

Electronic Supporting Information

Elucidating the Backbone Degradation Mechanism of Poly(7-Oxa- 2,3-diazanorbornene)

Na Zhang,^{a,c} Lianqiang Dong,^{b,c} Yu Wang,^{*,a} Xiaoyang Wang,^a Yixing Wen,^{b,c}
Xueguang Lu,^{b,c} Yuanchen, Dong,^{*,b,c} Wei You^{*,a,c}

^a Beijing National Laboratory for Molecular Sciences (BNLMS), CAS Key Laboratory of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China

^b Beijing National Laboratory for Molecular Sciences (BNLMS), CAS Key Laboratory of Colloid, Interface and Chemical Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China

^c University of Chinese Academy of Sciences, Beijing, China

Table of Contents

General Information.....	S2
Materials.....	S2
Characterization	S2
Synthetic Procedures.....	S3
Degradation Procedures	S5
TEM and DLS Characterization	S17
References.....	S18

General Information

Materials

Tetrahydrofuran (THF) and *d*-chloroform were purchased from Energy Chemical Co., Shanghai. Hydrochloric acid (HCl) was purchased from Sinopharm Chemical Reagent Co., Ltd. Shanghai, China. PS internal standard and TFA were purchased from Shanghai Macklin Biochemical Technology Co., Ltd. Chloroform (CHCl₃) was purchased from Concord Inc. Tianjin, China. Grubbs 3rd generation catalyst was purchased from Tjchemwizard Co., Ltd. Tianjin, China. All above-mentioned chemicals were used without further purification unless noted otherwise. Norbornene monomers NEO was prepared following reported procedures.¹ Polymer P-ODAN was prepared according to our previous report using 200:1 monomer to initiator ratio ($M_n = 44.1$ kDa, $D = 1.11$).²

Characterization

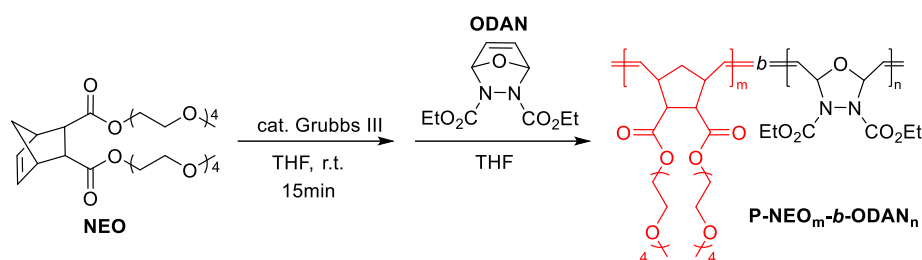
¹H NMR spectra were acquired on a Bruker Fourier 300 or Bruker Avance III 400 HD spectrometer in CDCl₃. Molecular weights (M_n and M_w) and polydispersity (D) were measured by gel permeation chromatography (Agilent 1260 Infinity II) in THF (40 °C) mobile phase based on narrowly distributed polystyrene (PS) standard with a flow rate of 0.3 mL/min.

Transmission electron microscopy (TEM) imaging was performed on a HT-7700 instrument to observe the self-assembly structure of copolymer. The sample was dropped on the treated hydrophilic copper grid (200 meshes). The copper grid was observed by transmission electron microscopy with an accelerated voltage of 100 kV at room temperature.

Dynamic light scattering (DLS) was performed on a BeNano 90 instrument to observe the diameter of particles with light scattering Angle about 90 degrees at room temperature.

Synthetic Procedures

Synthesis of P-NEO-*b*-ODAN



In a N₂-filled glovebox, NEO (112 mg, 0.2 mmol) was dissolved in 0.5 mL of THF, then a freshly prepared 1.9 mg Grubbs III catalyst (0.004 mmol) in 0.5 mL THF was added. The mixture was stirred at room temperature for 15 min. Next, a solution of ODAN (48 mg, 0.2 mmol) in 0.5 mL THF was added. After stirring at 25 °C overnight, the reaction was quenched with excess ethyl vinyl ether. SiliaMetS was used to remove the Ru-residue, and the filtered solution was concentrated. The polymer was quantitatively obtained without further purification ($M_n = 38.1$ kDa, = 1.17).

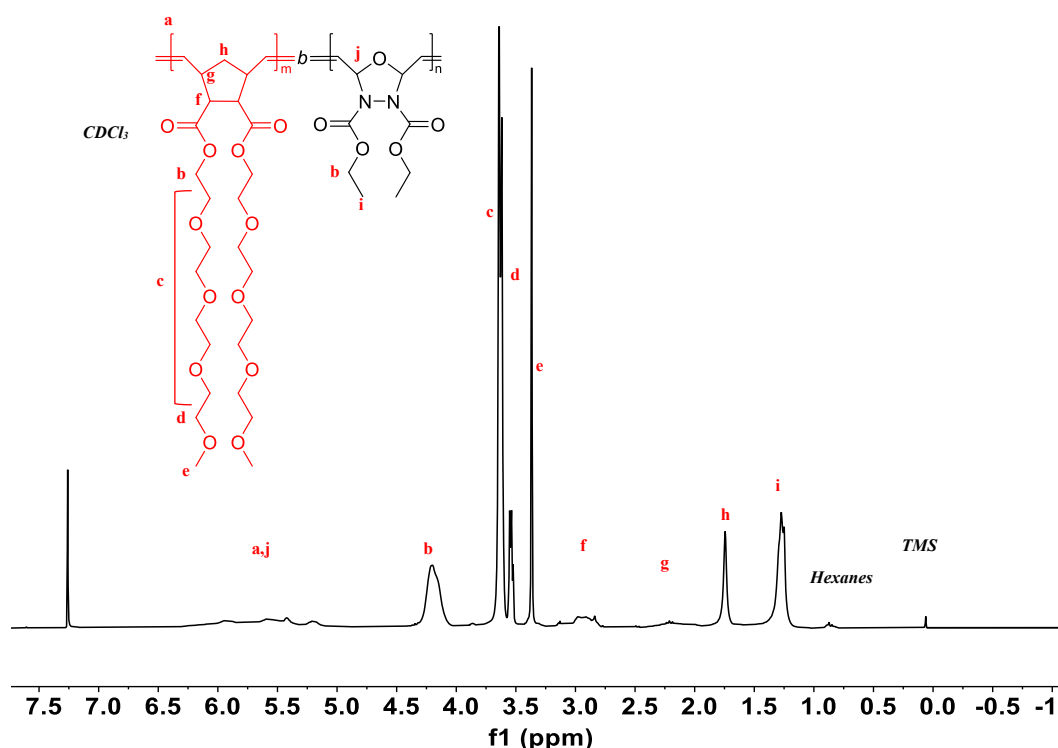
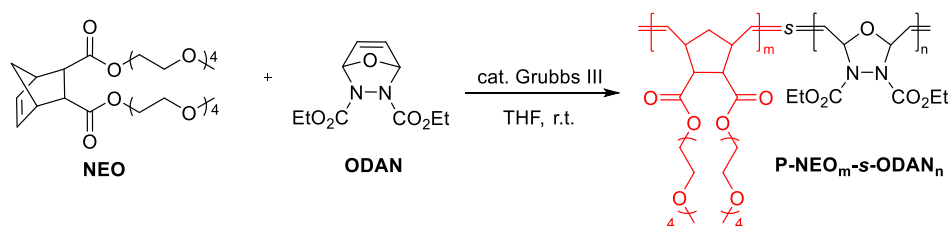


Figure S1. ¹H NMR Spectrum of P-NEO-*b*-ODAN.

