Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information

for

Luminescent Zinc Oxide Nanoparticles: From Stabilization to Slow Digestion Depending on the Nature of Polymer Coating.

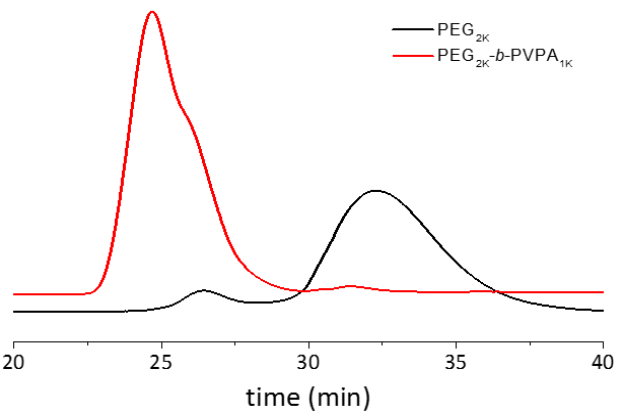


Figure S1. SEC-RI chromatograms of PEG$_{2k}$ (commercially available PEG-OH) and PEG$_{2k}$-*b*-PVPA$_{1k}$.

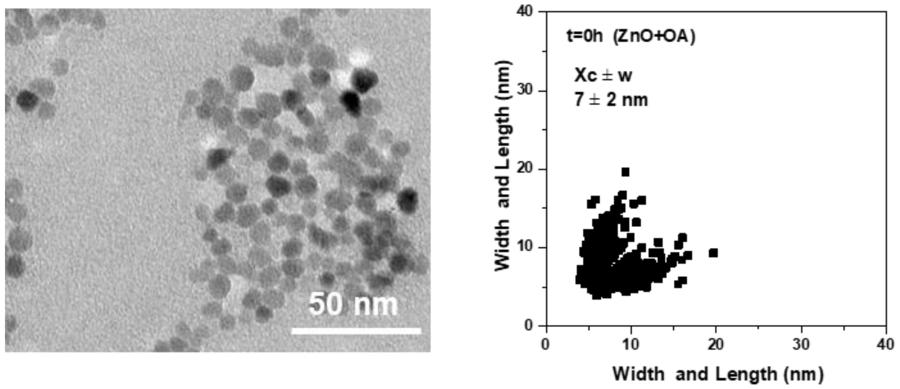


Figure S2. TEM image and particle size distribution of ZnO NPs formed in THF in presence of n-octyl amine OA (deposited immediately after NPs formation).

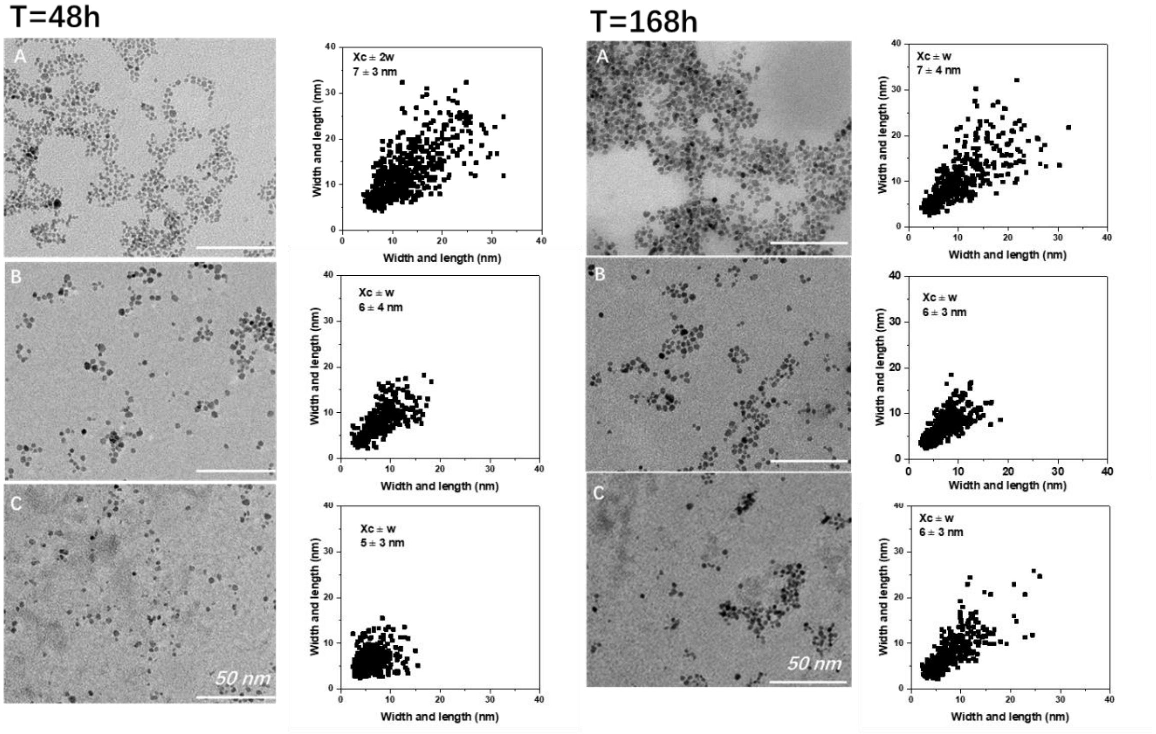


Figure S3. TEM images and particle size distribution of ZnO NPs formed in THF and stabilized by A: OA, B: OA+PEG$_{2k}$-b-PAA$_{1k}$, C: OA+PEG$_{2k}$-b-PVPA$_{1k}$ 48h and 168h after NPs formation and surface modification by polymer.

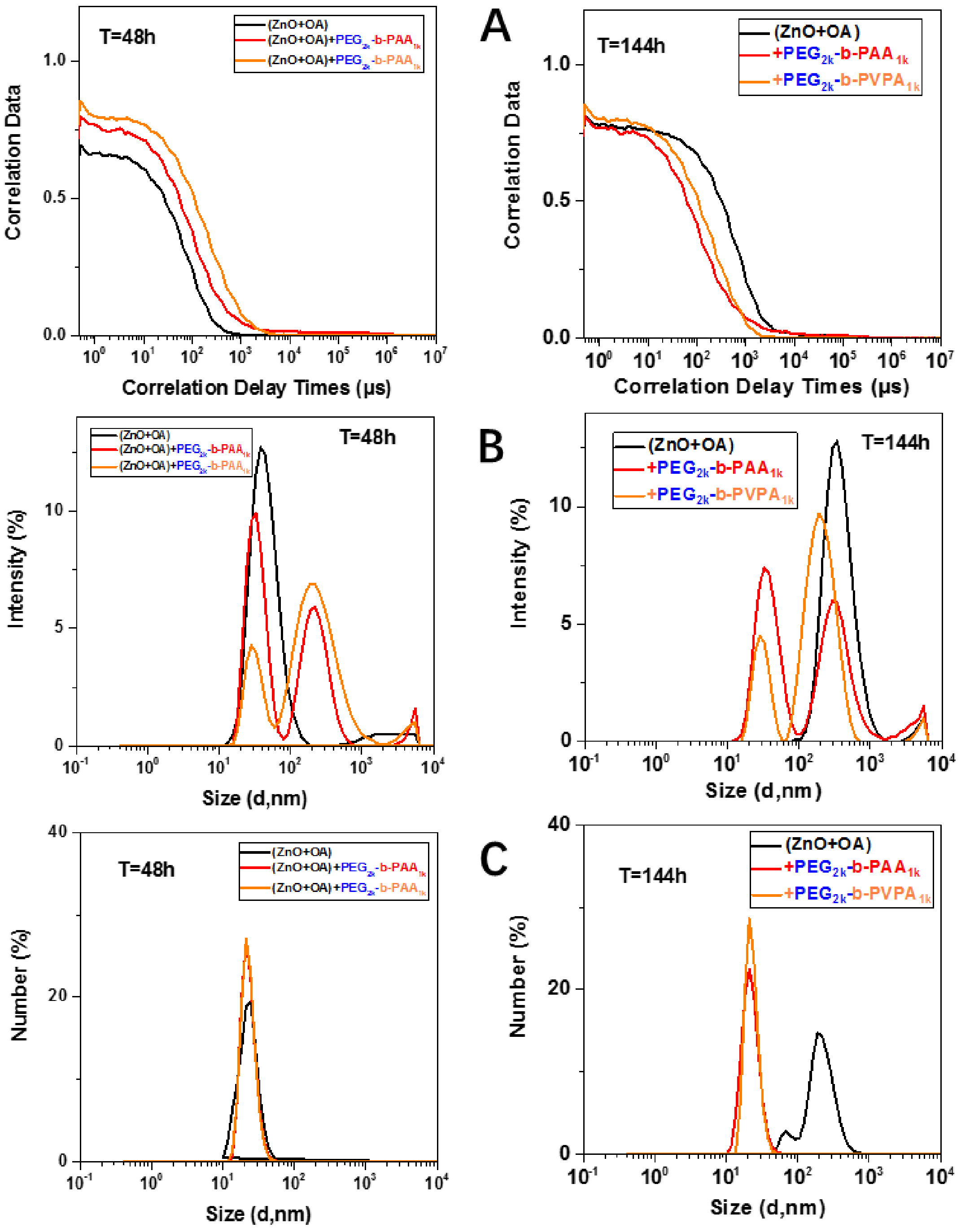


Figure S4. DLS Analysis of ZnO NPs formed in THF and stabilized by OA, OA+PEG$_{2k}$-*b*-PAA$_{1k}$ or OA+PEG$_{2k}$-*b*-PVPA$_{1k}$, 48h and 168h after NPs formation and surface modification by polymer. A: Correlograms, B: intensity-averaged size distribution, C: number-averaged size distribution.

