Supporting information

Achieving micelle control through core crystallinity

Lidija Glavas, Peter Olsén, Karin Odelius, Ann-Christine Albertsson

Fiber and Polymer Technology, School of Chemical Science and Engineering, KTH,

Royal Institute of Technology, SE-100 44 Stockholm, Sweden

CHARACTERIZATION OF COPOLYMERS

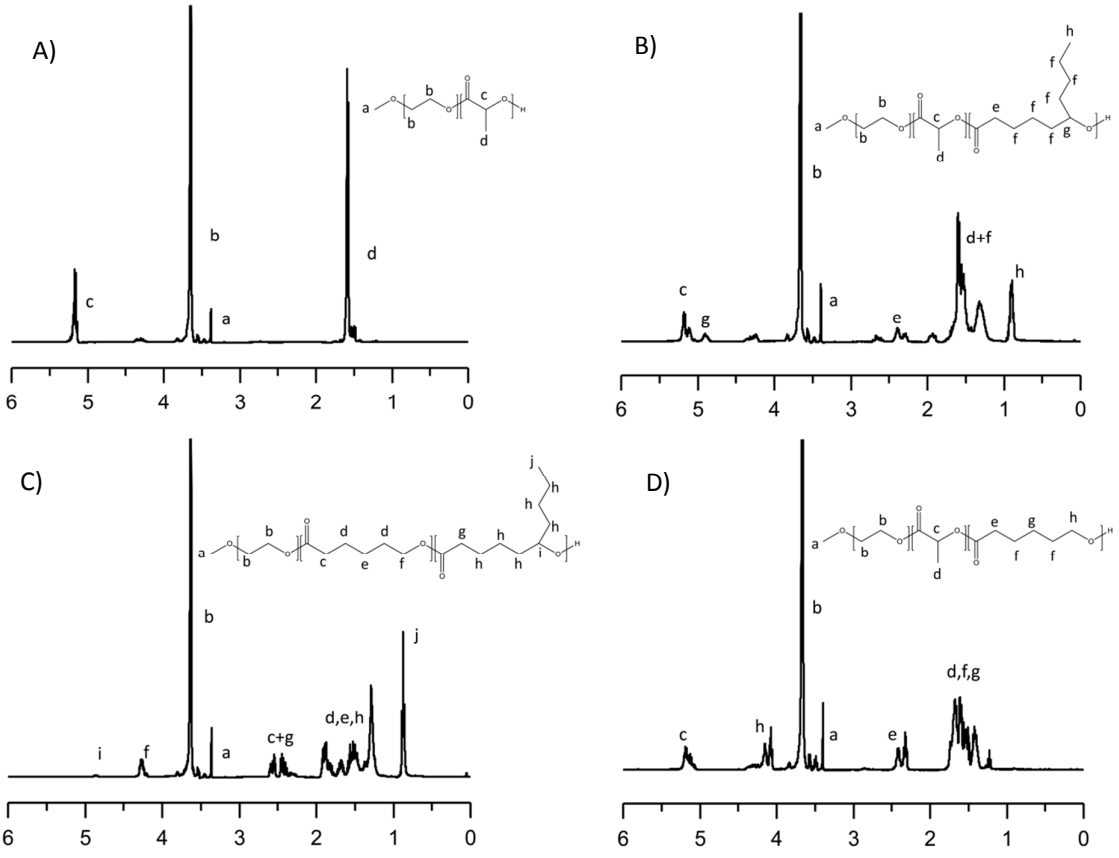

Figure 1. Determination of the chemical structure of A) PEG_{2k}-PLA_{2k}, B) PEG_{2k}-$P(LA/\varepsilon DL)_{2k}$, C) PEG_{2k}-$P(CL/\varepsilon DL)_{2k}$ and D) PEG_{2k}-$P(CL/LA)_{2k}$. The molecular weights were calculated using ^{1}H-NMR by integrating the methoxy peak of mPEG at 3.37 ppm and the peak for the repeating units of CL (at 4.06 ppm), ε-DL (at 0.86 ppm), and LA (at 5.17 ppm).

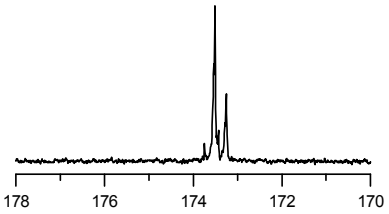

Figure 2. ^{13}C-NMR of PEG_{2k}-$P(CL/\varepsilon DL)_{2k}$ in the carbonyl region.