Synthesis of P-NEO-s-ODAN



In a N₂-filled glovebox, NEO (112 mg, 0.2 mmol) and ODAN (48 mg, 0.2 mmol) were dissolved in 1 mL of THF, then a freshly prepared 1.9 mg Grubbs III catalyst (0.004 mmol) in 0.5 mL THF was added. After stirring at 25 °C overnight, the reaction was quenched with excess ethyl vinyl ether. SiliaMetS was used to remove the Ru-residue, and the filtered solution was concentrated. The polymer was quantitatively obtained without further purification ($M_n = 38.1$ kDa, $\text{PDI} = 1.15$).

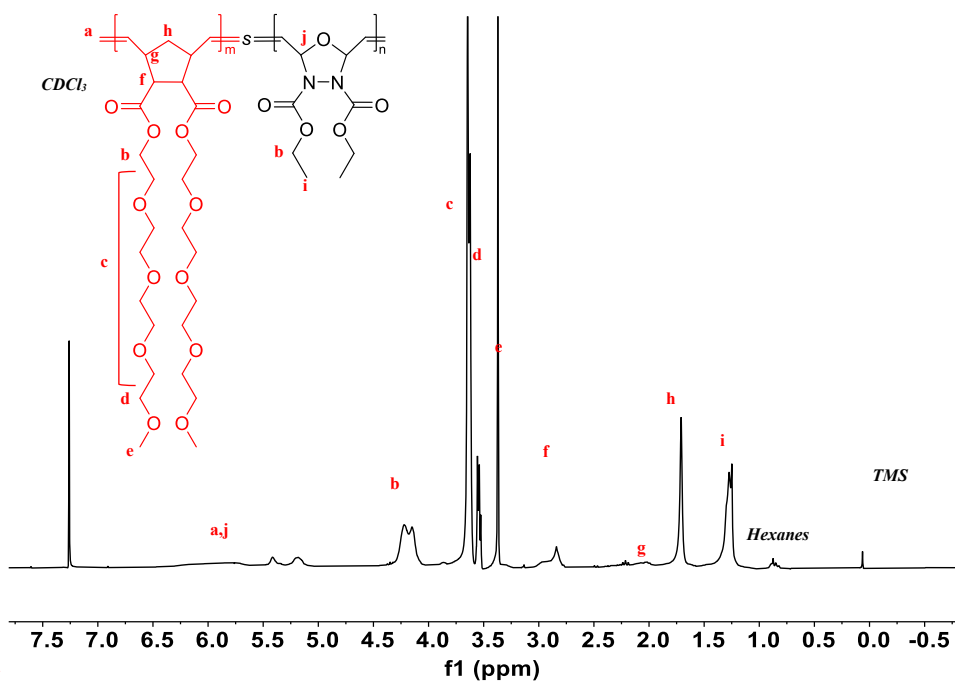


Figure S2. ¹H NMR Spectrum of P-NEO-s-ODAN.

Degradation Procedures

(A) General acidic degradation in THF

20 mg P-ODAN and 3~5 mg PS internal standard was diluted in 2 mL of THF, and 40 μ L 1.0 M HCl (or H₂O) was added to the solution. The mixture was stirred at 25 °C. At specific time intervals, 200 μ L of the solution was removed from the reaction, among which 100 μ L was diluted and subjected to GPC analysis directly, and another 100 μ L was mixed with excess sodium bicarbonate for neutralization. After sitting for 30 min, the mixture was filtered and subjected to GPC analysis.

(B) General acidic degradation in chloroform

20 mg P-ODAN and 3~5 mg PS internal standard was diluted in 2 mL of CHCl₃, and 40 μ L 1.0 M TFA (in CHCl₃ or MeOH) was added to the solution. The mixture was stirred at 25 °C. At specific time intervals, 200 μ L of the solution was removed from the reaction and mixed with excess sodium bicarbonate for neutralization. After sitting for 30 min, the mixture was dried under vacuum, redissolved in THF, filtered, and subjected to GPC analysis.

(C) General acidic degradation in water

20 mg P-NEO-b-ODAN or P-NEO-s-ODAN was diluted in 2 mL of H₂O, and 40 μ L 1.0 M HCl (H₂O) was added to the solution. The mixture was stirred at 25 °C. At specific time intervals, 200 μ L of the solution was removed from the reaction and mixed with excess sodium bicarbonate for neutralization. After sitting for 30 min, the mixture was dried under vacuum, redissolved in THF, filtered, and subjected to GPC analysis.

(D) General neutral degradation in THF (or chloroform)

20 mg P-ODAN and 3~5 mg PS internal standard was diluted in 2 mL of THF (or chloroform). The mixture was stirred at specific temperature (4 °C, 25 °C, 40 °C, and 60 °C). At specific time intervals, 200 μ L of the solution was removed from the reaction, filtered, and subjected to GPC analysis.

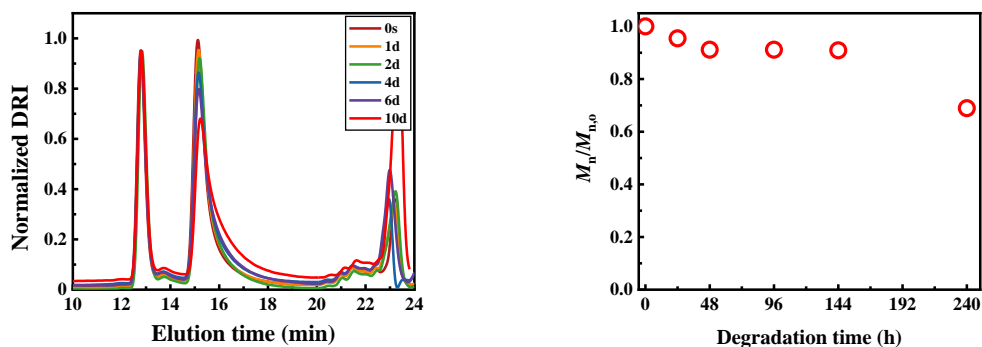


Figure S3. GPC traces and M_n changing trend for degradation of P-ODAN as a 1 mg/mL solution in THF at 25 °C (General Procedure D, except using low concentration).

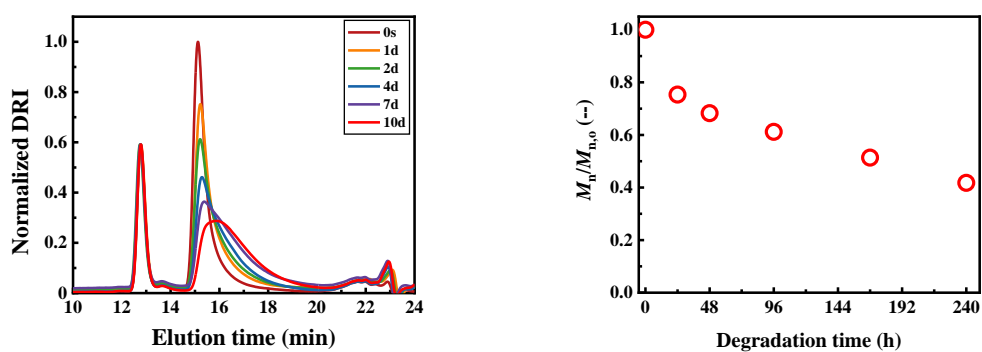


Figure S4. GPC traces and M_n changing trend for degradation of P-ODAN as a 10 mg/mL solution in THF at 25 °C (General Procedure D, Figure 2a in the main text).