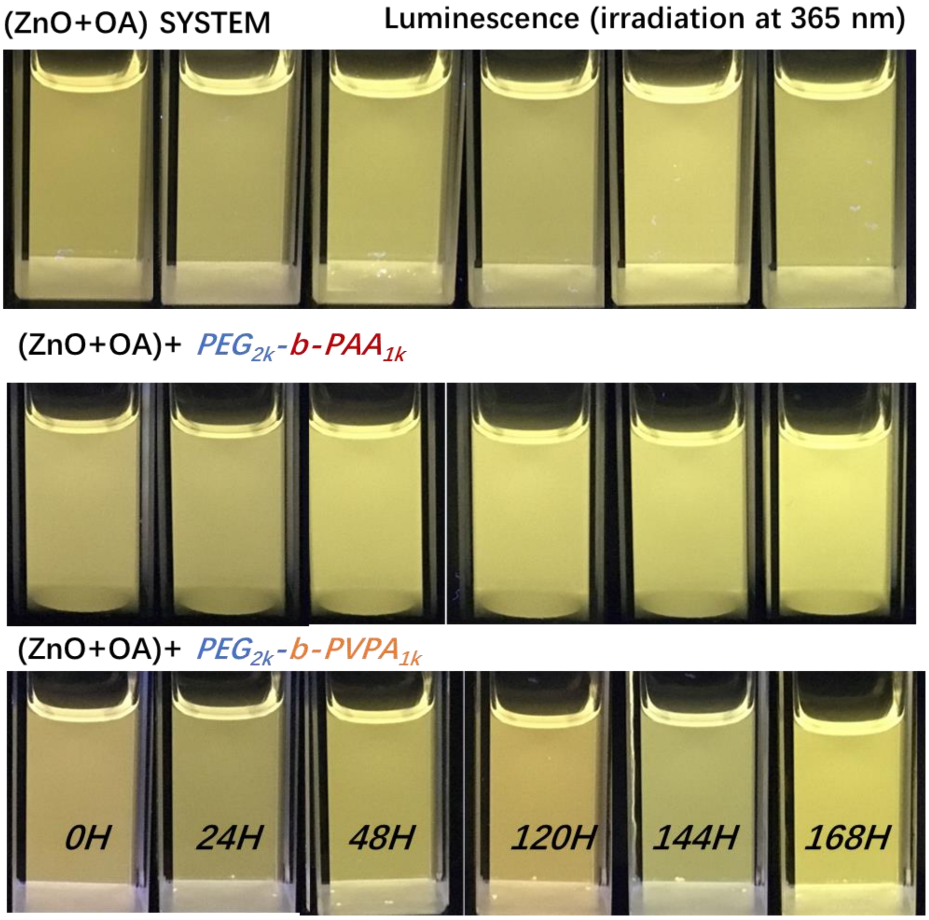


Figure S5. Evolution of luminescence as a function of time of ZnO NPs formed in THF and stabilized by OA, OA+PEG$_{2k}$-*b*-PAA$_{1k}$ or OA+PEG$_{2k}$-*b*-PVPA$_{1k}$ (irradiation at 365 nm).

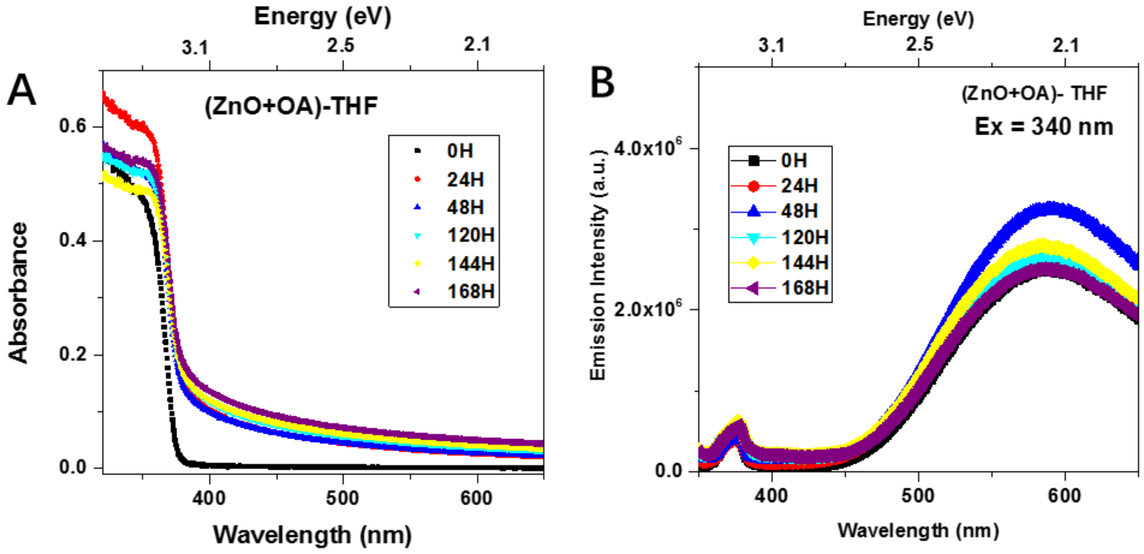


Figure S6. A: Evolution of absorbance as a function of time ZnO NPs coated by octyl amine in THF B: Evolution of fluorescence as a function of time ZnO NPs coated by OA in THF (λ_{exc} = 340 nm).

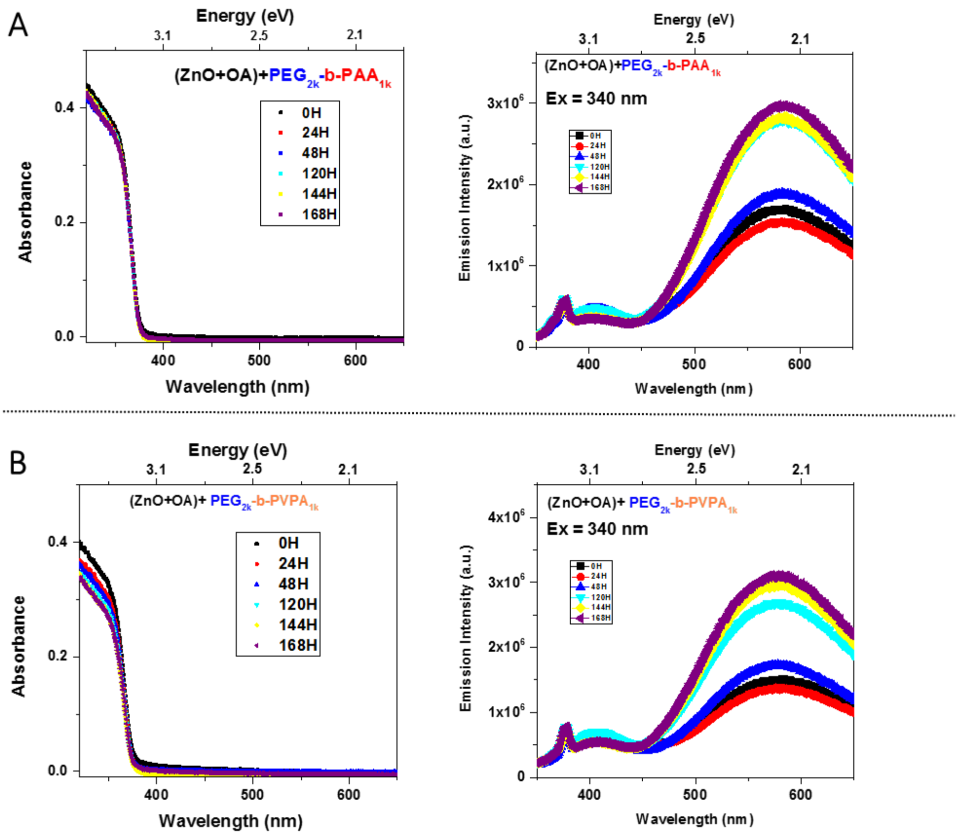


Figure S7. Evolution of absorbance and fluorescence (λ_{exc} = 340 nm) through time of ZnO NPs formed in the presence of OA and coated by A: PEG$_{2k}$-*b*-PAA$_{1k}$ and B: PEG$_{2k}$-*b*-PVPA$_{1k}$ in THF.

Normalization of data:

$$OD = \underbrace{10^{A+B*\log(\lambda)}}_{\text{Diffusion part}} + \underbrace{\frac{C}{\left(1+e^{\frac{\lambda-E}{D}}\right)}}_{\text{Absorbance of NPs}}$$

Figure 2a was obtained from absorbance spectra of Figure S6 an S7 after normalization as follows: each curve was fitted with the equation mentioned above to get rid of diffusion part. From the remaining absorbance part, the band gap is equal to Abs(350nm)-Abs(700nm) for each curve. As normalized Abs(700nm) is equal to 0, this value is roughly equal to Abs(350nm). Original emission spectra were divided by the band gap value to obtain the emission spectra presented here. This normalization enable to get rid of ZnO NPs concentration effect. Figure 2B was obtained from this normalized emission spectra.

