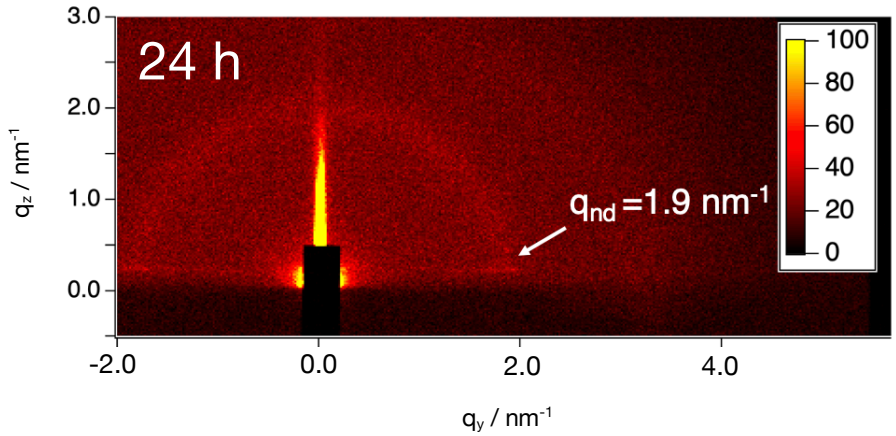
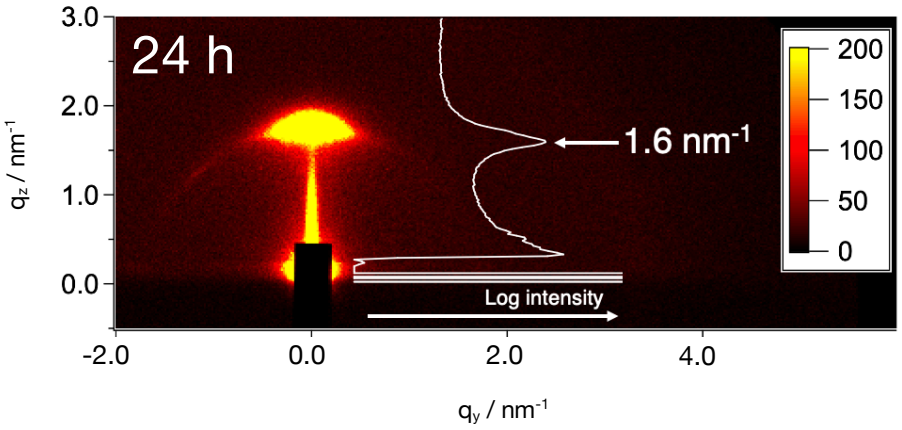
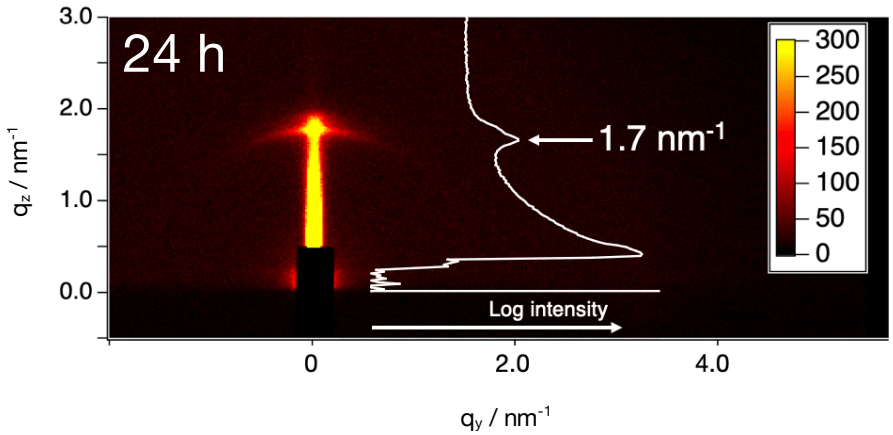



**Figure S8** 2D-XRD image for (a) p(ODA40/HEAm60) and (b) p(ODA90/HEAm10). All the films were thermally annealed for 24 h.