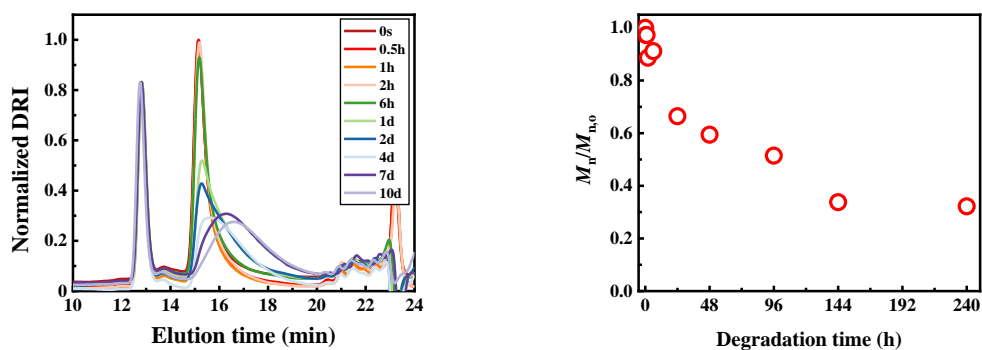


Figure S5. GPC traces and M_n changing trend for degradation of P-ODAN as a 10 mg/mL solution in THF at 25 °C with the addition of 40 μL H_2O (General Procedure D, Figure 2d in the main text).

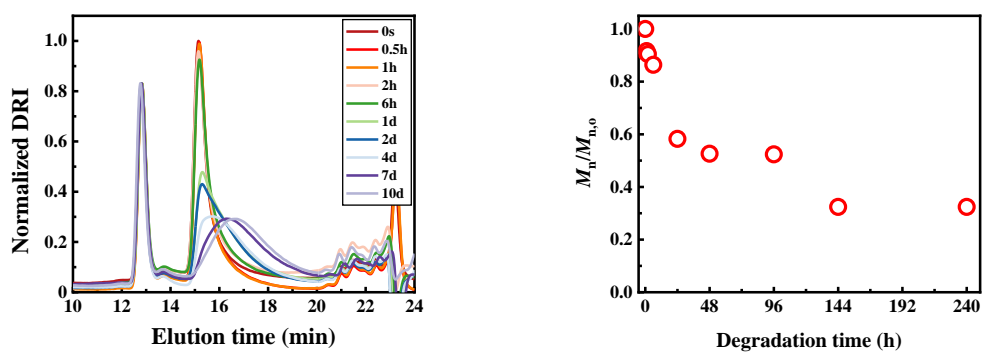


Figure S6. GPC traces and M_n changing trend for degradation of P-ODAN as a 10 mg/mL solution in THF at 25 °C with the addition of 40 μL H_2O and treated with Na_2CO_3 before GPC analysis (General Procedure D).

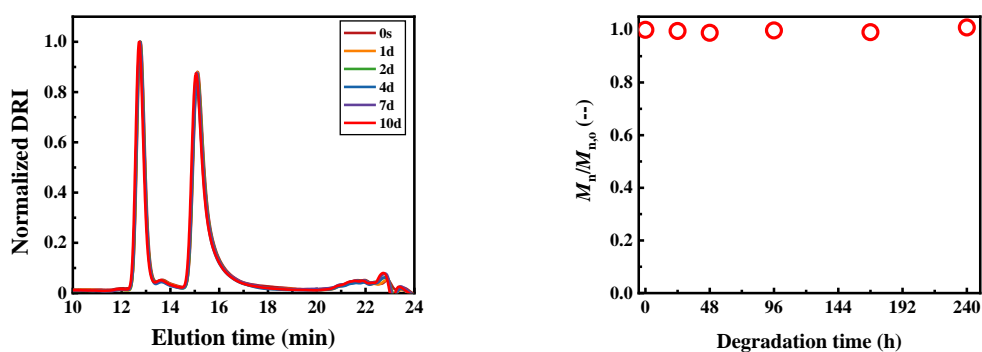


Figure S7. GPC traces and M_n changing trend for degradation of P-ODAN as a 10 mg/mL solution in THF at 4 °C (General Procedure D).

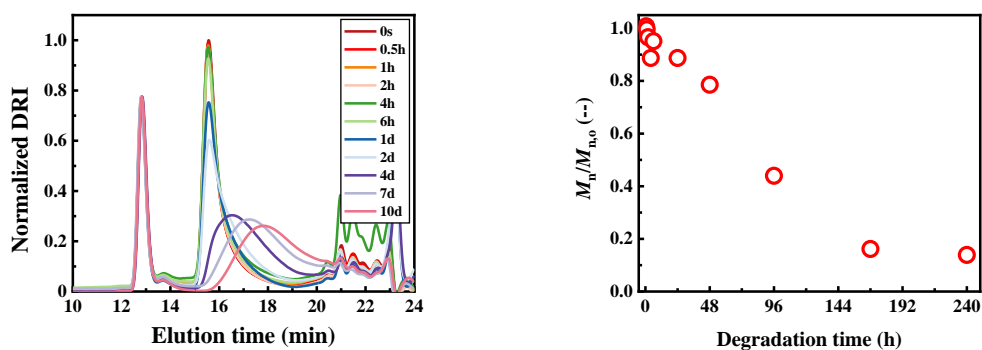


Figure S8. GPC traces and M_n changing trend for degradation of P-ODAN as a 10 mg/mL solution in THF at 40 °C (General Procedure D).

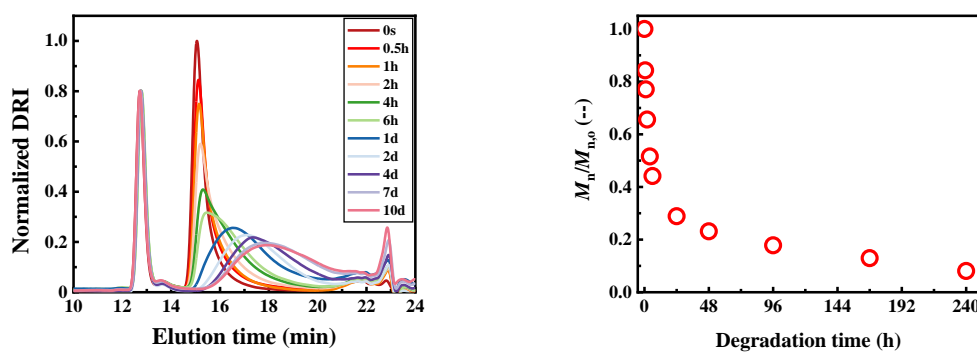


Figure S9. GPC traces and M_n changing trend for degradation of P-ODAN as a 10 mg/mL solution in THF at 60 °C (General Procedure D, Figure 2e in the main text).

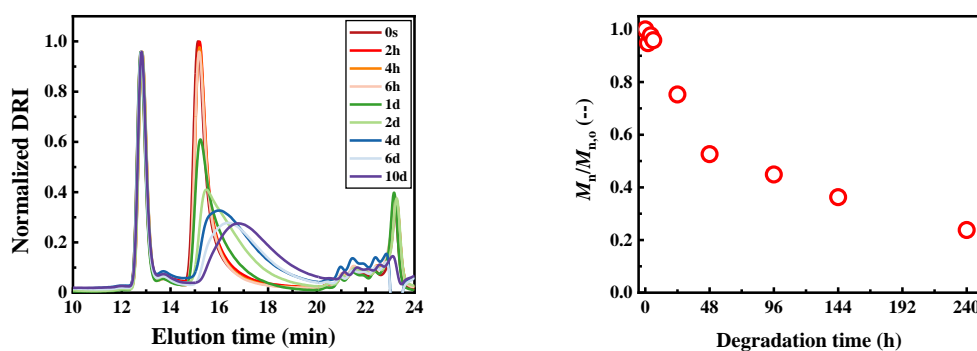


Figure S10. GPC traces and M_n changing trend for degradation of P-ODAN as a 10 mg/mL solution in THF at 25 °C in the presence of 200 mg Na_2CO_3 (General Procedure D).