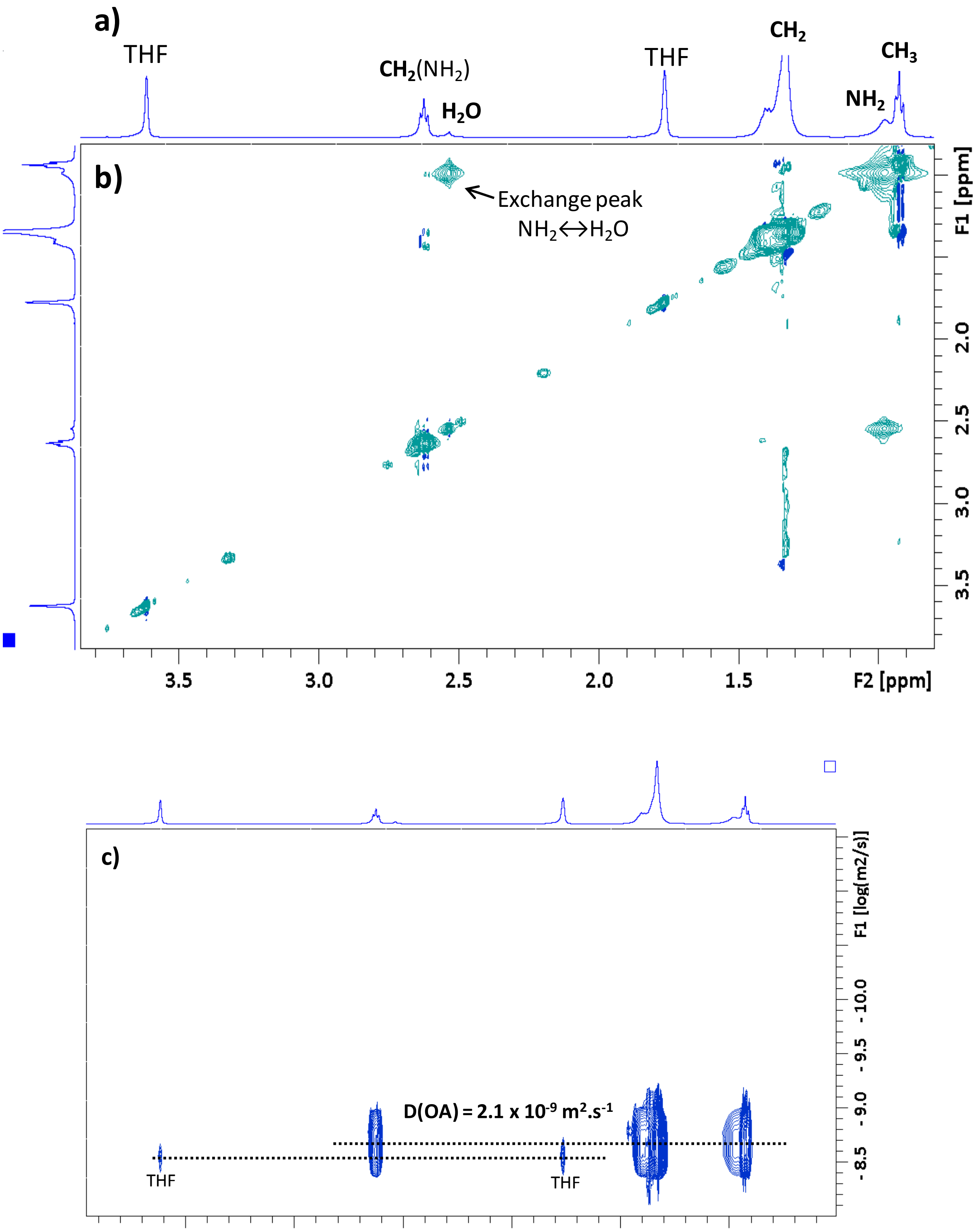
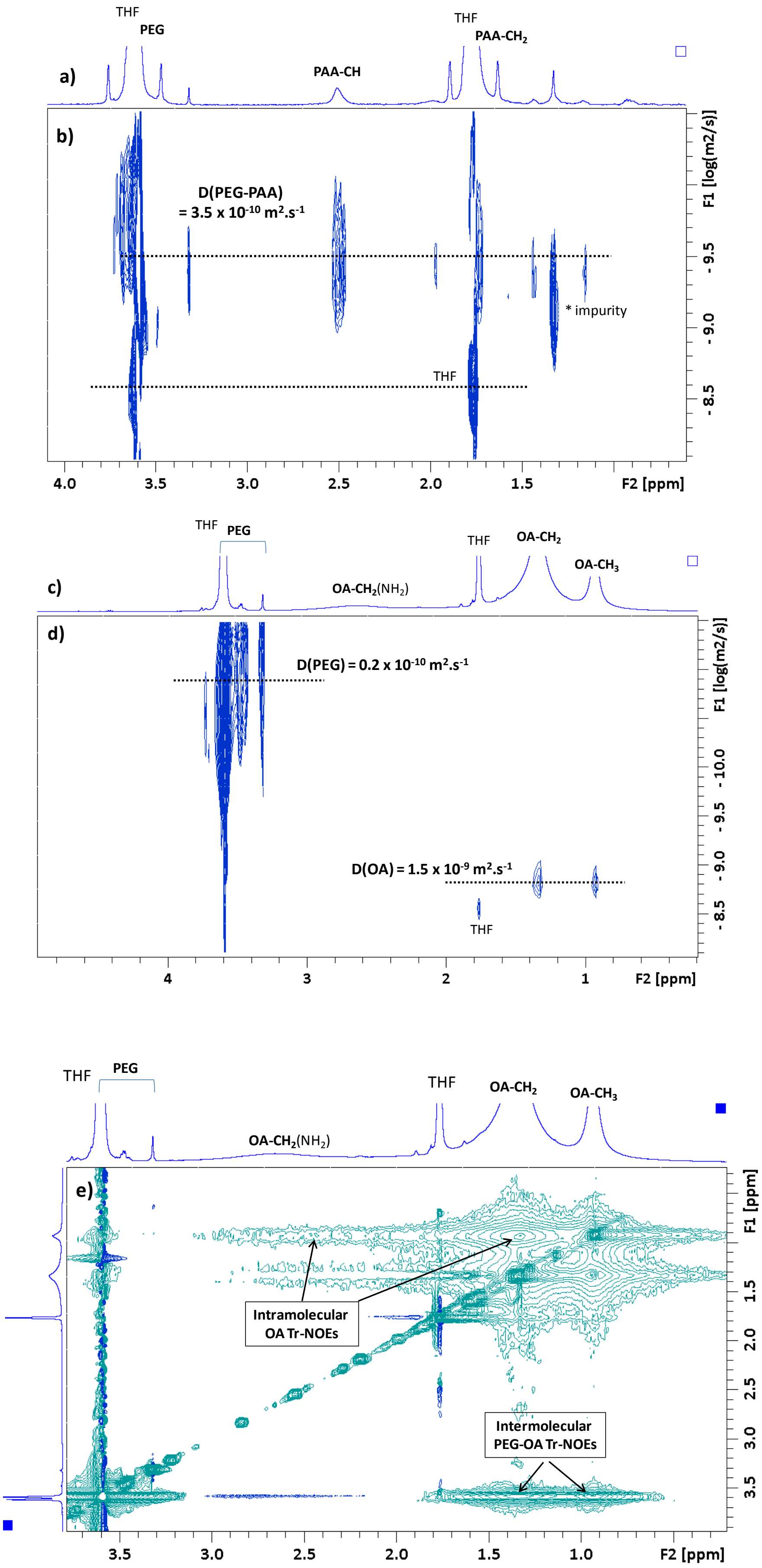


Figure S8. Liquid-state NMR spectra of ZnO/OA system in THF-d_8 at 295K. a) ^{1}H NMR, b) ^{1}H NOESY (mixing time 100ms) and c) ^{1}H DOSY.


a)
THF
PEG
PAA-CH
THF
PAA-CH$_2$
b)
D(PEG-PAA)
= 3.5 x 10^{-10} m^2.s^{-1}
* impurity
THF
F1 [log(m2/s)]
- 9.5
- 9.0
- 8.5
4.0
3.5
3.0
2.5
2.0
1.5
F2 [ppm]
c)
THF
PEG
OA-CH$_2$(NH$_2$)
THF
OA-CH$_2$
OA-CH$_3$
d)
D(PEG) = 0.2 x 10^{-10} m^2.s^{-1}
D(OA) = 1.5 x 10^{-9} m^2.s^{-1}
THF
F1 [log(m2/s)]
- 10.0
- 9.5
- 9.0
- 8.5
4
3
2
1
F2 [ppm]
THF
PEG
OA-CH$_2$(NH$_2$)
THF
OA-CH$_2$
OA-CH$_3$
e)
Intramolecular
OA Tr-NOEs
Intermolecular
PEG-OA Tr-NOEs
F1 [ppm]
1.5
2.0
2.5
3.0
3.5
3.5
3.0
2.5
2.0
1.5
1.0
F2 [ppm]

