Supporting information for:

Fluorescent monitoring on the degradation evolution for aliphatic polyesters

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Experimental section

Chemicals and materials. Fluorescent 6-aminofluorescein (AF), 1-(3-dimethylaminopropyl)-3-ethyl carbodiimide hydrochloride (EDC), N-hydroxysuccinimide (NHS) were purchased from HWRK Chem Co. Ltd. (Beijing, China). Dimethyl sulfoxide (DMSO) was obtained from Beijing Chemical Reagent Company. Poly(butylene adipate-co-terephthalate) (PBAT) was supplied by Chinese Academy of Agricultural Sciences.

Preparation of fluorescent solutions. The AF was first dissolved in DMSO at a concentration of 10 mM. This AF stock solution was then diluted to 15.6 μM by EDC (1.0 mM), NHS (1.0 mM) and buffer solution (pH = 5).

Thermal and photothermal treatment of PBAT films. Thermal treatment of PBAT films was implemented under the temperature of 60 ºC in a JZ401A aging chamber, and the films were sampled every two hours. Photothermal treatment of PBAT films was carried out in a Q-Lab QUV UV/Spray accelerated weathering equipment under the simultaneously treatment of heating and UV irradiation. The temperature was set at 60 ºC, and the UV irradiation was set under conditions of 1.0 W/m^2 at 340 nm.

Furthermore, in order to make a comparison, a weathering treatment was carried out for PBAT films according to the ISO 4892-2:2006 standard: irradiation of 0.51 W/m^2 at 340 nm, relative humidity of 65%, temperature of 40 °C, and spray period of 18 min with water within a 120 min-irradiation cycle. This reference sample was treated for 14 days (336 h).

Fluorescent labeling and in situ monitoring. The acquired PBAT films were first rinsed by absolute ethyl alcohol to remove the impurities on the surface. To implement an in-situ monitoring, a piece of PBAT film (1.2 × 1.5 cm^2) was pasted on a glass slide, and a tiny hole was poked in the film as a tracking sign. The same location in one

sample was tracked based on the specific morphology under bright field. This film was then placed under the photothermal or thermal treatment for 2 h. Afterwards, the film was dipped into the as-prepared AF solution and sonicated for 15 min for a complete labelling process, followed by the washing of ethanol to remove the excess AF solution. After labelling process, the film was dried and observed on fluorescent confocal microscopy to capture the variations in the same place. This procedure was repeated until 8 h of treatment.

Two fluorescent channels were employed to capture the fluorescent variations for PBAT after treatment. To acquire the changes for the intrinsic fluorescence, laser of 405 nm was used, and the collection was set in the range 415−485 nm. Another laser of 488 nm was utilized to monitor the carboxyl groups in PBAT films, with the fluorescent emission in 510−550 nm.

Controlled labelling experiments. To verify the accuracy of the fluorescent labelling process, the effect of diffusion for AF molecules in the polymer matrix was studied. The PBAT films after photothermal treatment for 8 h were immersed in the AF solution in the presence and absence of NHS/EDC under ultrasonic treatment for 15 min and dried for fluorescence imaging. Afterwards, the PBAT films were then washed in ethanol by ultrasonic treatment (5 min) to remove the unlabeled AF molecules.

Titration process for the carboxyl groups. The potentiometric titration was performed for sodium polymethacrylate (PMAA) and PBAT leaching solution on a ZDJ-3A auto potentiometric titrator. PMAA solution were diluted from the mother liquor (30 wt%) to achieve the solutions with the theoretical concentration of carboxyl groups as 0.025, 0.050, 0.075, 0.100 and 0.125 M. These solutions were titrated by HCl (pre-titrated as 53.50 mM), and the endpoints of the titration were determined when the values of $\Delta E/\Delta V$ reached the maximum.