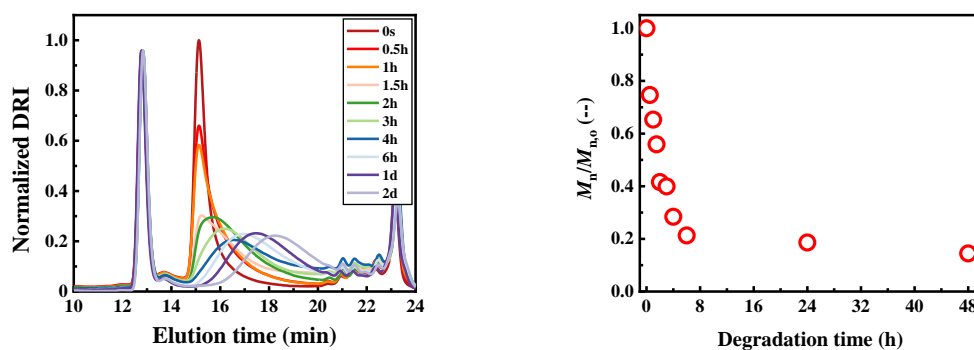


Figure S11. GPC traces and M_n changing trend for degradation of P-ODAN as a 10 mg/mL solution in dilute HCl/THF solution (0.02 M) at 25 °C *without* Na_2CO_3 neutralization (General Procedure A, Figure 2b in the main text).

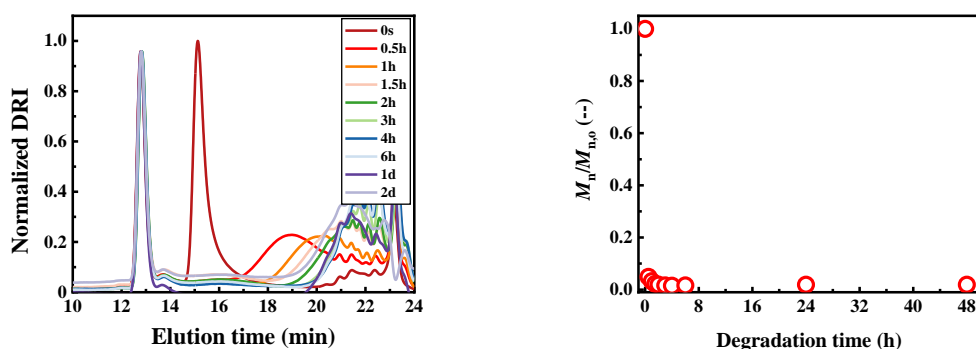


Figure S12. GPC traces and M_n changing trend for degradation of P-ODAN as a 10 mg/mL solution in dilute HCl/THF solution (0.02 M) at 25 °C with Na_2CO_3 neutralization (General Procedure A, Figure 2c in the main text).

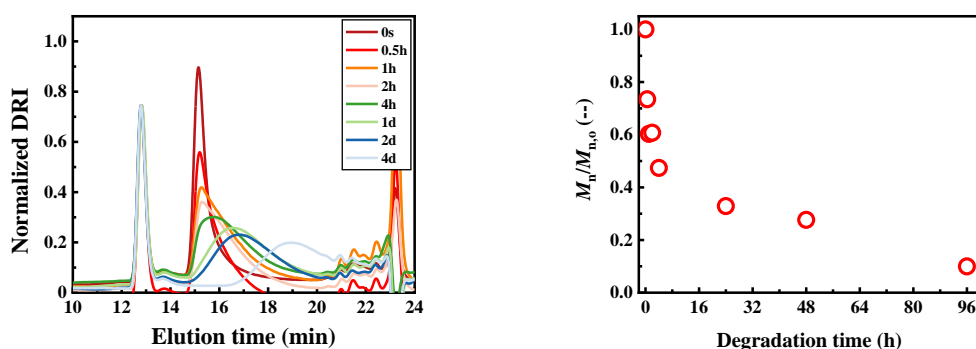


Figure S13. GPC traces and M_n changing trend for degradation of P-ODAN as a 10 mg/mL solution in dilute HCl/THF solution (0.002 M) at 25 °C *without* Na_2CO_3 neutralization (lower acid and water concentration than General Procedure A).

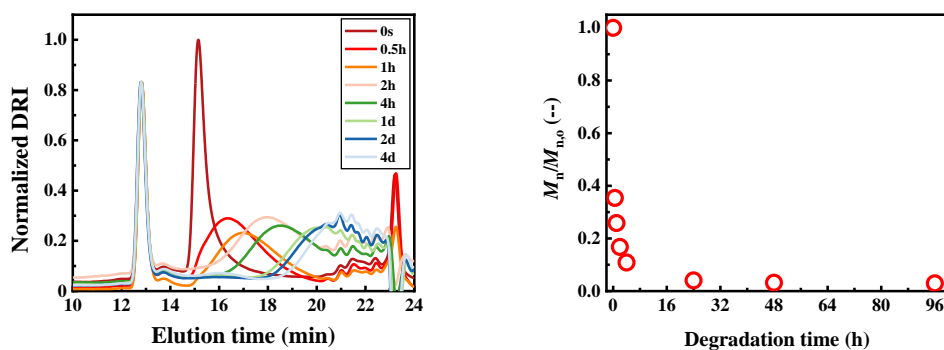


Figure S14. GPC traces and M_n changing trend for degradation of P-ODAN as a 10 mg/mL solution in dilute HCl/THF solution (0.002 M) at 25 °C *with* Na_2CO_3 neutralization (lower acid and water concentration than General Procedure A).

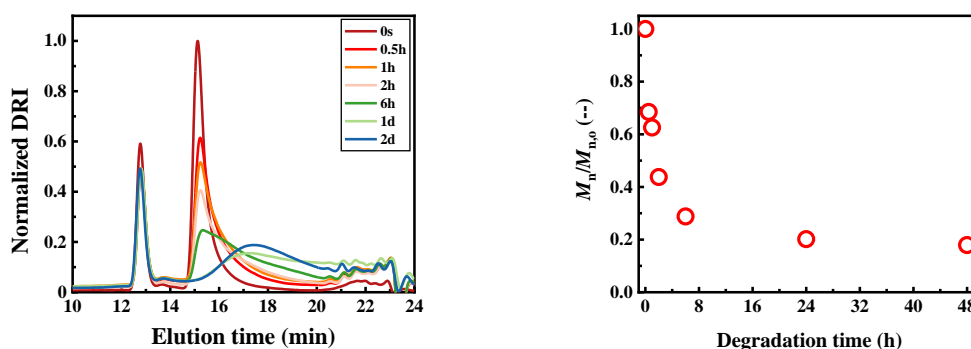


Figure S15. GPC traces and M_n changing trend for degradation of P-ODAN as a 10 mg/mL solution in dilute HCl/THF solution (0.002 M) with additional 36 μL of H_2O at 25 $^\circ\text{C}$ *without* Na_2CO_3 neutralization (lower acid concentration than General Procedure A).