(a)




(b)




(c)

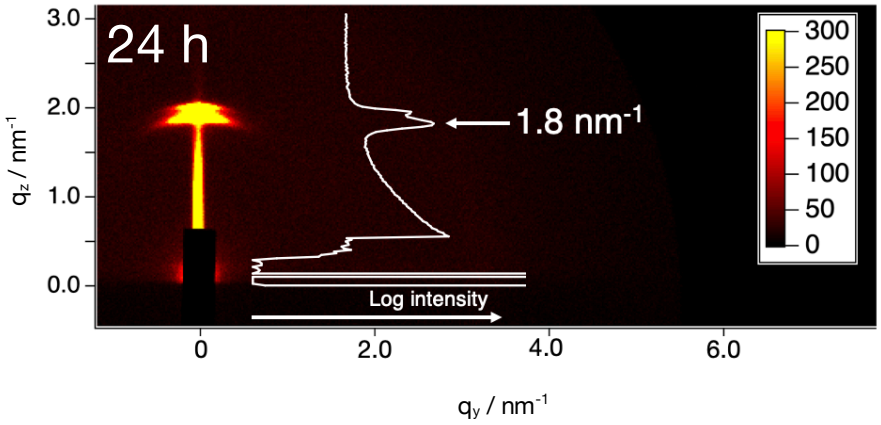
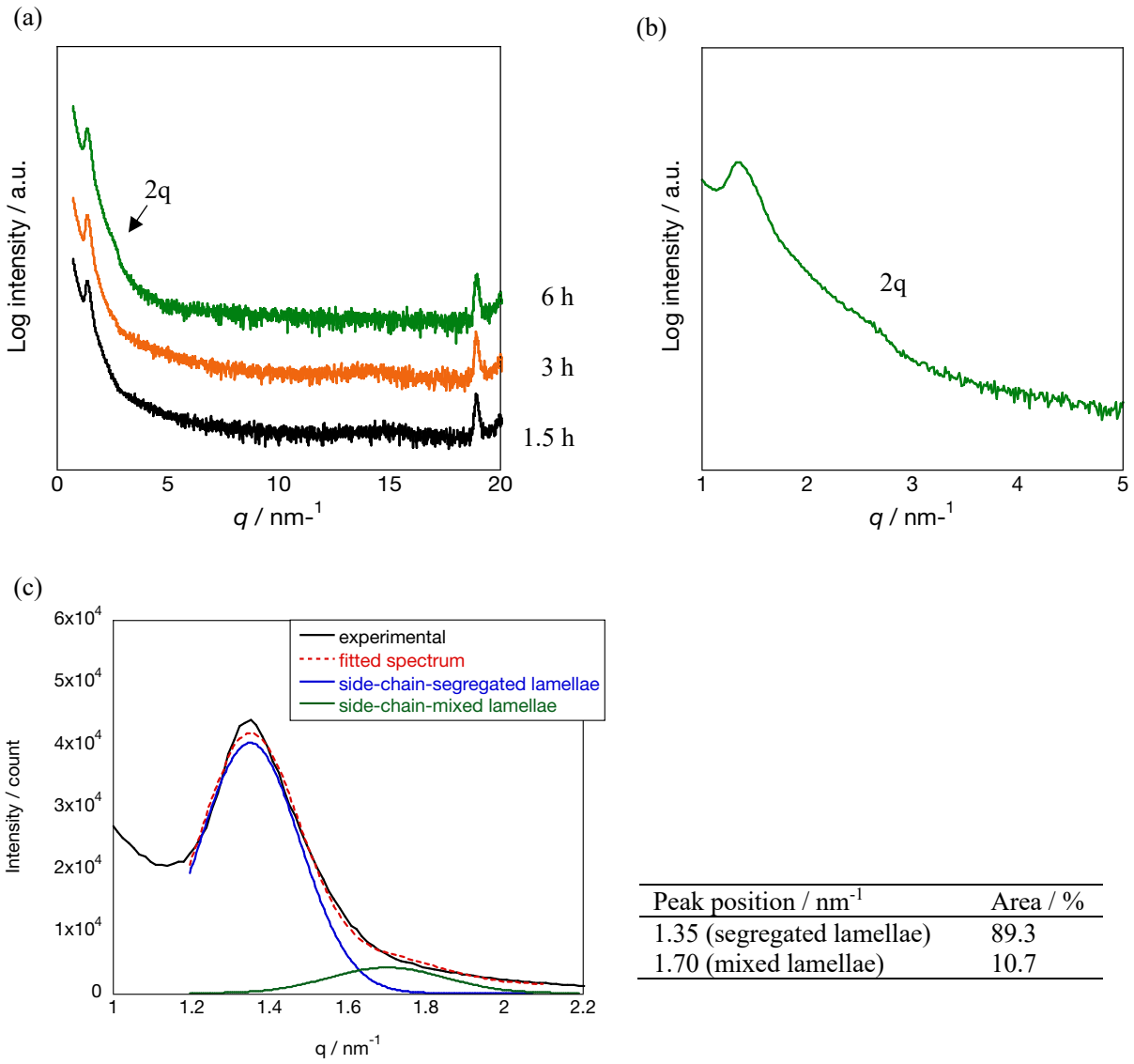