Furthermore, the titration was also carried out for PBAT films. Firstly, the PBAT films (5×5 cm^2) were soaked in KCl (10 mM) solution overnight to acquire leaching solutions. Afterwards, the leaching solution was titrated by KOH (10.11 mM), and the results were calculated quantitatively.

Sample characterizations. Leica TCS SP8 confocal laser scanning microscope was implemented to capture the fluorescent variations of PBAT films, and the quantitative data was obtained from Leica Application Suite X. Excitation and emission spectra of PBAT films were acquired on a F-7000 fluorescence spectrometer (Hitachi), and emission spectrum of AF was collected in the range 500−650 nm under the excitation of 490 nm. Fourier transform infrared spectra (FT-IR) of PBAT films were recorded on a Nicolet 6700 (Thermo Electron) in range of 400–4000 cm^{-1}. X-ray photoelectron spectroscopy (XPS) was carried out on ESCALAB 250 (Thermo Fisher Scientific, USA) using an monochromated Al Kalph 150W source.

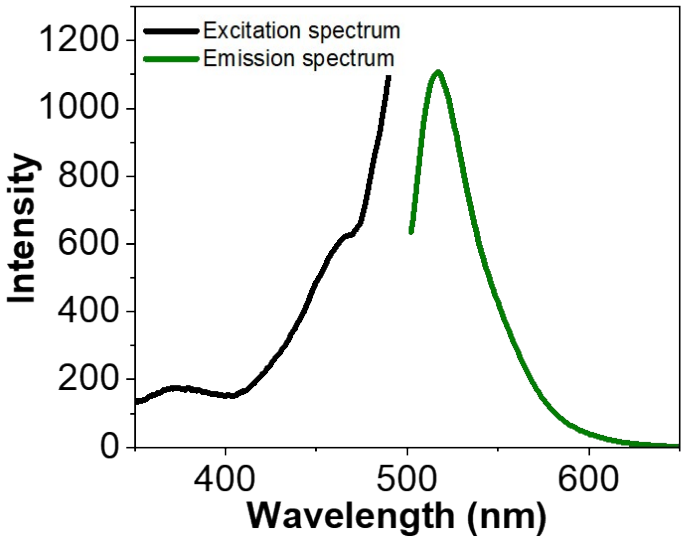
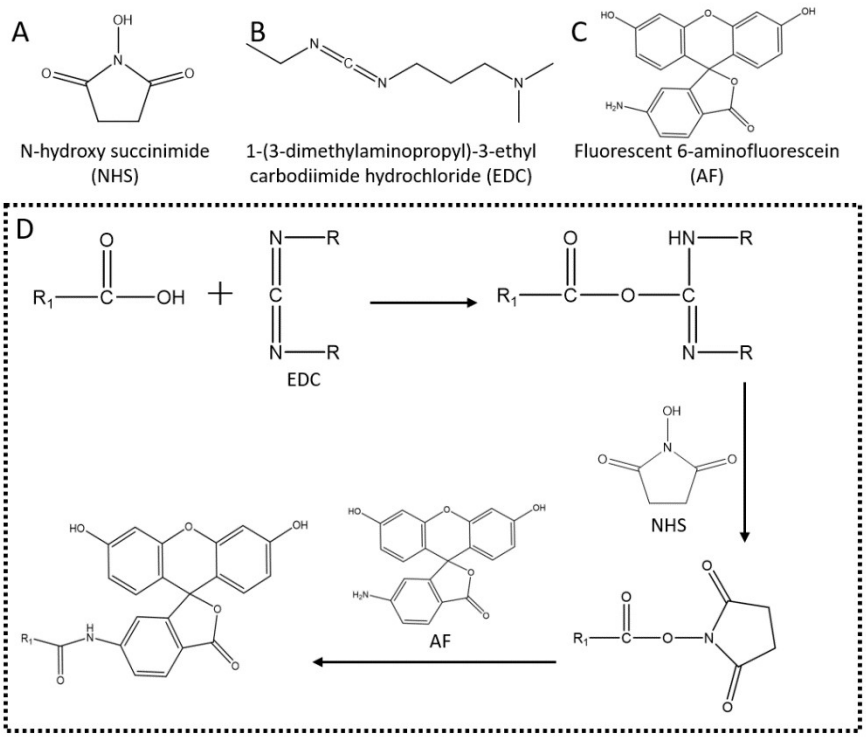


Fig. S1 Fluorescent excitation and emission spectra of AF molecules.