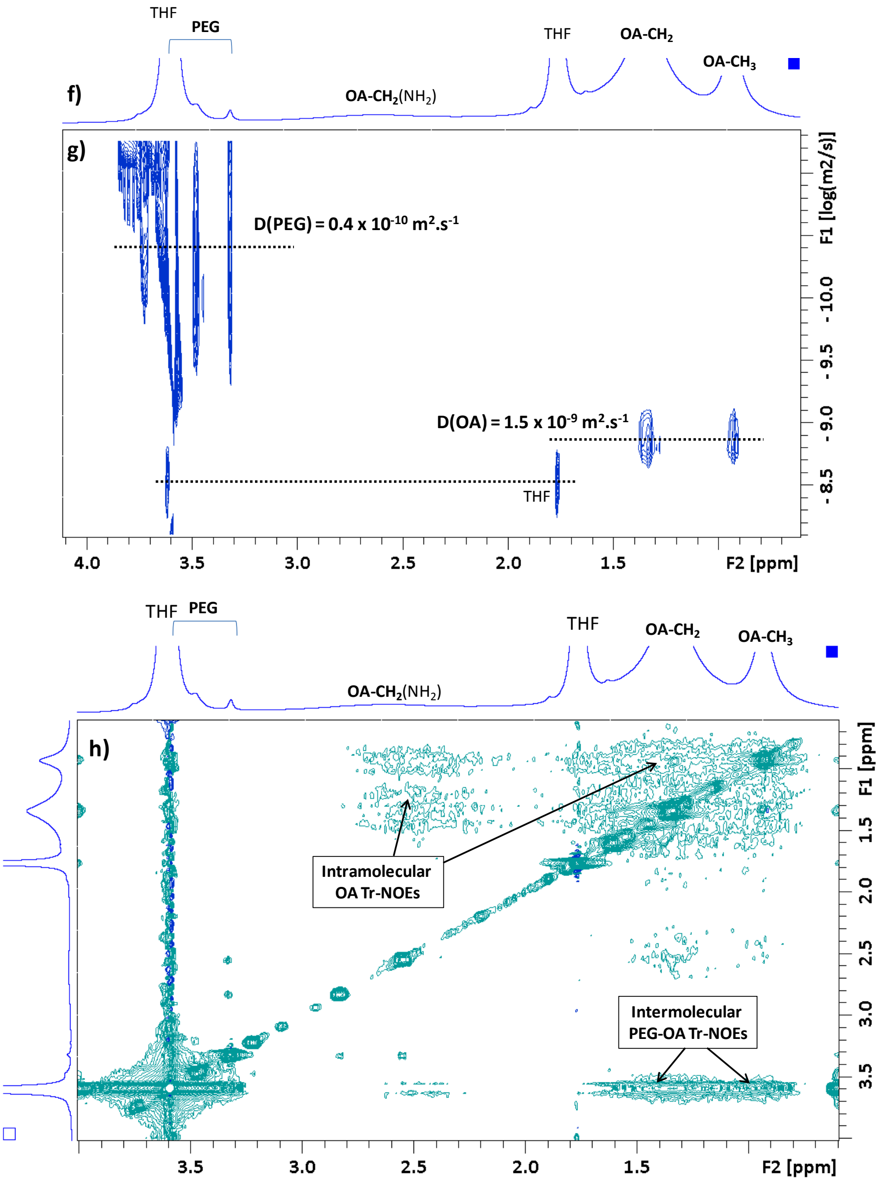


Figure S9. Liquid-state NMR spectra of PEG$_{2k}$-*b*-PAA$_{1k}$, ZnO/OA/PEG$_{2k}$-*b*-PAA$_{1k}$ and OA/PEG$_{2k}$-*b*-PAA$_{1k}$ systems in THF-d$_8$ at 295K. a) ^{1}H NMR and b) ^{1}H DOSY of PEG$_{2k}$-*b*-PAA$_{1k}$; c) ^{1}H NMR, d) ^{1}H DOSY and e) ^{1}H NOESY (mixing time 100ms) of ZnO/OA/PEG$_{2k}$-*b*-PAA$_{1k}$; f) ^{1}H NMR, g) ^{1}H DOSY and h) ^{1}H NOESY (mixing time 100ms) of OA/PEG$_{2k}$-*b*-PAA$_{1k}$. Note that the DOSY signal of the PEG$_{2k}$-*b*-PAA$_{1k}$ polymer are very broad probably because of size heterogeneity. The diffusion coefficient indicated for PEG$_{2k}$-*b*-PAA$_{1k}$ corresponds to an average diffusion coefficient.

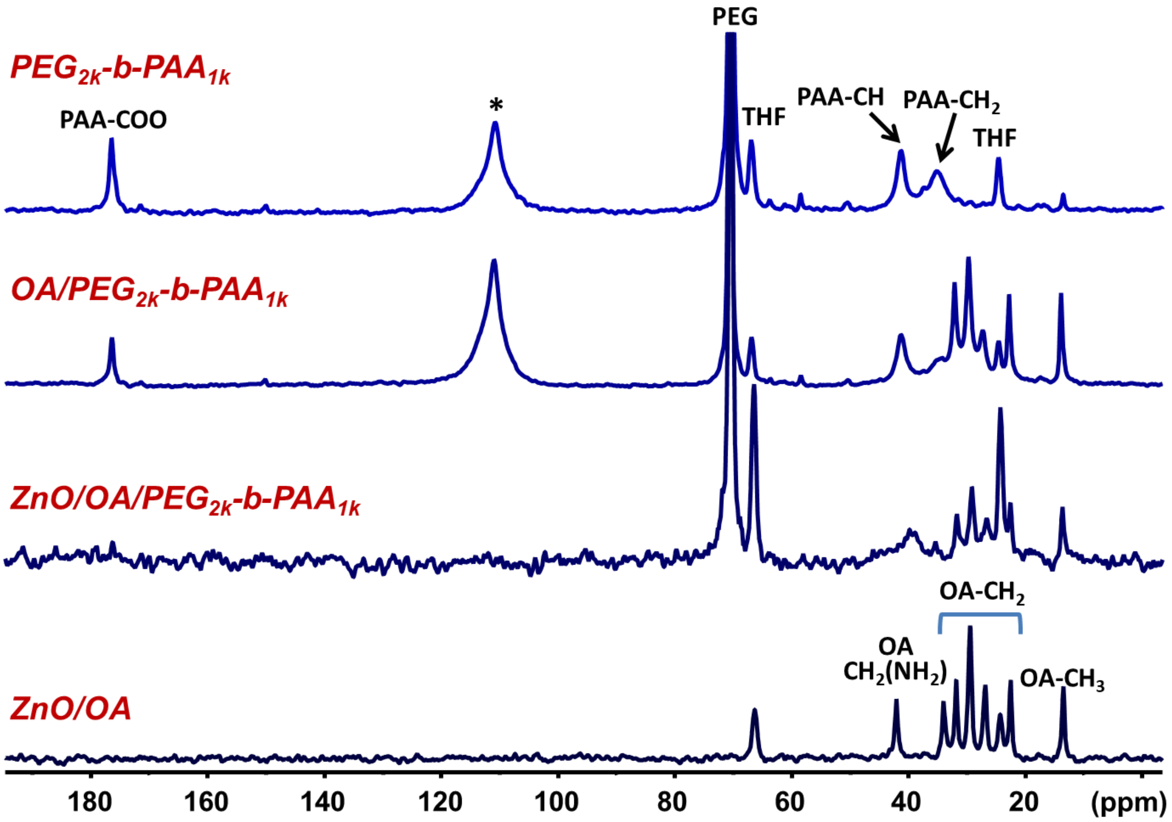
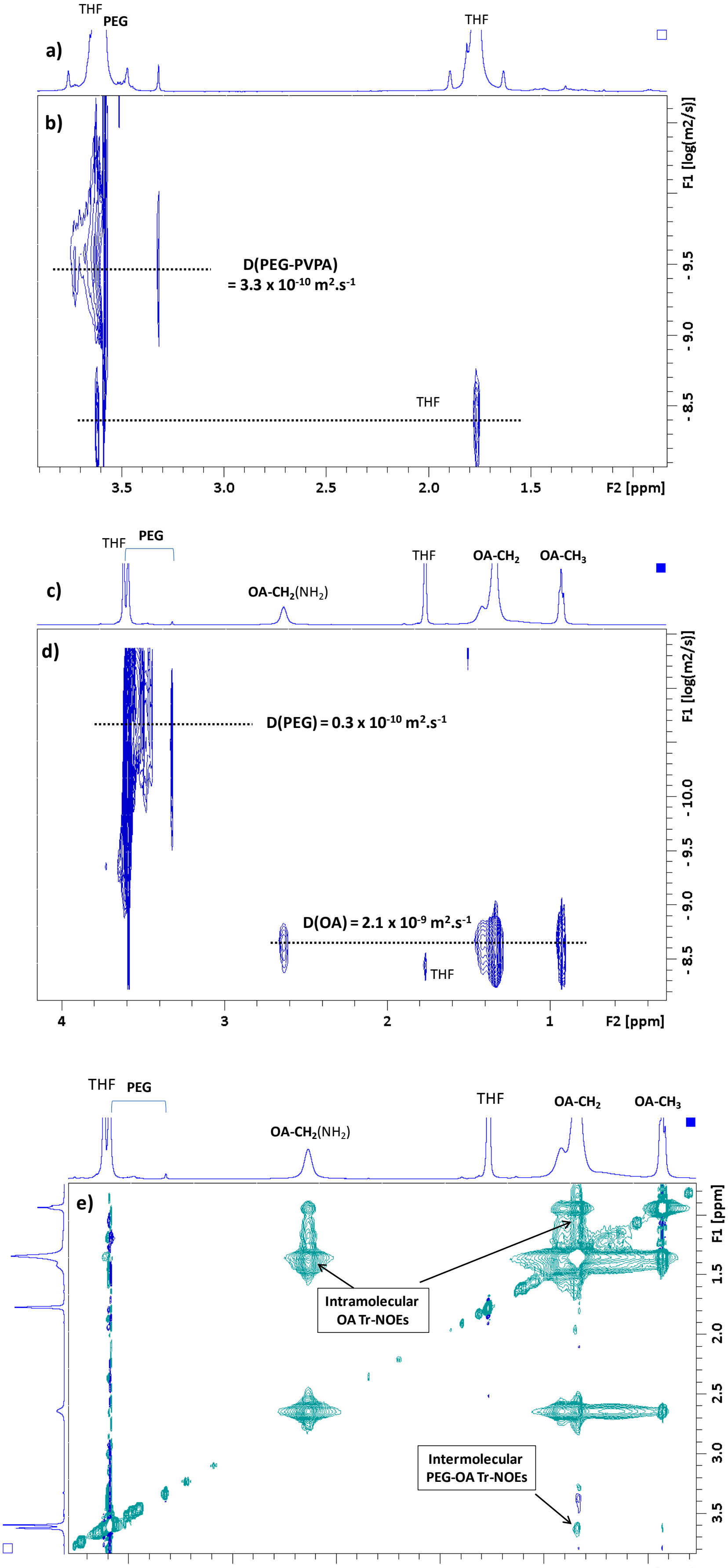


Figure S10. Solid state ^{13}C MAS spectrum of ZnO/OA/PEG$_{2k}$-*b*-PAA$_{1k}$ system compared with the one issued from ZnO/OA, the polymers alone and from a mixture of OA/polymer. Note the absence of the PAA-COO(H) signal in the ZnO/OA/PEG$_{2k}$-*b*-PAA$_{1k}$ sample due to i) strong signal broadening (see PAA-COO(H) shape in CPMAS spectrum in Figure 3) and probably strong increase of ^{13}C relaxation times due to the rigidification of carboxylate groups at the ZnO NP surface. * Teflon insert.