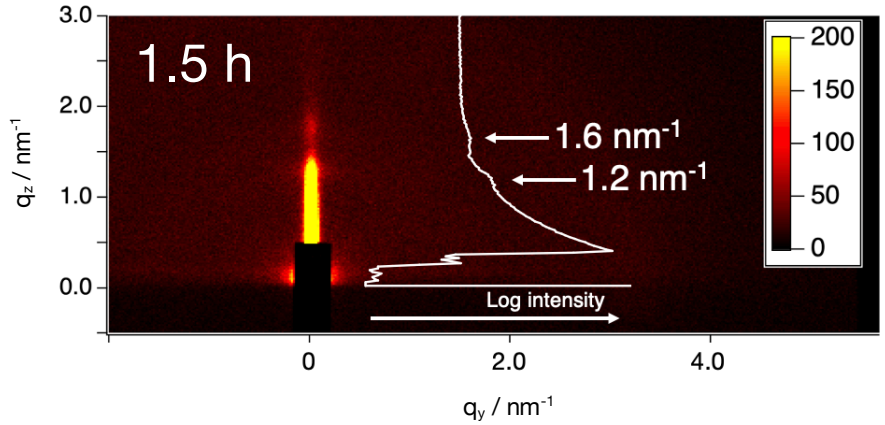

**Figure S9** 2D-XRD image and 1D intensity profile for out of plane for (a) p(ODA50/HEAm50), (b) p(ODA60/HEAm40), (c) p(ODA70/HEAm30). All the films were thermally annealed at ~*Tg* + 10 ˚C for 24 h. The 1D intensity profiles were extracted from the 2D images. The side peak appeared in *q* higher than the Bragg peak is originated from a diffraction from the reflected X-ray beam.[2]



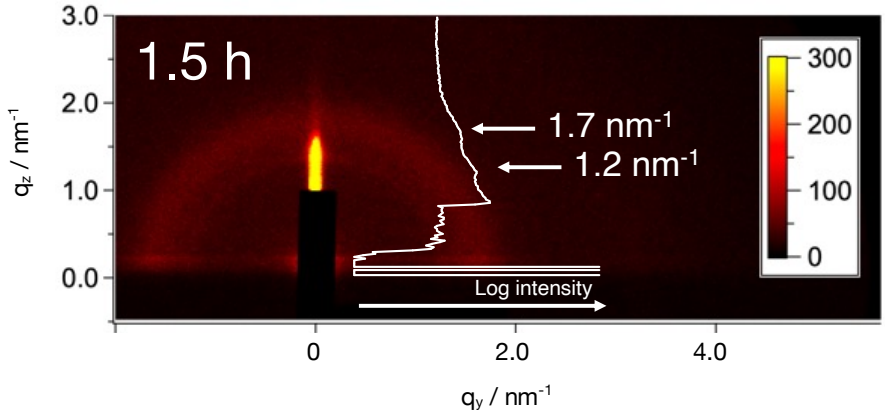

| Peak position / $nm^{-1}$ | Area / % |
|---|---|
| 1.35 (segregated lamellae) | 89.3 |
| 1.70 (mixed lamellae) | 10.7 |

**Figure S10** (a)XRD patterns of p(ODA50/HEAm50) annealed at 160 ˚C at different times. (b) Expand graph of XRD pattern for 6 h annealed film. (c) Deconvolution of first-order Bragg peak in figure (b). Right table is the fitting results.