Scheme S1. Chemical structures of (A) N-hydroxysuccinimide (NHS), (B) 1-(3-dimethylaminopropyl)-3-ethyl carbodiimide hydrochloride (EDC), and (C) fluorescent 6-aminofluorescein (AF); (D) Reaction schematic of AF to target carboxyl groups.

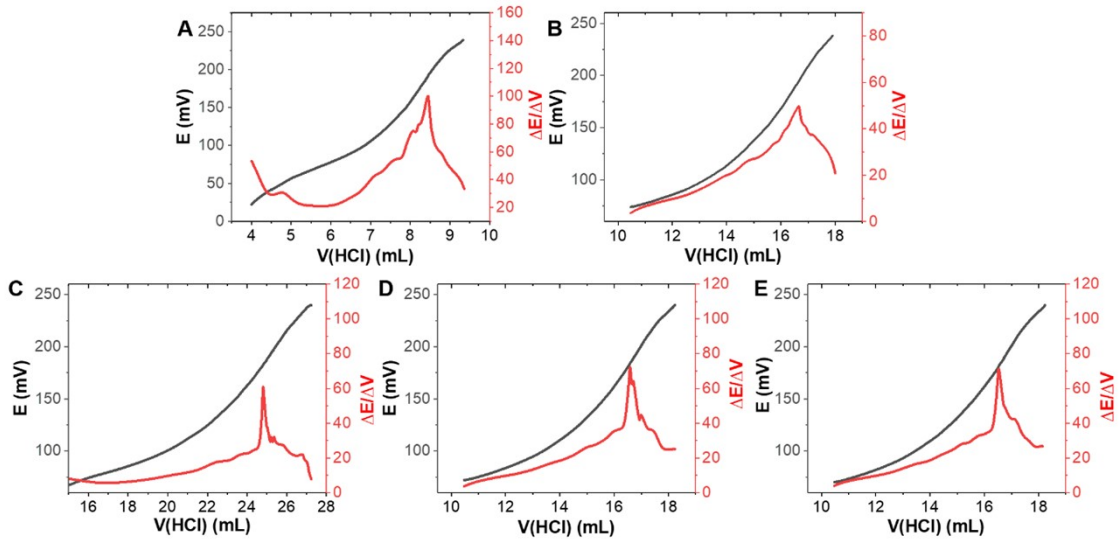


Fig. S2 Titration curves for sodium polymethacrylate solutions with the theoretical concentrations of carboxyl groups of (A) 0.025 M, (B) 0.050 M, (C) 0.075 M, (D) 0.100 M (diluted for 2 folds) and (E) 0.125 M (diluted for 2.5 folds).