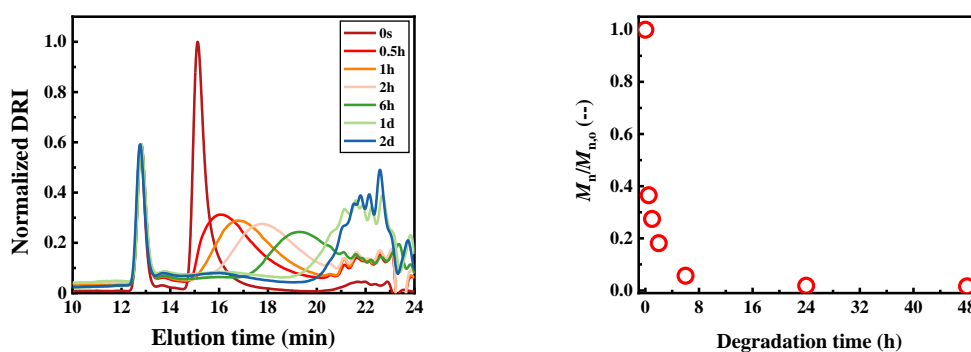


Figure S16. GPC traces and M_n changing trend for degradation of P-ODAN as a 10 mg/mL solution in dilute HCl/THF solution (0.002 M) with additional 36 μL of H_2O at 25 $^\circ\text{C}$ *with* Na_2CO_3 neutralization (lower acid concentration than General Procedure A).

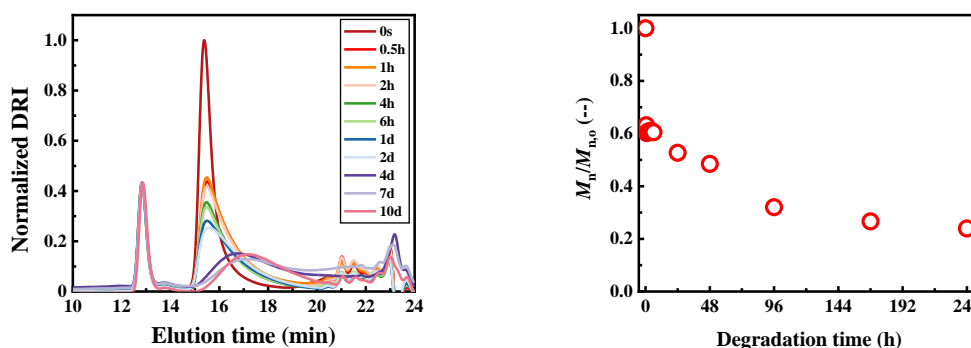


Figure S17. GPC traces and M_n changing trend for degradation of P-ODAN as a 10 mg/mL solution in dilute HCl/THF solution (0.02 M) at 4 $^\circ\text{C}$ *without* Na_2CO_3 neutralization (lower temperature than General Procedure A).

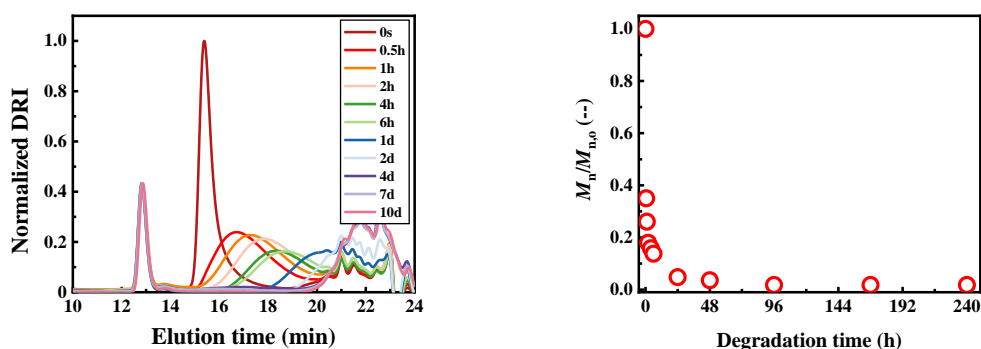


Figure S18. GPC traces and M_n changing trend for degradation of P-ODAN as a 10 mg/mL solution in dilute HCl/THF solution (0.02 M) after quenching with Na_2CO_3 salts at 4 °C *with* Na_2CO_3 neutralization (lower temperature than General Procedure A).

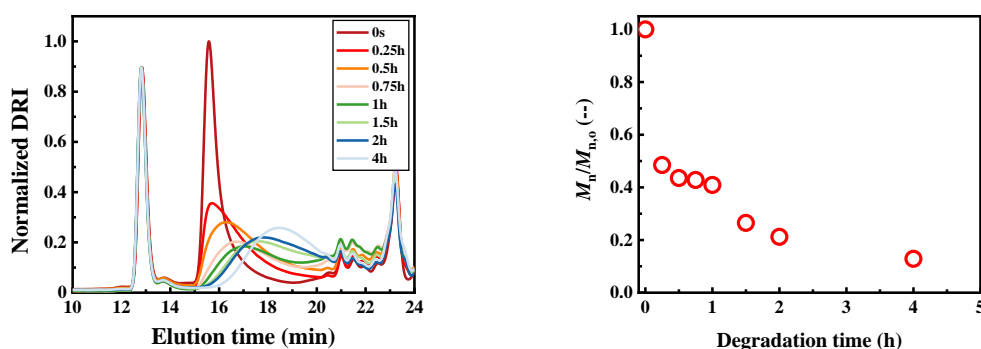


Figure S19. GPC traces and M_n changing trend for degradation of P-ODAN as a 10 mg/mL solution in dilute HCl/THF solution (0.02 M) at 40 °C *without* Na_2CO_3 neutralization (higher temperature than General Procedure A).

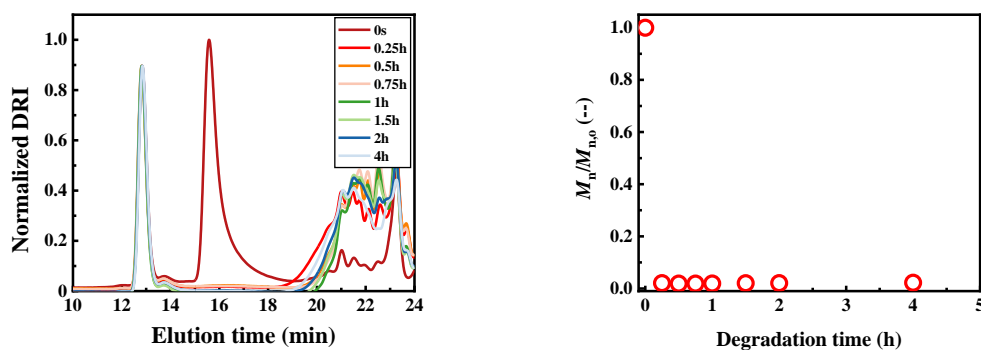


Figure S20. GPC traces and M_n changing trend for degradation of P-ODAN as a 10 mg/mL solution in dilute HCl/THF solution (0.02 M) after quenching with Na_2CO_3 salts at 40 °C *without* Na_2CO_3 neutralization (higher temperature than General Procedure A).