(a)




(b)




(c)

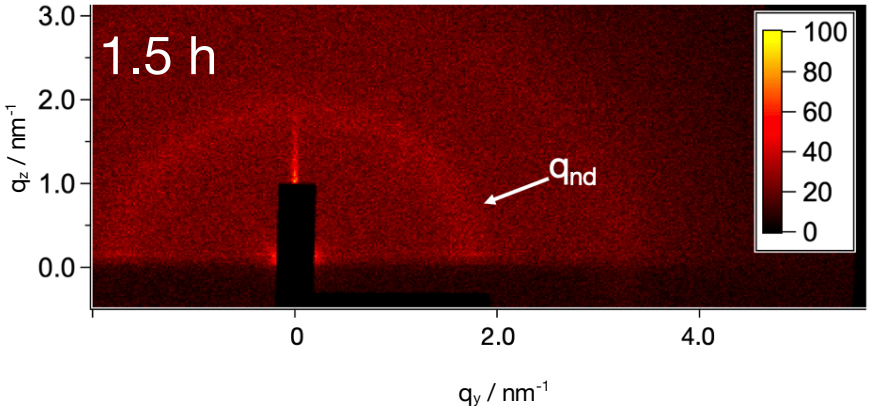



**Figure S11** 2D-XRD image (right) and 1D intensity profile for out of plane (left) for (a) p(ODA50/HEAm50), (b) p(ODA60/HEAm40), (c) p(ODA70/HEAm30). All the films were thermally annealed at 160 ˚C for 1.5 h. The 1D intensity profiles were extracted from the 2D images. The higher q value peak in p(ODA50/HEAm50) (q = 1.6 $nm^{-1}$) and p(ODA60/HEAm40) (q = 1.7 $nm^{-1}$) is attributed to remaining monolayer lamellar structure.