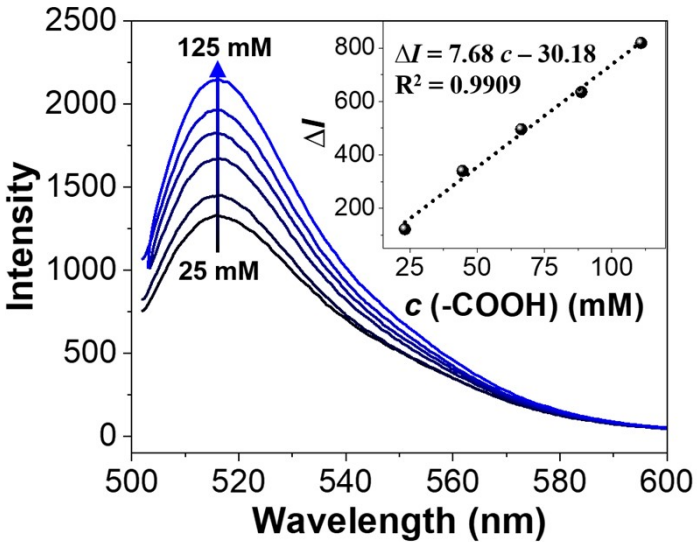


Fig. S3 Fluorescent intensity variations of AF (15.6 μM) in the presence of different concentrations of carboxyl groups in polymethylacrylic acid (PMAA) and the linear fitting equation (λ_{ex} = 490 nm).

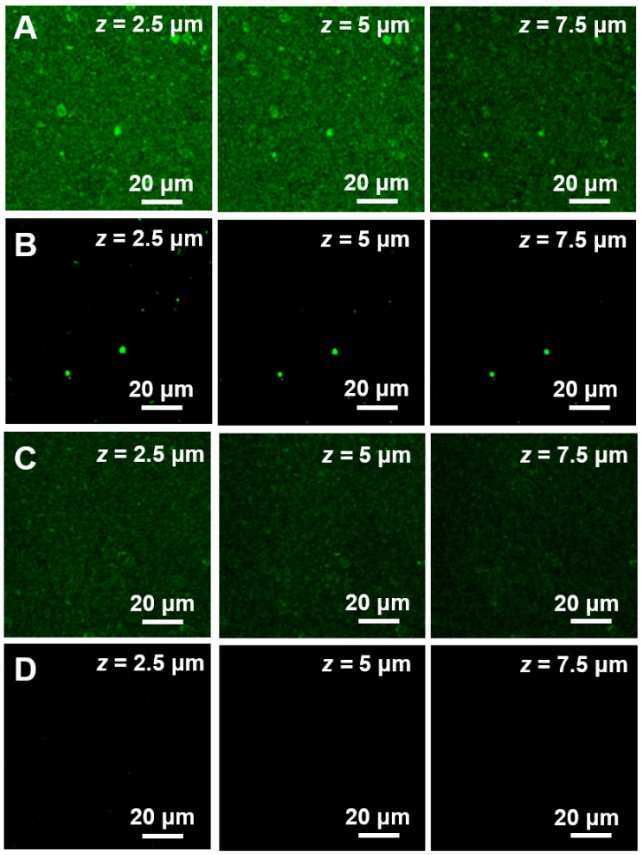


Fig. S4 Two-dimensional fluorescent images captured at different depths of PBAT films after photothermal treatment for 8 h: (A) degraded PBAT films immersed in AF solution with NHS and EDC, (B) degraded PBAT films immersed in AF solution with NHS and EDC, followed by washing; (C) degraded PBAT films immersed in AF solution without NHS and EDC, (D) degraded PBAT films immersed in AF solution without NHS and EDC, followed by washing.