a)
THF
PEG
THF
b)
D(PEG-PVPA)
= 3.3 x 10^{-10} m^2.s^{-1}
THF
F1 [log(m2/s)]
-9.5
-9.0
-8.5
3.5
3.0
2.5
2.0
1.5
F2 [ppm]
c)
THF
PEG
OA-CH$_2$(NH$_2$)
THF
OA-CH$_2$
OA-CH$_3$
d)
D(PEG) = 0.3 x 10^{-10} m^2.s^{-1}
D(OA) = 2.1 x 10^{-9} m^2.s^{-1}
THF
F1 [log(m2/s)]
-10.0
-9.5
-9.0
-8.5
4
3
2
1
F2 [ppm]
THF
PEG
OA-CH$_2$(NH$_2$)
THF
OA-CH$_2$
OA-CH$_3$
e)
Intramolecular
OA Tr-NOEs
Intermolecular
PEG-OA Tr-NOEs
F1 [ppm]
1.5
2.0
2.5
3.0
3.5
3.5
3.0
2.5
2.0
1.5
F2 [ppm]

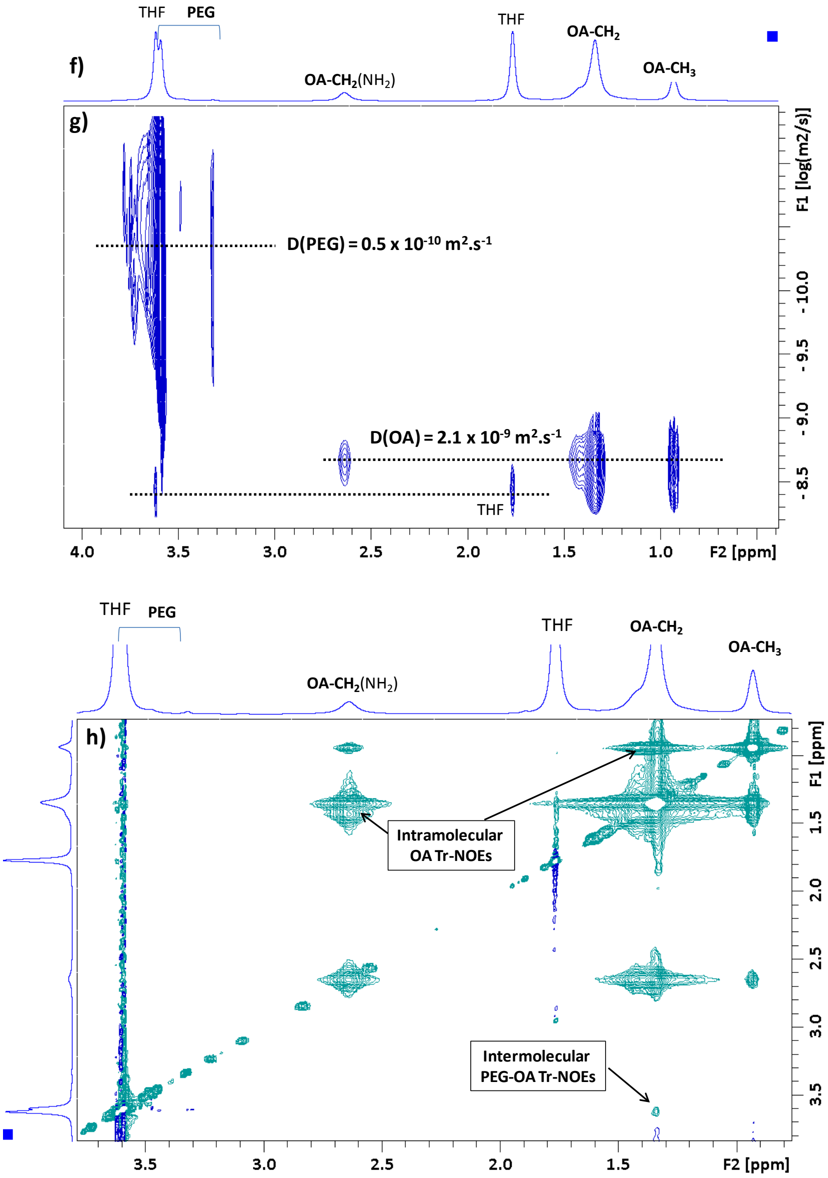


Figure S11. Liquid-state NMR spectra of PEG$_{2k}$-*b*-PVPA$_{1k}$, ZnO/OA/PEG$_{2k}$-*b*-PVPA$_{1k}$ and OA/PEG$_{2k}$-*b*-PVPA$_{1k}$ systems in THF-d$_8$ at 295K. a) ^{1}H NMR and b) ^{1}H DOSY of PEG$_{2k}$-*b*-PVPA$_{1k}$; c) ^{1}H NMR, d) ^{1}H DOSY and e) ^{1}H NOESY (mixing time 100ms) of ZnO/OA/PEG$_{2k}$-*b*-PVPA$_{1k}$; f) ^{1}H NMR, g) ^{1}H DOSY and h) ^{1}H NOESY (mixing time 100ms) of OA/ PEG$_{2k}$-*b*-PVPA$_{1k}$. Note that the DOSY signal of the PEG polymer are very broad probably because of size heterogeneity. The diffusion coefficient indicated for PEG$_{2k}$-*b*-PVPA$_{1k}$ corresponds to an average diffusion coefficient. The linewidth broadening of OA signals, the decrease of the OA diffusion coefficient and the Tr-NOE intensities observed with PEG$_{2k}$-*b*-PVPA$_{1k}$ (especially the intermolecular Tr-NOEs) are significantly weaker than the ones observed with PEG$_{2k}$-*b*-PAA$_{1k}$. This indicates that the population of OA in weak interaction with the PEG$_{2k}$-*b*-PVPA$_{1k}$ polymer is smaller than the one in weak interaction with PEG$_{2k}$-*b*-PAA$_{1k}$.

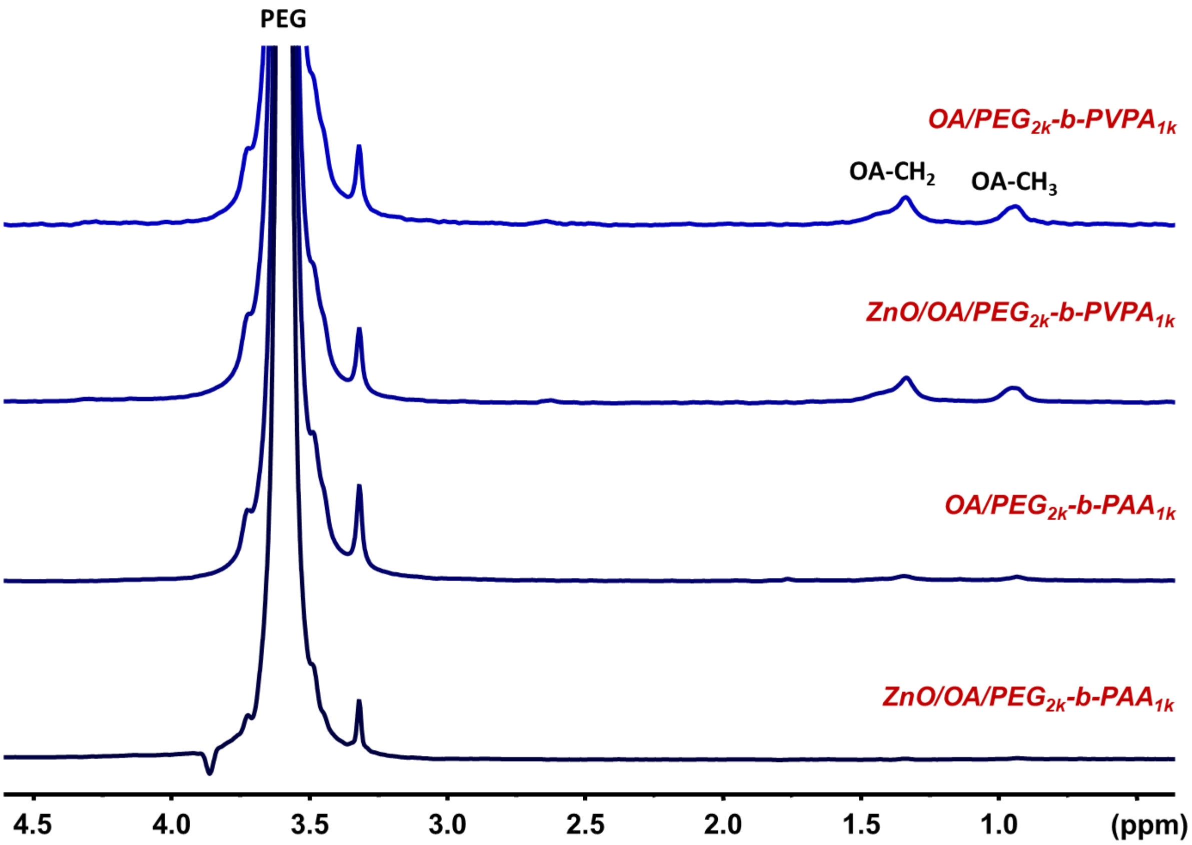


Figure S12. ^{1}H NMR spectra with diffusion filter of ZnO/OA/PEG$_{2k}$-*b*-PAA$_{1k}$, OA/PEG$_{2k}$-*b*-PAA$_{1k}$, ZnO/OA/PEG$_{2k}$-*b*-PVPA$_{1k}$ and OA/PEG$_{2k}$-*b*-PVPA$_{1k}$ systems in THF-d$_8$ at 295K. All the experiment were performed with the same experimental parameters. The PEG signal was set at the same intensity in all the experiments. Residual signal of OA aliphatic groups are observed with PVPA polymer due to the presence of slow diffusing OA species in strong interaction with the PVPA polymer.