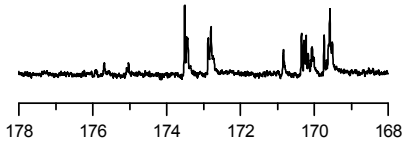

Figure 3. ^{13}C-NMR of PEG_{2k}-$P(LA/\varepsilon DL)_{2k}$ in the carbonyl region.

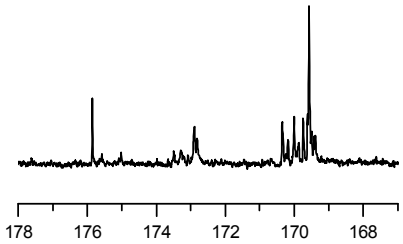

Figure 4. ^{13}C-NMR of PEG_{2k}-$P(CL/LA)_{2k}$ in the carbonyl region.

Table 1. The mass ratio of the hydrophobic block of the copolymers with two monomers in the hydrophobic block. The ratios were calculated using values obtained from ^{1}H-NMR.

Sample name	Mass ratio of the hydrophobic block [M_1:M_2]
PEG_{2k}-$P(CL/\varepsilon DL)_{2k}$	40:60
PEG_{2k}-$P(LA/\varepsilon DL)_{2k}$	46:54
PEG_{2k}-$P(CL/LA)_{2k}$	44:56

Table 2. The melting enthalpies of the all the copolymers.

Sample name	Melting enthalpy [J/g]
PEG_{2k}-PCL_{1k}	141[a]
PEG_{2k}-PCL_{2k}	121[a]
PEG_{2k}-PCL_{3k}	97[a]
PEG_{2k}-PCL_{4k}	89[a]
PEG_{2k}-$P\varepsilon DL_{1k}$	107
PEG_{2k}-$P\varepsilon DL_{2k}$	85
PEG_{2k}-$P\varepsilon DL_{3k}$	71
PEG_{2k}-$P\varepsilon DL_{4k}$	55
PEG_{2k}-PLA_{2k}	83[a]
PEG_{2k}-$P(CL/\varepsilon DL)_{2k}$	85
PEG_{2k}-$P(LA/\varepsilon DL)_{2k}$	79
PEG_{2k}-$P(CL/LA)_{2k}$	87

[a] The melting enthalpies reported are combined enthalpies for both the PEG and the PCL/PLA-block.