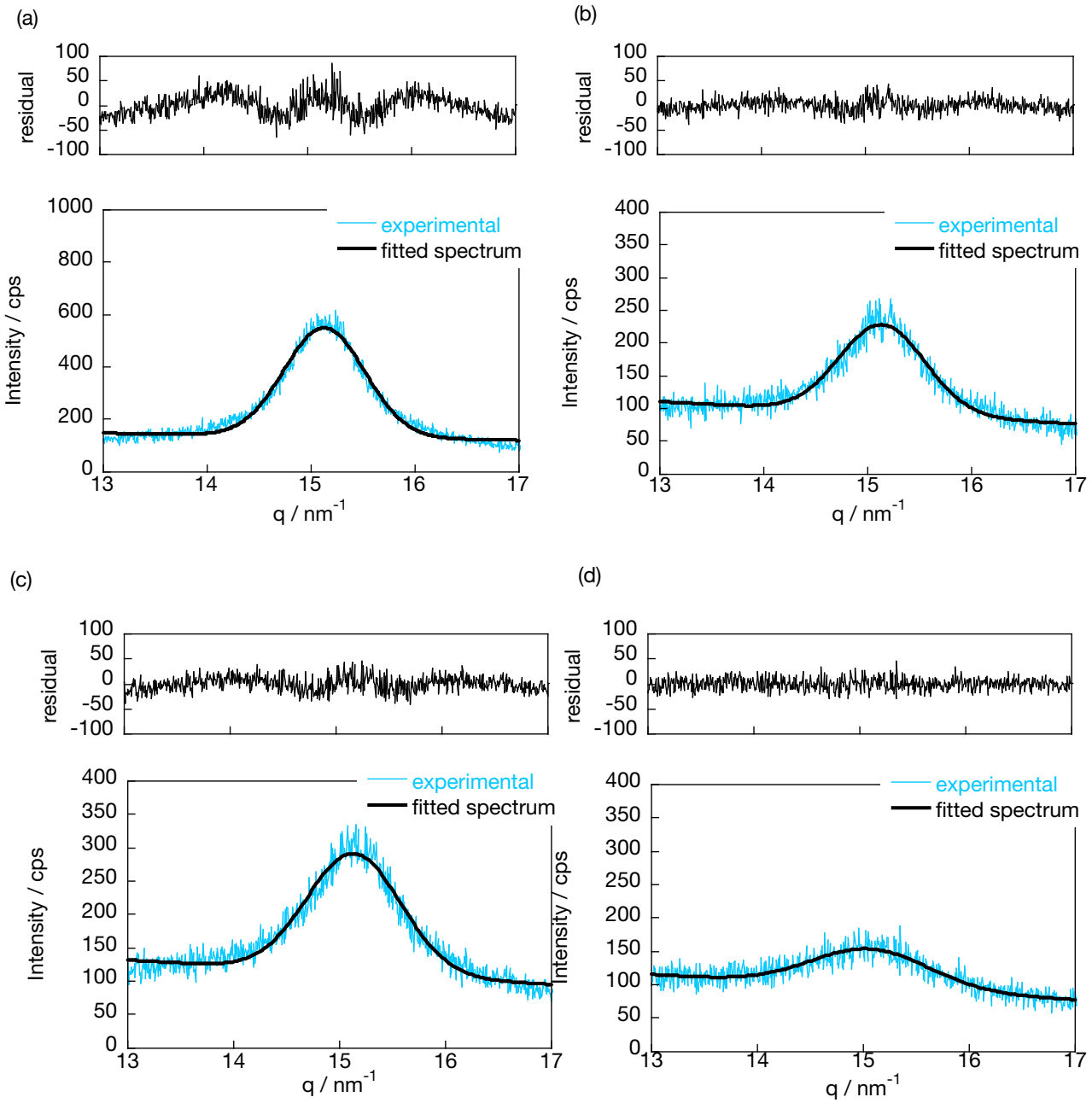
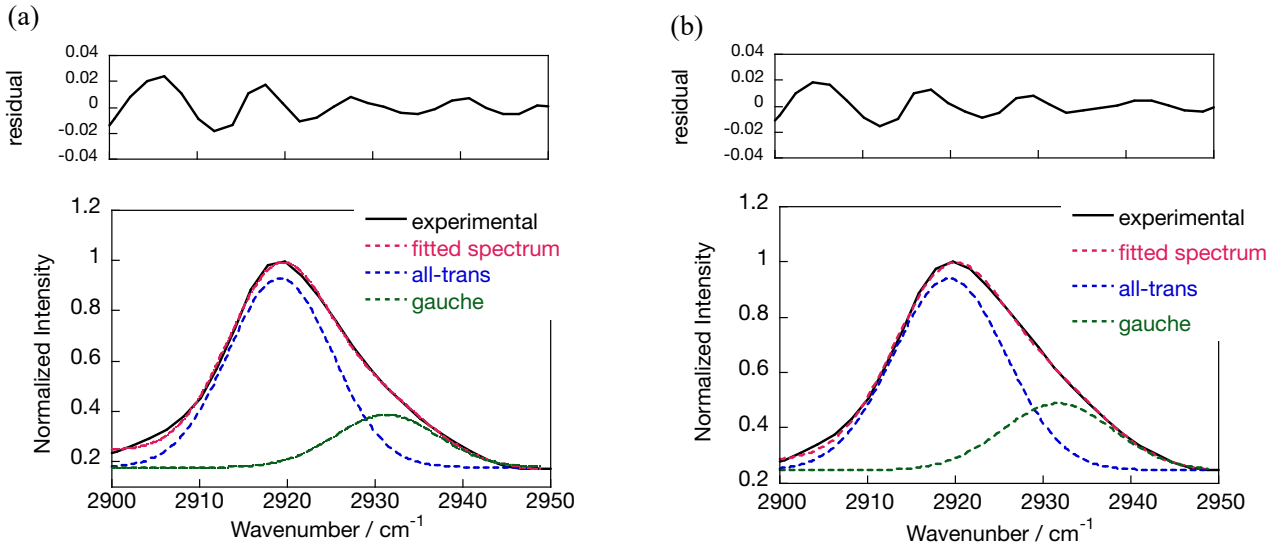