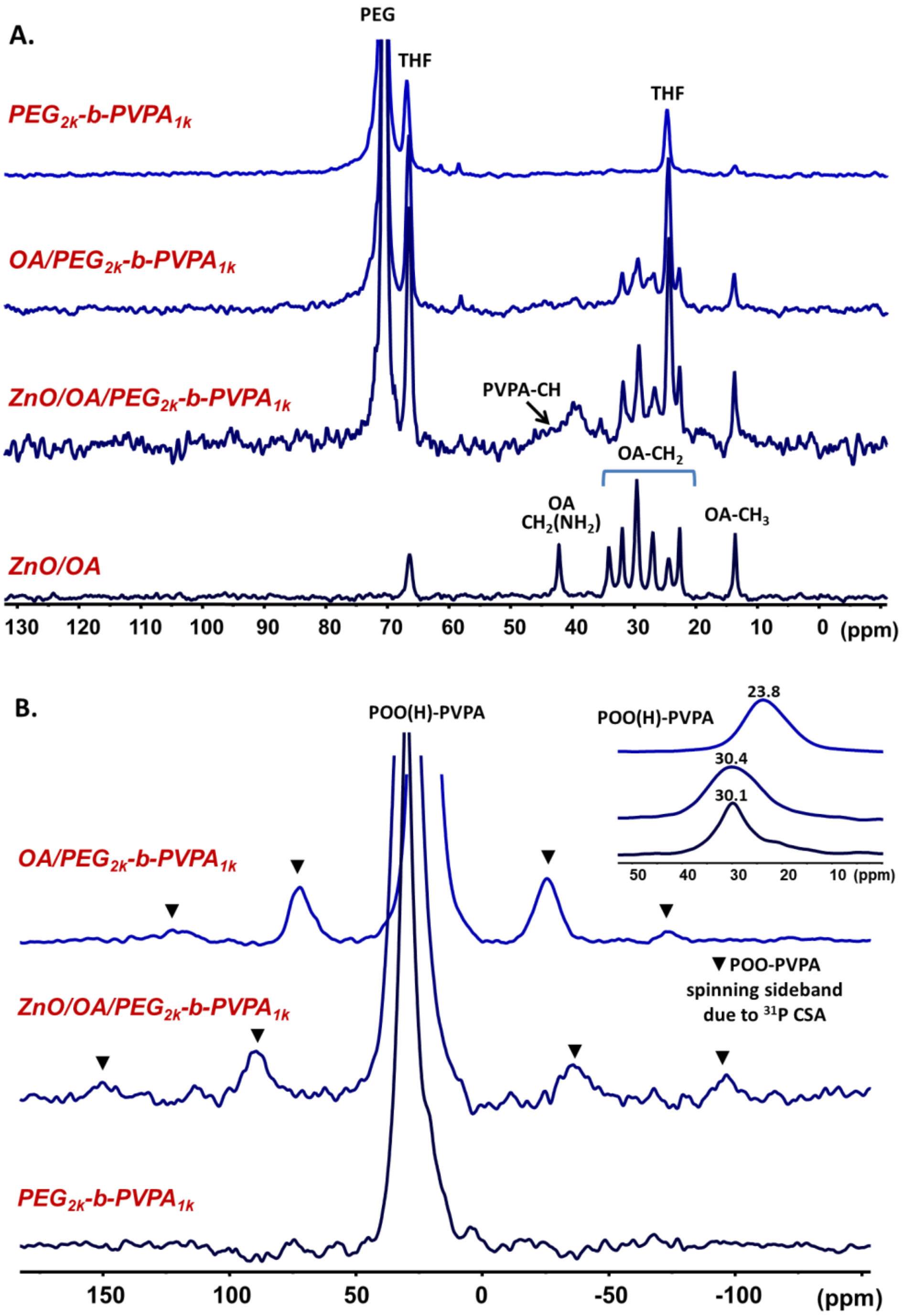


Figure S13. ^{13}C MAS (A) and ^{31}P CPMAS (B) spectra of ZnO/OA/PEG$_{2k}$-*b*-PVPA$_{1k}$ system. Spectra obtained for these systems were compared with the one issued from ZnO/OA, the polymers alone and from a mixture of OA/polymer. Note the absence of the PVPA signals in the PEG$_{2k}$-*b*-PVPA$_{1k}$ sample due to strong signal broadening associated with high chemical/structural disorder at the PVPA functions. ▼: spinning sideband due to ^{31}P chemical shift anisotropy (CSA) associated with a rigidification of the POO(H) functions of PEG-PVPA. Note that the spinning rate for ZnO/OA/PEG$_{2k}$-*b*-PVPA$_{1k}$ sample was of 10 kHz while it was of 8 kHz for OA/PEG$_{2k}$-*b*-PVPA$_{1k}$ and PEG$_{2k}$-*b*-PVPA$_{1k}$ sample. Inset in figure B: Zoom on ^{31}P POO(H) NMR resonances with their chemical shift.

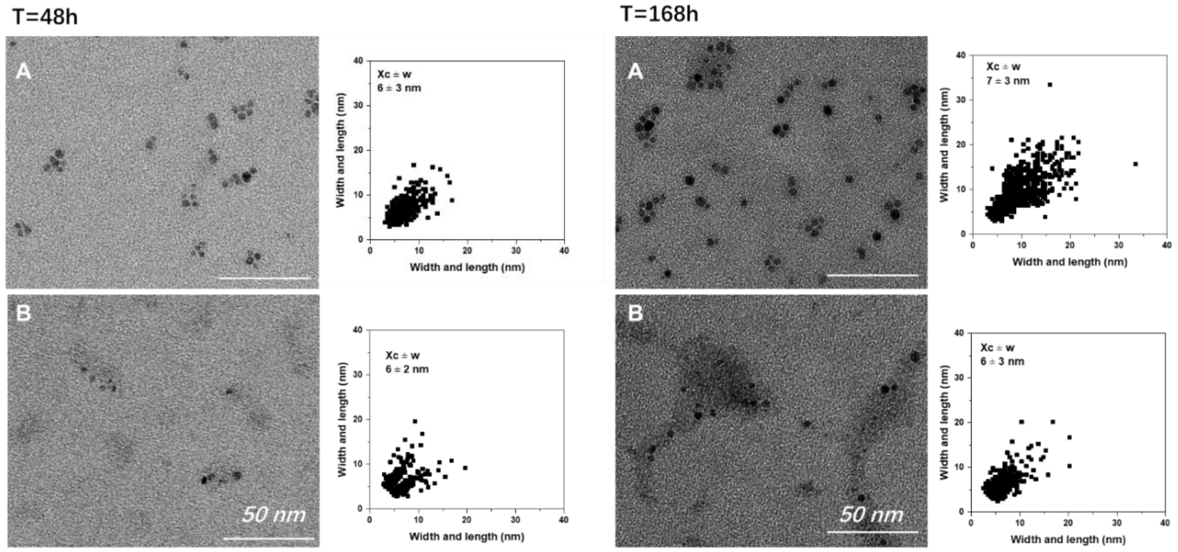


Figure S14. TEM images and particle size distribution of ZnO NPs formed in THF 48h or 168h after transfer in water, stabilized by A: OA+PEG$_{2k}$-*b*-PAA$_{1k}$ or B: OA+PEG$_{2k}$-*b*-PVPA$_{1k}$.