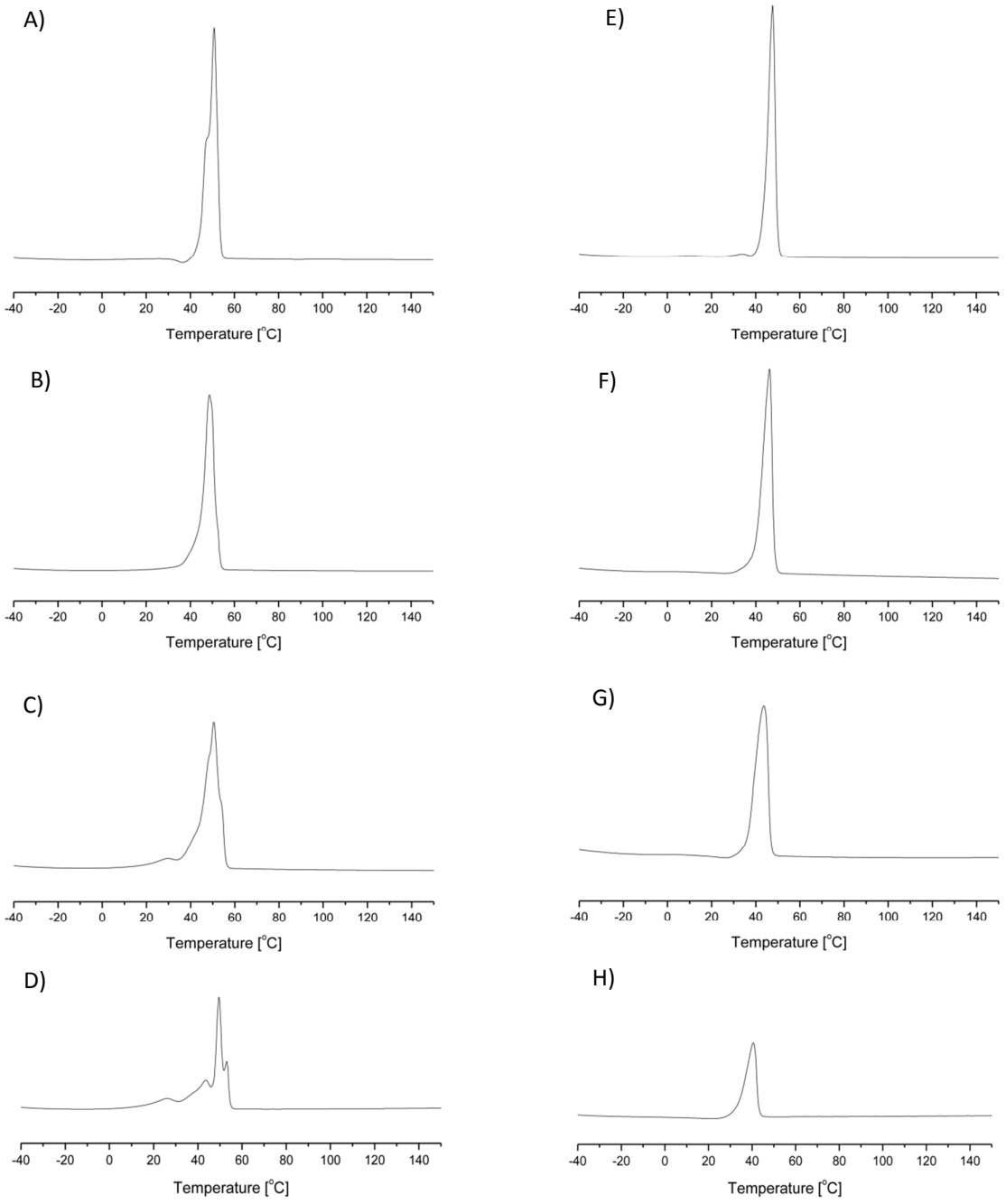

Figure 5. The DSC traces of A) PEG_{2k}-PCL_{1k}, B) PEG_{2k}-PCL_{2k}, C) PEG_{2k}-PCL_{3k}, D) PEG_{2k}-PCL_{4k}, E) PEG_{2k}-$P\varepsilon DL_{1k}$, F) PEG_{2k}-$P\varepsilon DL_{2k}$, G) PEG_{2k}-$P\varepsilon DL_{3k}$ and H) PEG_{2k}-$P\varepsilon DL_{4k}$.

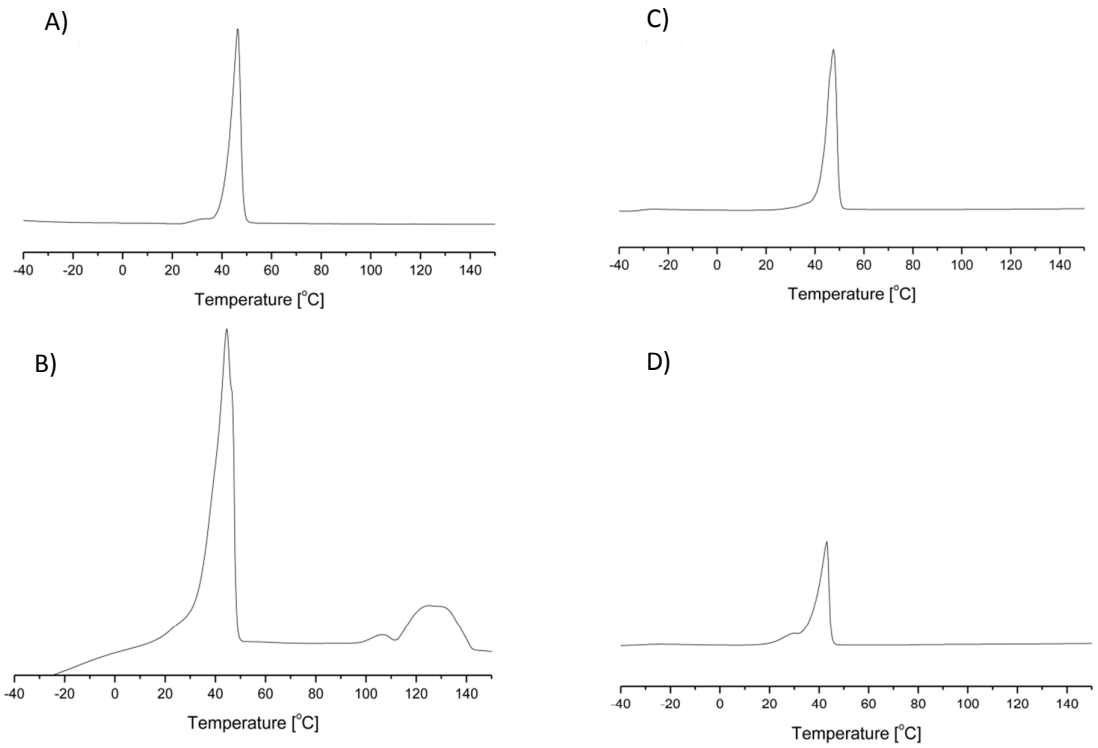

Figure 6. The DSC traces of A) PEG_{2k}-$P(CL/\varepsilon DL)_{2k}$, B) PEG_{2k}-PLA_{2k}, C) PEG_{2k}-$P(LA/CL)_{2k}$, D) PEG_{2k}-$P(LA/\varepsilon DL)_{2k}$.