**Figure S12** Fitting result for $q_{hex}$ peak of copolymer lamellar film for (a) p(ODA70/HEAm30), (b) p(ODA60/HEAm40) (c) p(ODA50/HEAm50) annealed at 115 ˚C for 24 h and (d) p(ODA50/HEAm50) annealed at 160 ˚C for 6 h Upper graph in each spectrum is the residual for the fitting results.




| Peak position / $cm^{-1}$ | Area / % |
|---|---|
| 2919.2 (*trans*) | 78.6 |
| 2932.3 (*gauche*) | 21.5 |

| Peak position / $cm^{-1}$ | Area / % |
|---|---|
| 2919.3 (*trans*) | 74.4 |
| 2931.7 (*gauche*) | 25.6 |

**Figure S13** Deconvolution of $CH_2$ asymmetric stretching ($\nu_a$) for p(ODA50/HEAm50) film annealed at (a) 115 ˚C for 24 h and (b) 160 ˚C for 6 h Upper graph in each spectrum is the residual for the fitting results and bottom table is the fitting results.

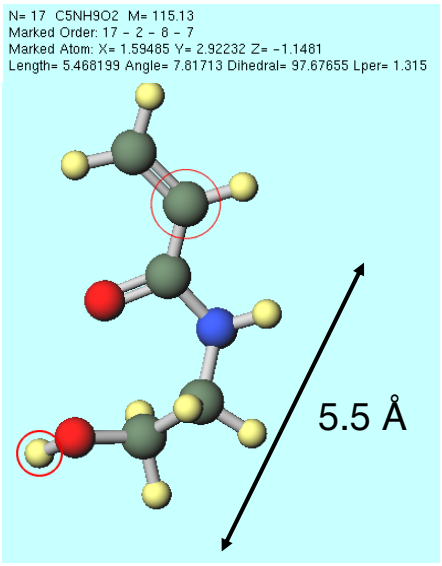



**Figure S14** Length calculation of HEAm side chains. yellow: hydrogen, red: oxygen, green: carbon and blue: nitrogen

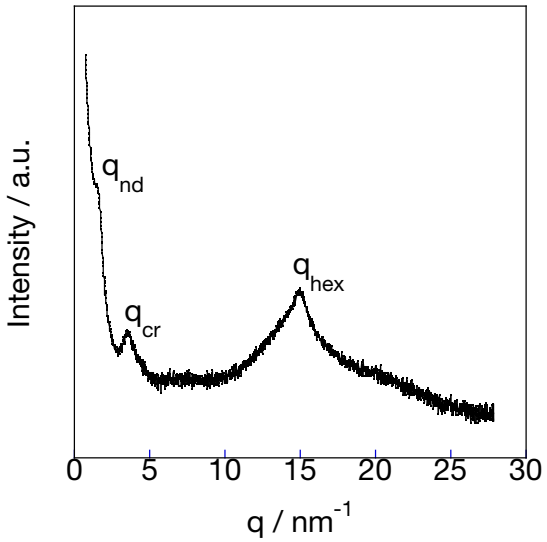



**Figure S15** XRD pattern of p(ODA50/HEAm50) powder annealed at 115 ˚C for 24h. Strong diffraction at q = 15 $nm^{-1}$ is attributed to diffraction from hexagonally packed alkyl side chains.

## Reference

(1) *Young, R. J.; Lovell, P. A. Introduction to Polymers; Third Edition ed.; Tailor & Francis: Florida, 2011.*

(2) Lee, B.; Park, I.; Yoon, J.; Park, S.; Kim, J.; Kim, K. W.; Chang, T.; Ree, M. Structural analysis of block copolymer thin films with grazing incidence small-angle X-ray scattering. *Macromolecules* **2005**, *38*, 4311-4323.