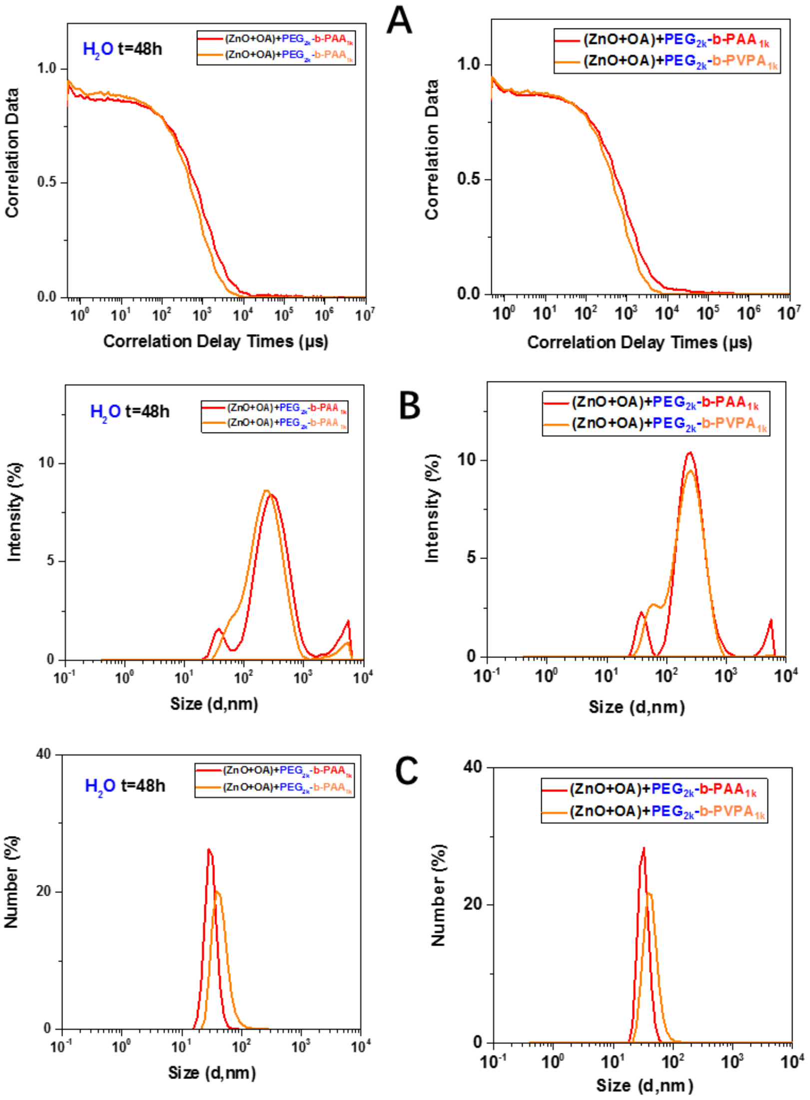
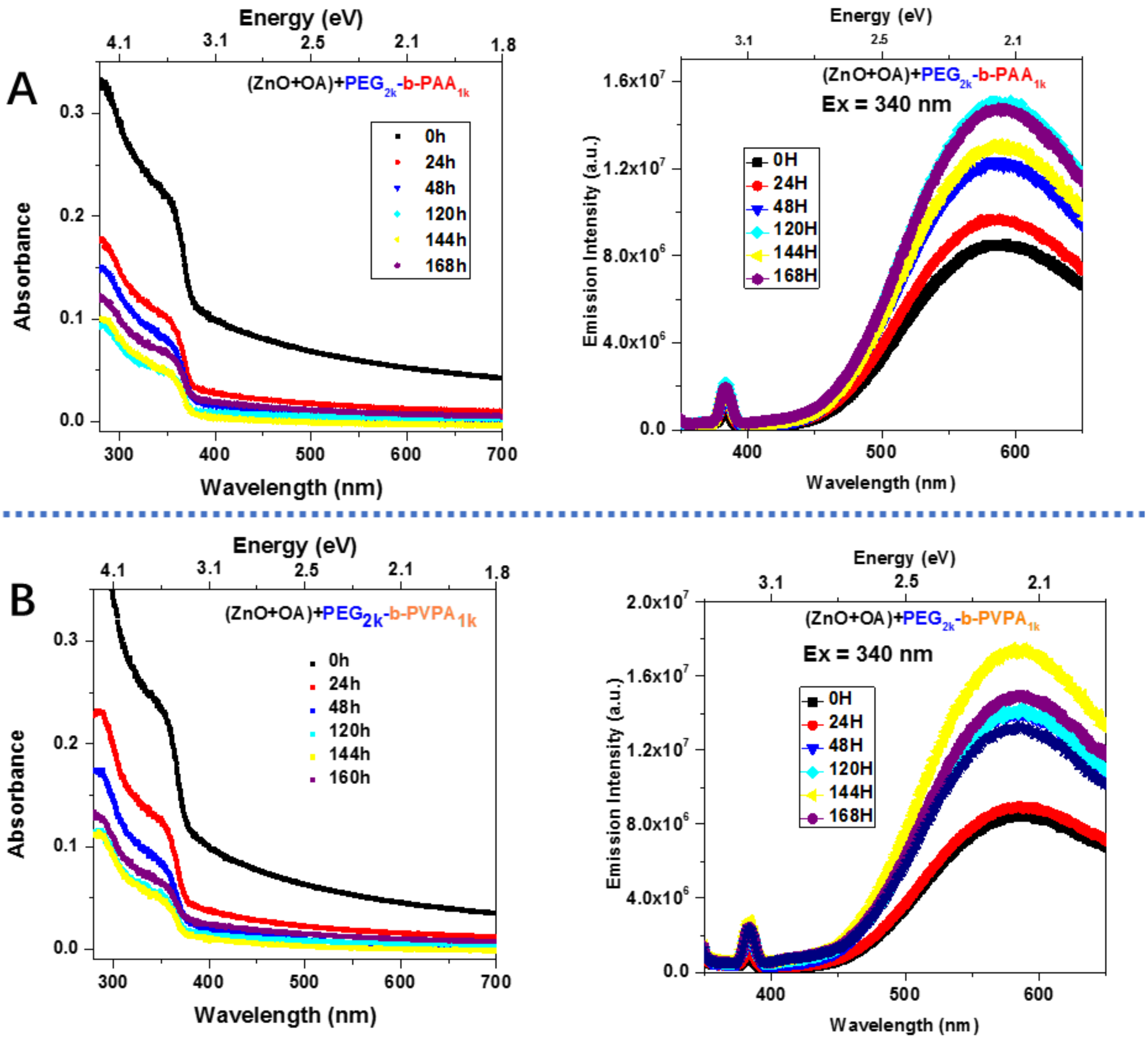


Figure S15. DLS Analysis of ZnO NPs formed in THF and stabilized by OA, OA+PEG$_{2k}$-*b*-PAA$_{1k}$ or OA+PEG$_{2k}$-*b*-PVPA$_{1k}$, 48h and 144h after transfer in water solution. A: Correlograms, B: intensity-averaged size distribution, C: number-averaged size distribution of hydrodynamic diameter.



$$OD = \underbrace{10^{A+B*\log(\lambda)}}_{\text{Diffusion part}} + \underbrace{\frac{C}{\left(1+e^{\frac{\lambda-E}{D}}\right)}}_{\text{Absorbance of NPs}}$$

Figure S16. Evolution of absorbance and fluorescence (λ_{exc} = 340 nm) through time of ZnO NPs formed in the presence of octyl amine and coated by A: PEG$_{2k}$-*b*-PAA$_{1k}$ and B: PEG$_{2k}$-*b*-PVPA$_{1k}$ after transfer in water. Figure 6A was obtained from absorbance spectra after normalization as follows : each curve was fitted with the equation mentioned above to get rid of diffusion part. From the remaining absorbance part, the band gap is equal to Abs(350nm)-Abs(700nm) for each curve. As normalized Abs(700nm) is equal to 0, this value is roughly equal to Abs(350nm).

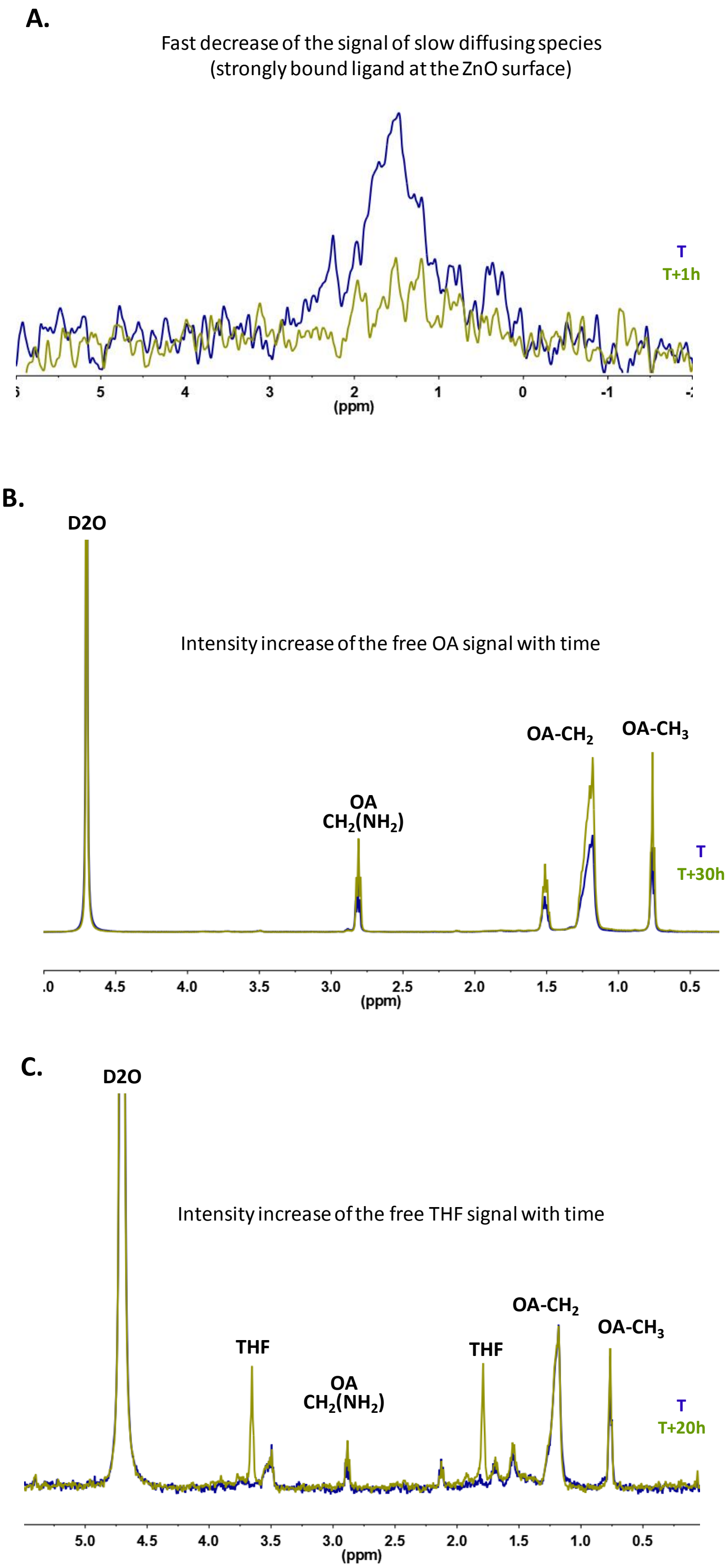


Figure S17. Time evolution of ^1H diffusion filter NMR experiment (A) and of liquid state ^1H NMR spectra of ZnO/OA system in D_2O for two components (B-C).