SELF-ASSEMBLY

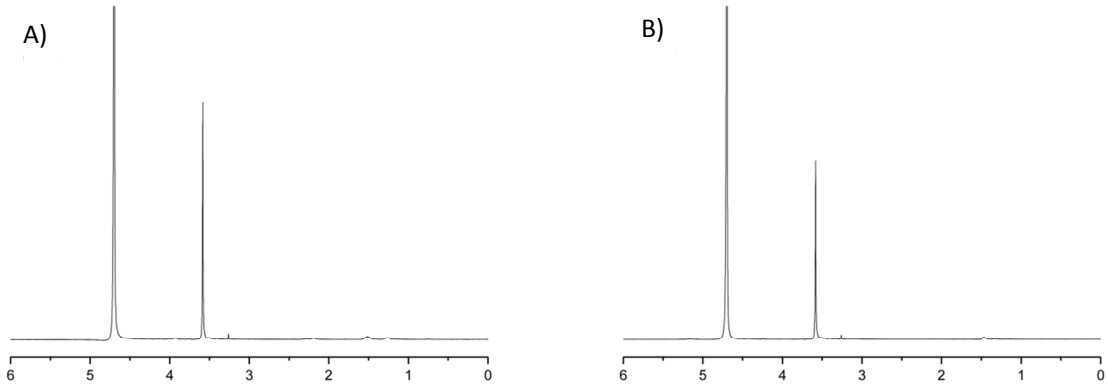

Figure 7. Evidence of the self-assembly of A) PEG_{2k}- PCL_{2k} and B) PEG_{2k}- PLA_{2k}. ^{1}H-NMR in D_2O.

MORPHOLOGY

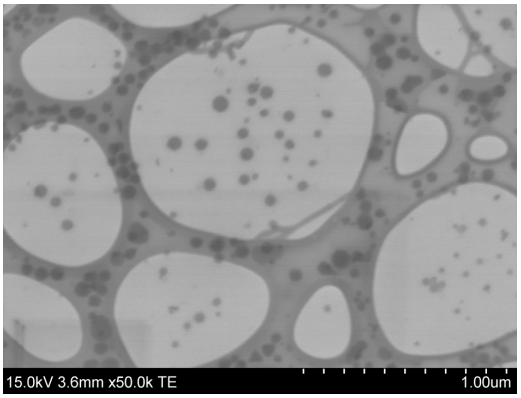

Figure 8. Morphology of PEG_{2k}-$P\varepsilon DL_{2k}$ at 0.6 mg/mL.

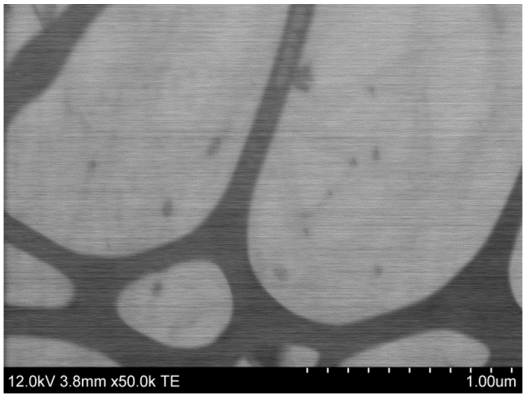

Figure 9. Morphology of PEG_{2k}-PCL_{2k} at 0.6 mg/mL

MICELLE STABILITY

Table 3. The stability of the micelles (0.6 mg/mL) after 4 weeks measured by DLS.

Sample name	Size [a] [nm]	Size [b] [nm]
PEG_{2k}-PCL_{2k}	29	42
PEG_{2k}-PLA_{2k}	57	62
PEG_{2k}-$P\varepsilon DL_{2k}$	27	27
PEG_{2k}-$P(CL/\varepsilon DL)_{2k}$	41	46
PEG_{2k}-$P(LA/\varepsilon DL)_{2k}$	24	38
PEG_{2k}-$P(LA/CL)_{2k}$	27	26

[a] Z-average value

[b] Z-average value after 4 weeks