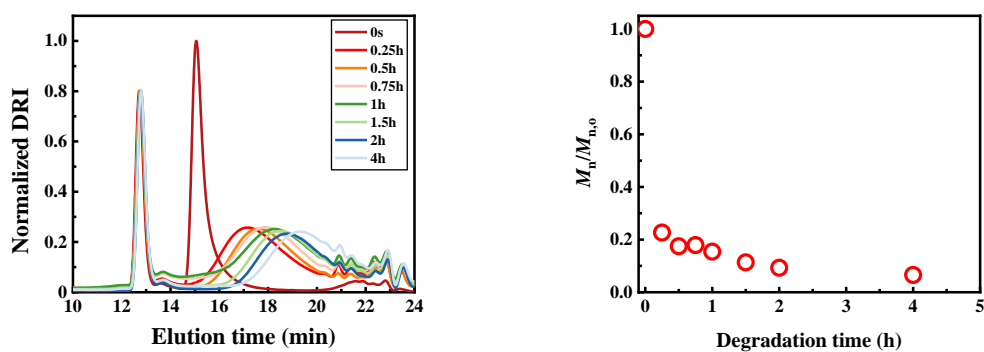


Figure S21. GPC traces and M_n changing trend for degradation of P-ODAN as a 10 mg/mL solution in dilute HCl/THF solution (0.02 M) at 60 °C *without* Na_2CO_3 neutralization (higher temperature than General Procedure A).

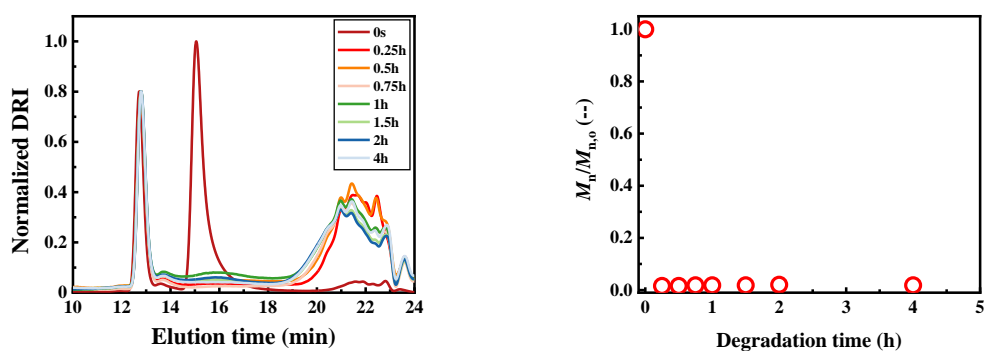


Figure S22. GPC traces and M_n changing trend for degradation of P-ODAN as a 10 mg/mL solution in dilute HCl/THF solution (0.02 M) at 60 °C *with* Na_2CO_3 neutralization (higher temperature than General Procedure A).

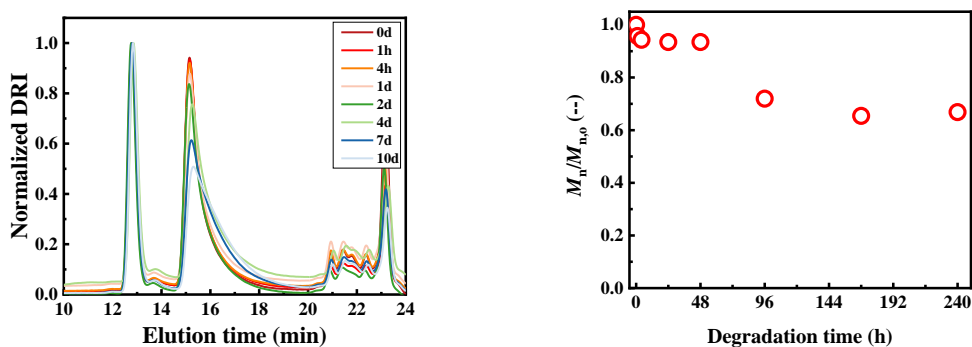


Figure S23. GPC traces and M_n changing trend for degradation of P-ODAN as a 10 mg/mL solution in CHCl_3 at 25 °C (General Procedure D).

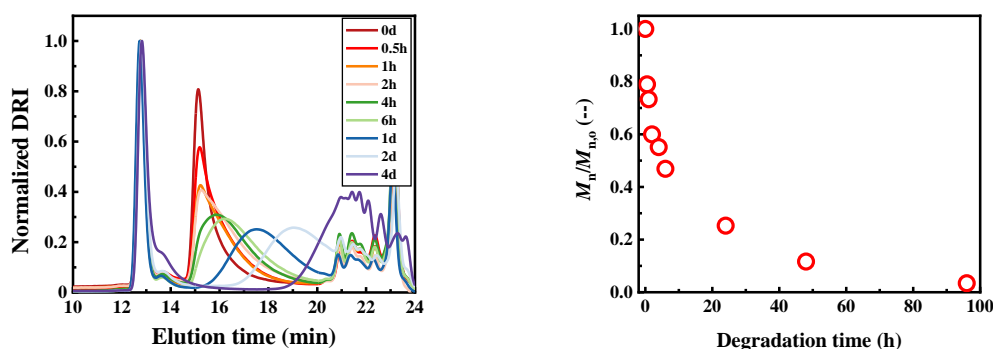


Figure S24. GPC traces and M_n changing trend for degradation of P-ODAN as a 10 mg/mL solution in CHCl_3 at 60 °C (General Procedure D).

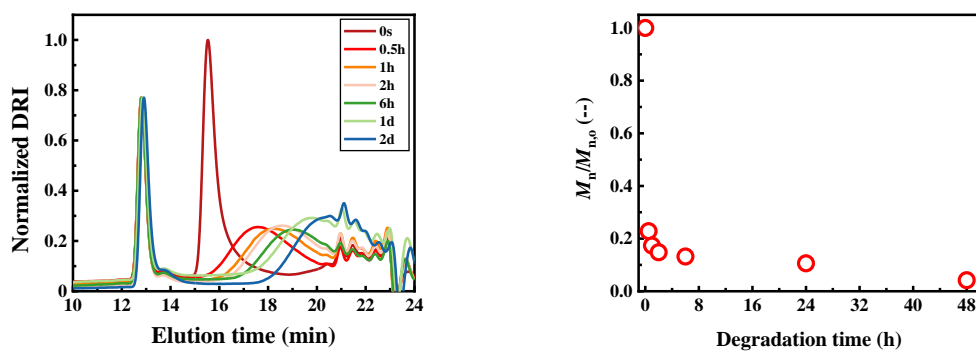


Figure S25. GPC traces and M_n changing trend for degradation of P-ODAN as a 10 mg/mL solution in dilute TFA/ CHCl_3 solution (0.02 M) at 25 °C *without* Na_2CO_3 neutralization (General Procedure B).

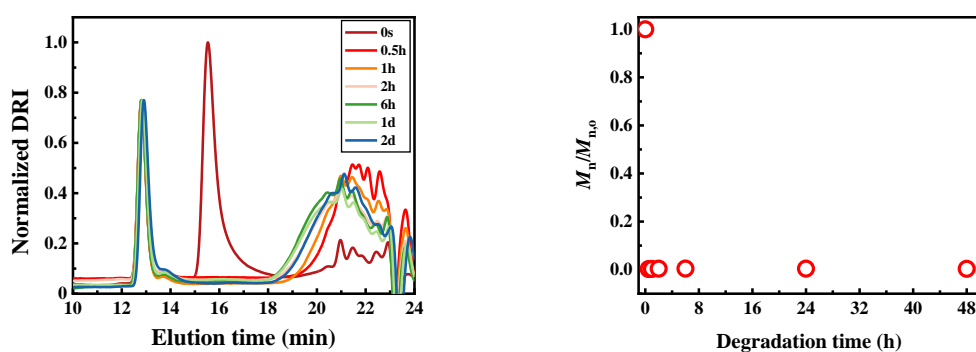


Figure S26. GPC traces and M_n changing trend for degradation of P-ODAN as a 10 mg/mL solution in dilute TFA/ CHCl_3 solution (0.02 M) at 25 °C *with* Na_2CO_3 neutralization (General Procedure B).