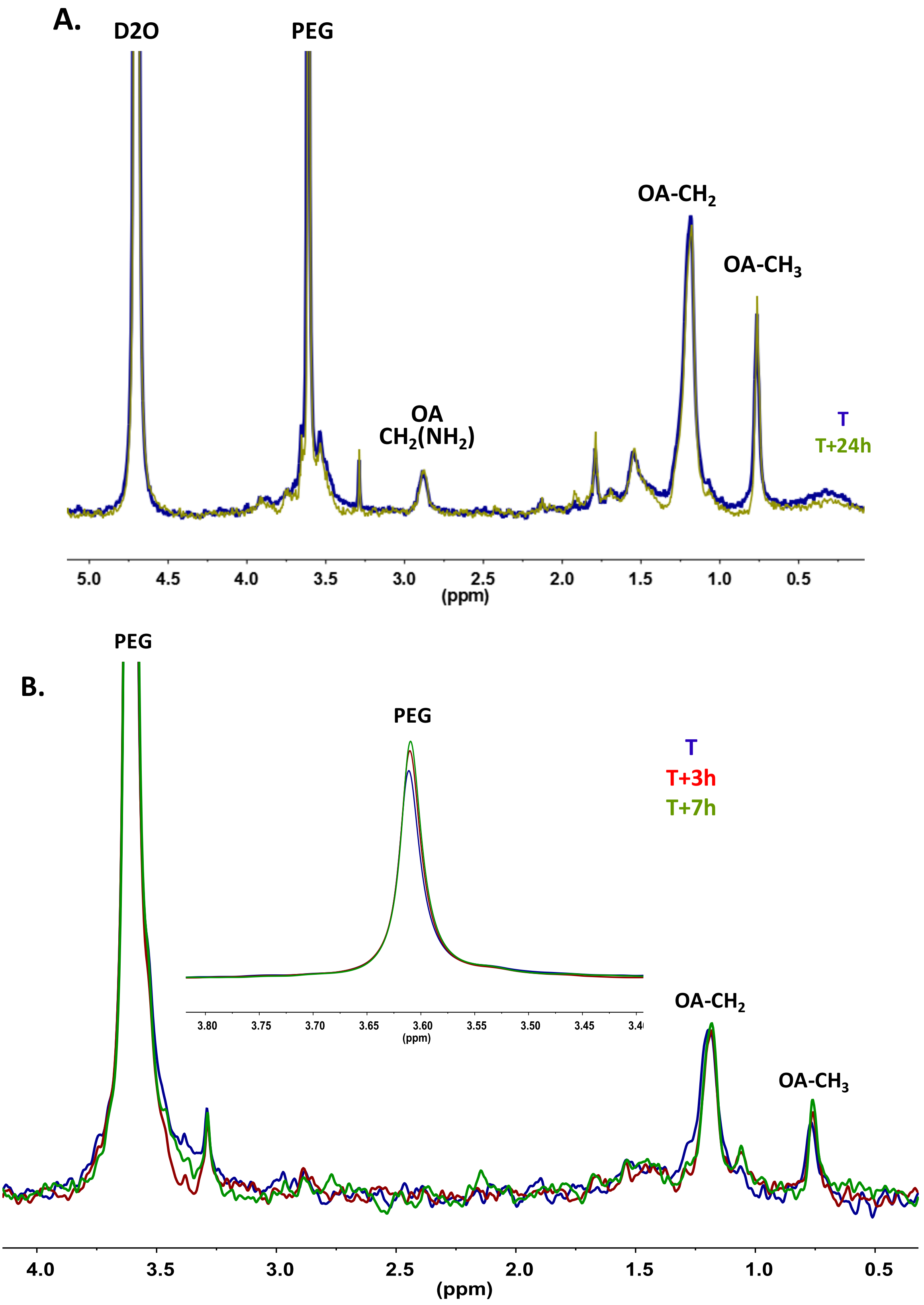


Figure S18. Time evolution of liquid state ^{1}H NMR spectra of ZnO/OA in the presence of PEG$_{2k}$-*b*-PAA$_{1k}$ (A) and of ^{1}H diffusion filter NMR experiment (B).

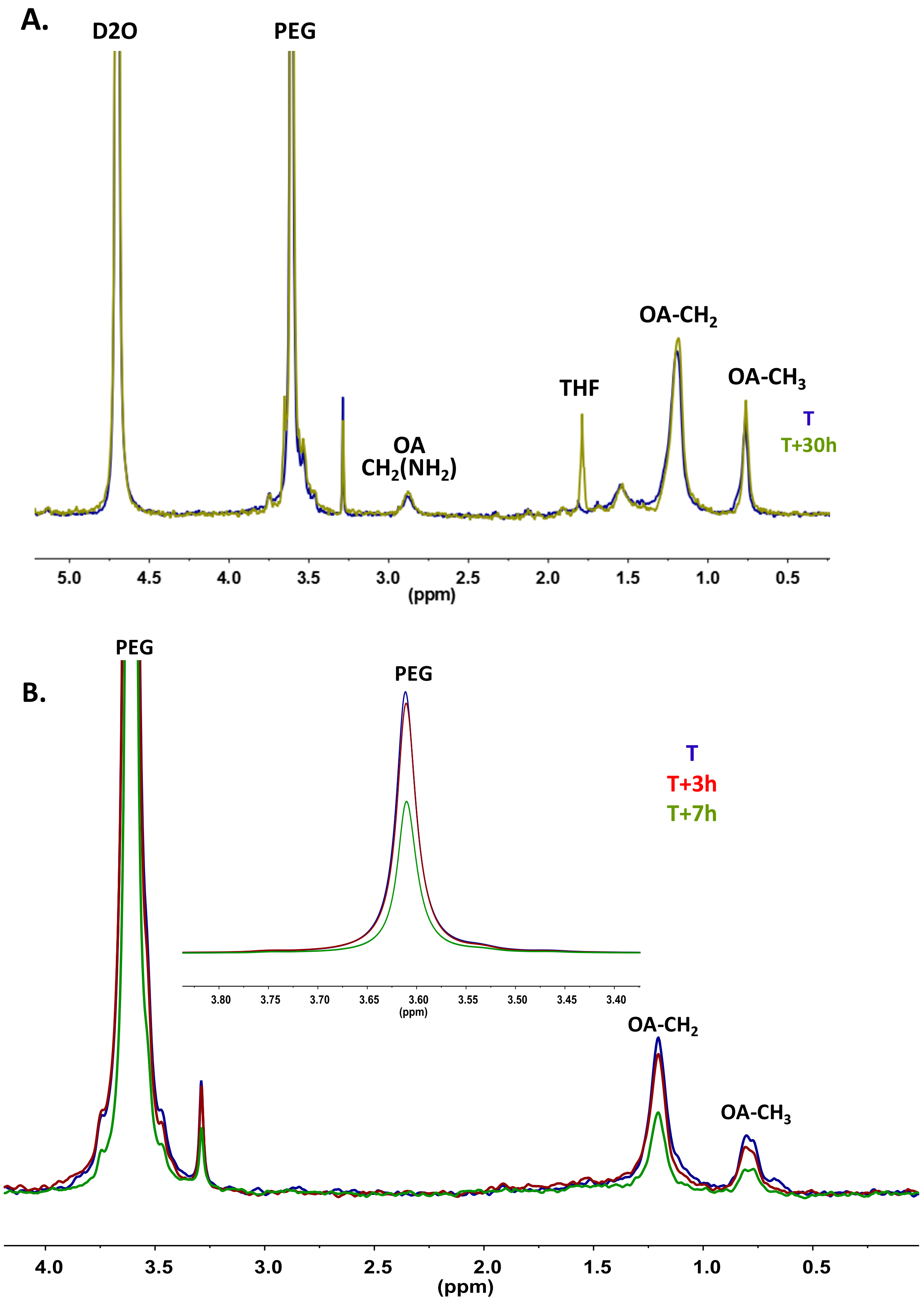


Figure S19. Time evolution of liquid state ^{1}H NMR spectra of ZnO/OA in the presence of PEG$_{2k}$-*b*-PVPA$_{1k}$ (A) and of ^{1}H diffusion filter NMR experiment (B).

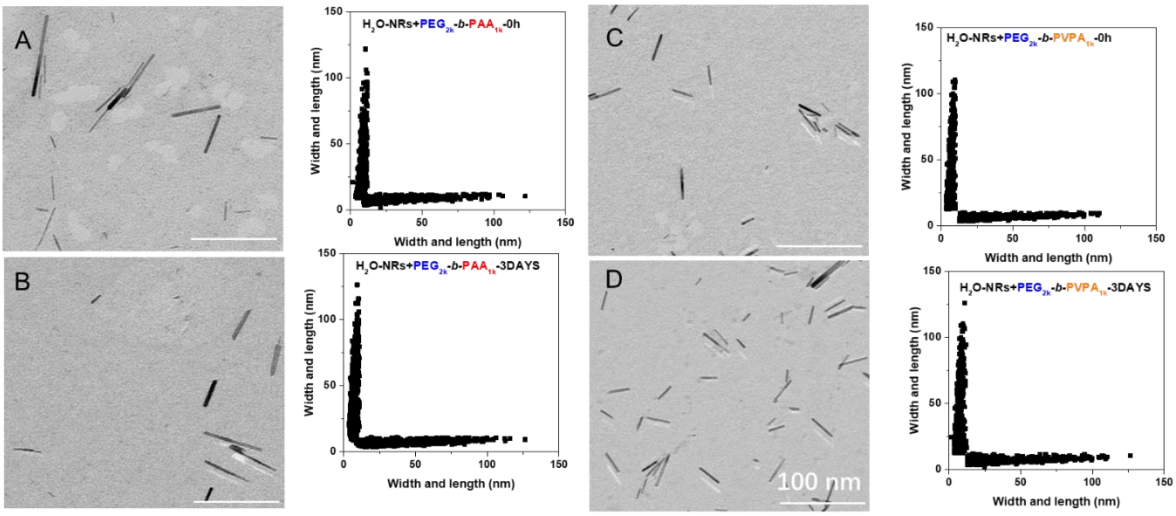


Figure S20. TEM images and corresponding 2D-plots of ZnO nanorods coated by PEG$_{2k}$-*b*-PAA$_{1k}$ (A and B) or by PEG$_{2k}$-*b*-PVPA$_{1k}$ (C and D) transferred in water recorded immediately after transfer (A and C) or after 3-days aging in water (B and D).

Table S1. Average dimensions of ZnO nanorods coated (or not) in THF by PEG_{2k}-*b*-PAA_{1k} or by PEG_{2k}-*b*-$PVPA_{1k}$ transferred in water obtained from TEM measurements immediately after transfer and after storage in water solutions during 3 days.

(Xc±w)	No Polymers (nm)	+PEG_{2k}-*b*-PAA_{1k} (nm)	+PEG_{2k}-*b*-$PVPA_{1k}$ (nm)
Length -0h	31±17	33±21	38±25
Width-0h	7±2	8±2	7±2
Length-3days	-	36±21	35±24
Width-3days	-	7±1	7±2