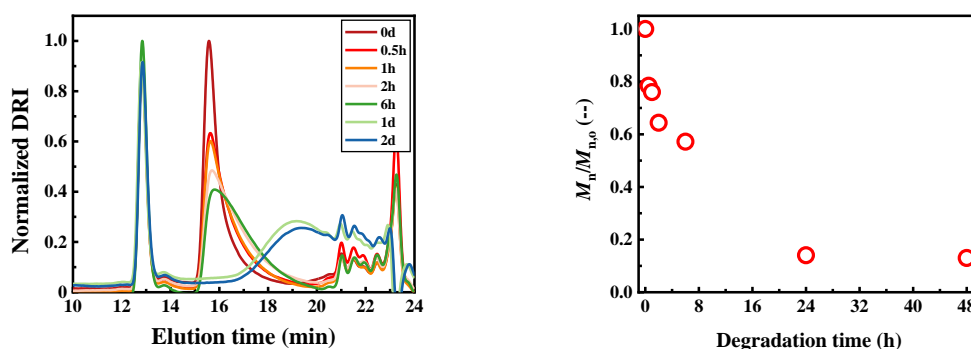


Figure S27. GPC traces and M_n changing trend for degradation of P-ODAN as a 10 mg/mL solution in dilute TFA/MeOH/ CHCl_3 solution (0.02 M) and the addition of at 25 °C *without* Na_2CO_3 neutralization (General Procedure B).

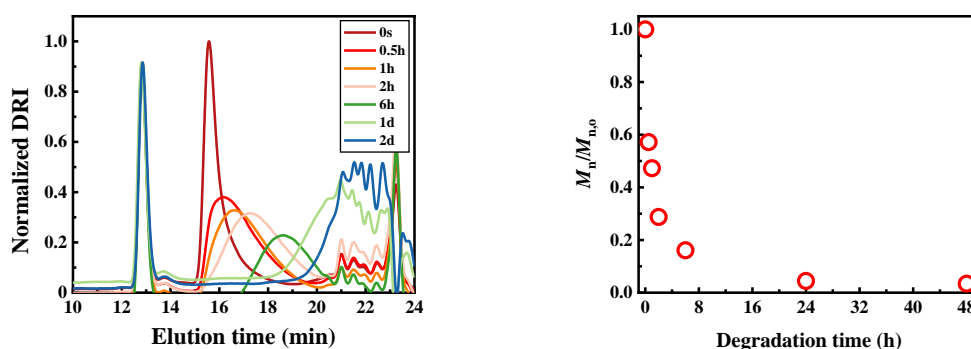


Figure S28. GPC traces and M_n changing trend for degradation of P-ODAN as a 10 mg/mL solution in dilute TFA/MeOH/ CHCl_3 solution (0.02 M) and the addition of at 25 °C *with* Na_2CO_3 neutralization (General Procedure B).

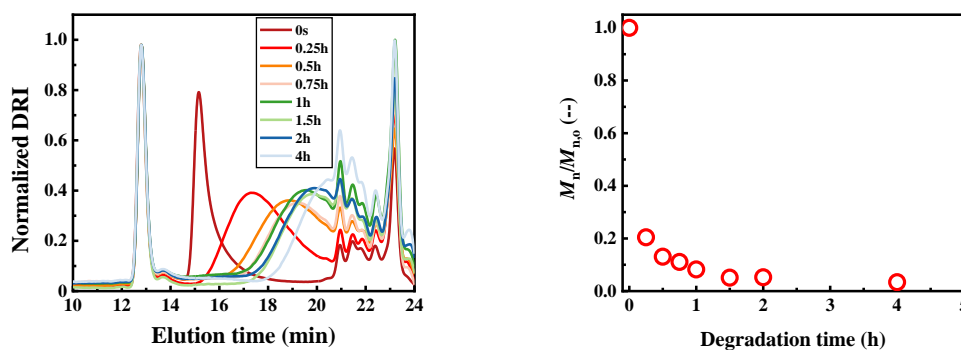


Figure S29. GPC traces and M_n changing trend for degradation of P-ODAN as a 10 mg/mL solution in dilute TFA/MeOH/ CHCl_3 solution (0.02 M) and the addition of at 60 °C *without* Na_2CO_3 neutralization (higher temperature than General Procedure B).

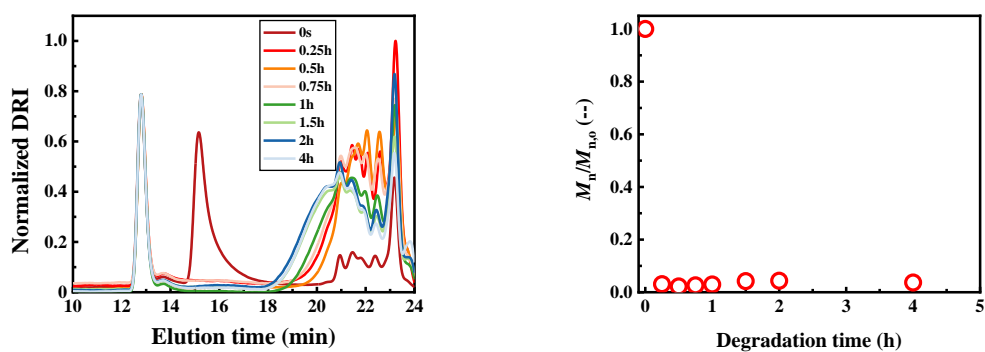


Figure S30. GPC traces and M_n changing trend for degradation of P-ODAN as a 10 mg/mL solution in dilute TFA/MeOH/ CHCl_3 solution (0.02 M) and the addition of at 60 °C *with* Na_2CO_3 neutralization (higher temperature than General Procedure B).

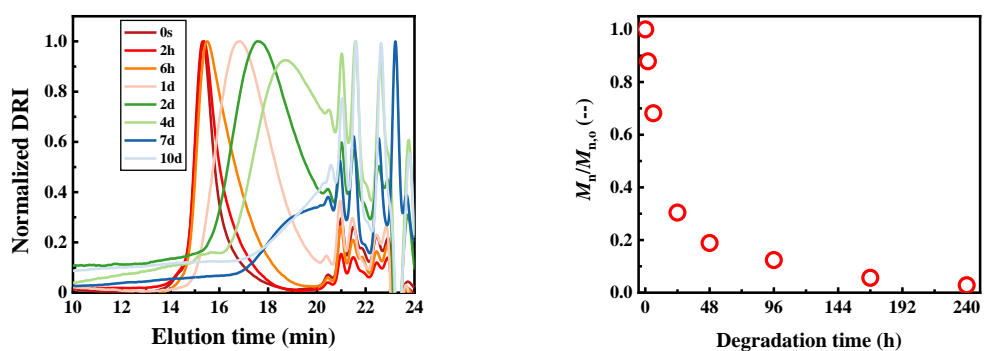


Figure S31. GPC traces and M_n changing trend for degradation of P-NEO-*s*-ODAN as a 10 mg/mL solution in H_2O solution after quenching at 25 °C *without* Na_2CO_3 neutralization (General Procedure C).

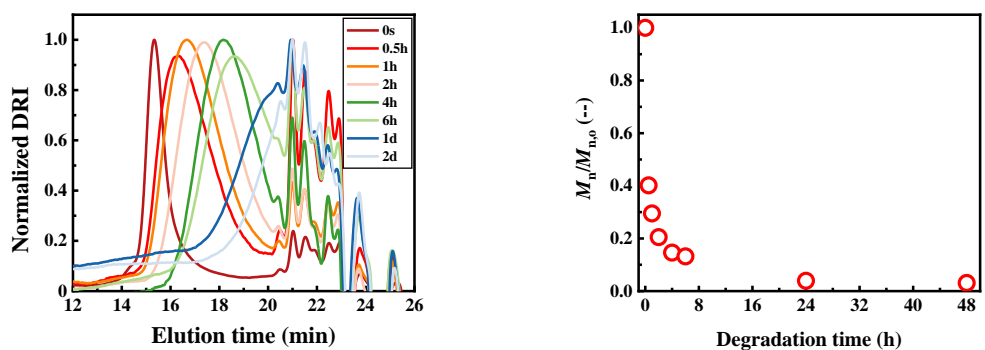


Figure S32. GPC traces and M_n changing trend for degradation of P-NEO-*s*-ODAN as a 10 mg/mL solution in dilute HCl/ H_2O solution (0.02 M) at 25 °C *with* Na_2CO_3 neutralization (General Procedure C).

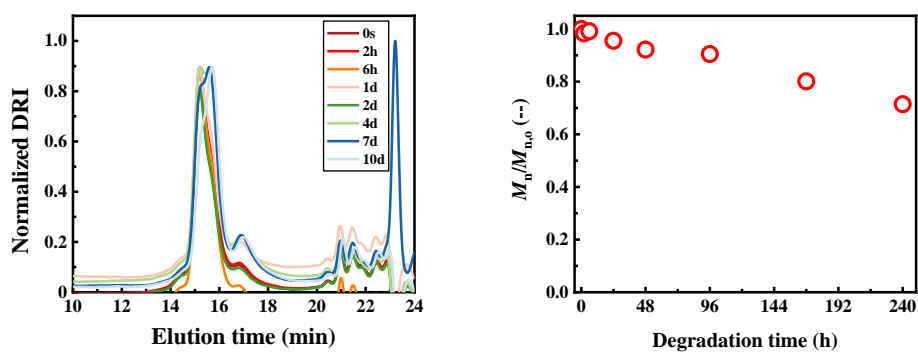


Figure S33. GPC traces and M_n changing trend for degradation of P-NEO-*b*-ODAN as a 10 mg/mL solution in H₂O solution after quenching at 25 °C *without* Na₂CO₃ neutralization (General Procedure C).

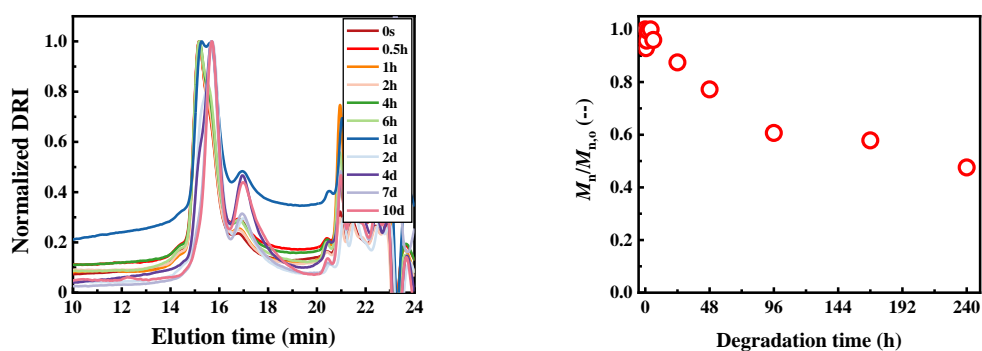


Figure S34. GPC traces and M_n changing trend for degradation of P-NEO-*b*-ODAN as a 10 mg/mL solution in dilute HCl/H₂O solution (0.02 M) at 25 °C *with* Na₂CO₃ neutralization (General Procedure C).

TEM and DLS Characterization

(A) TEM characterization of P-NEO-*b*-ODAN assembled in water

Add 500 μL ultra-pure water slowly into 100 μL P-NEO-*b*-ODAN solution (5 mM in DMF). After mixing the solution by vortex fully, the sample was kept at room temperature for 30 minutes. The samples were transferred to a dialysis bag with a molecular weight of 10 kDa and the dialysis was performed against ultra-pure water (1 L) at room temperature for 24 hours. The dialysate was changed every 8 hours. After the dialysis, the sample was diluted 10 times with ultra-pure water. Then 5 μL diluted sample were dropped on the treated hydrophilic copper grid (200 meshes). The sample was applied to a carbon grid by adding 5 μL sample solution to the grid and carefully removed by using a filter paper after 5 min immersion. Then, the grid was washed with 5 μL water and uranyl acetate (0.7 wt%) twice alternately. After carefully removing the residue of uranyl acetate, the grid was allowed to dry for at least 5 min again. Then the copper grid was observed by transmission electron microscopy (HT-7700, Japan) with an accelerated voltage of 100 kV.

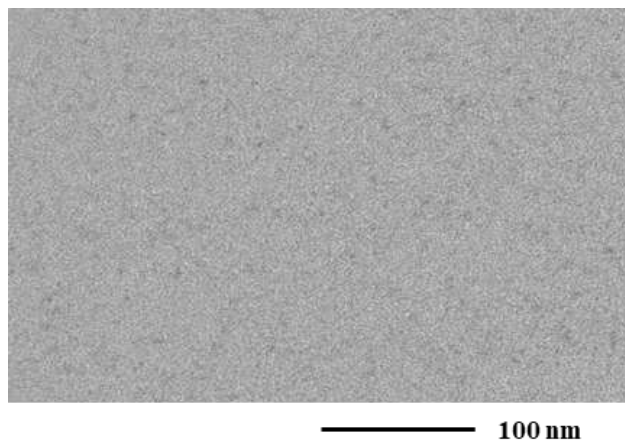


Figure S35. TEM image of the degradation of P-NEO-*b*-ODAN in water.

(B) DLS characterization of P-NEO-*b*-ODAN assembled in water

After the dialysis as discussed above, the samples are diluted 10 times with ultra-pure water at room temperature for DLS (BeNano 90, China) test.

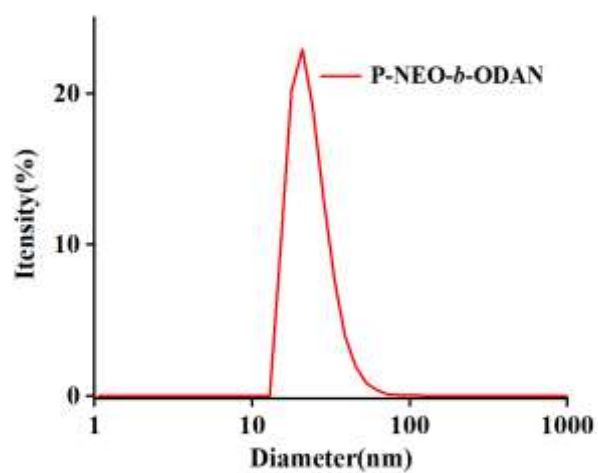


Figure S 36. DLS test result of P-NEO-*b*-ODAN assembled in water at room temperature.

References

1. W. Hou, X. Yin, Y. Chen, J. Du, Y. Chen and Y. Shi, *ACS Macro Lett.*, 2023, **12**, 794–800.
2. X. Wang, Y. Wen, Y. Wang, W. Li, X. Lu and W. You, *CCS Chemistry*, 2024, **6**, 2305–2317.