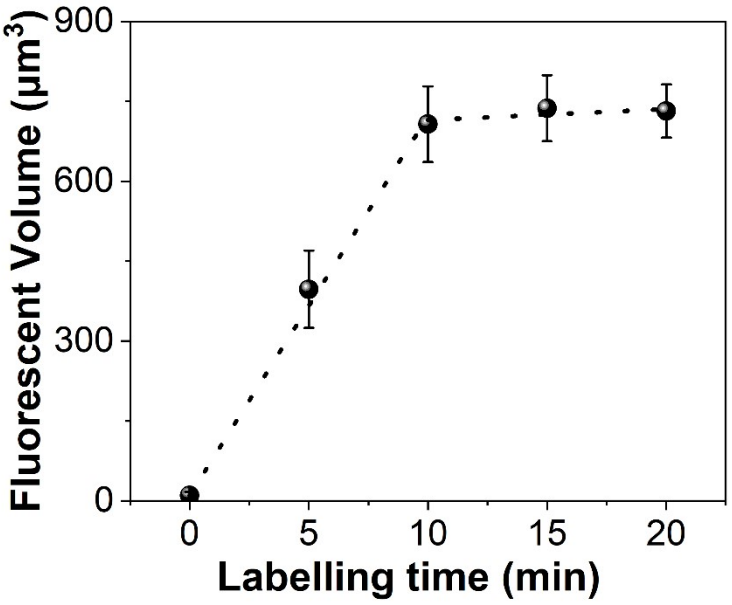


Fig. S5 Fluorescent volume variations of AF-labelled PBAT films (200 × 200 μm^2) for different labelling time for PBAT film after thermal treatment for 8 h.

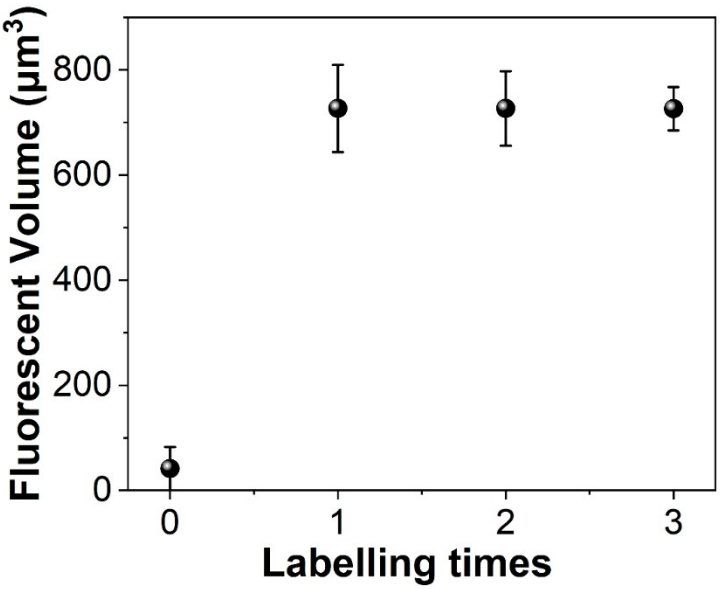


Fig. S6 Fluorescent volume variations of PBAT films (thermally treated for 8 h) after repeat labelling by AF solution for once, twice and three times.

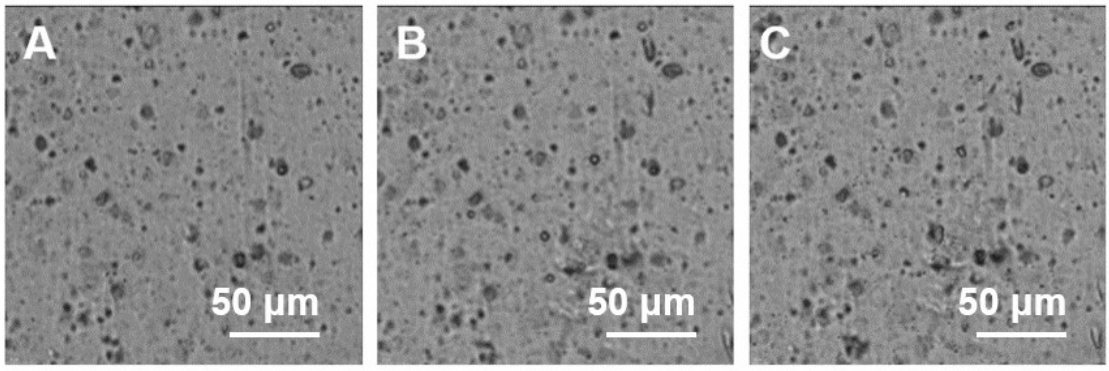


Fig. S7 Bright-field images (200 × 200 μm^2) of PBAT films after thermal treatment for 8 h and repeat fluorescent labelling process for (A) once, (B) twice, and (C) three times.

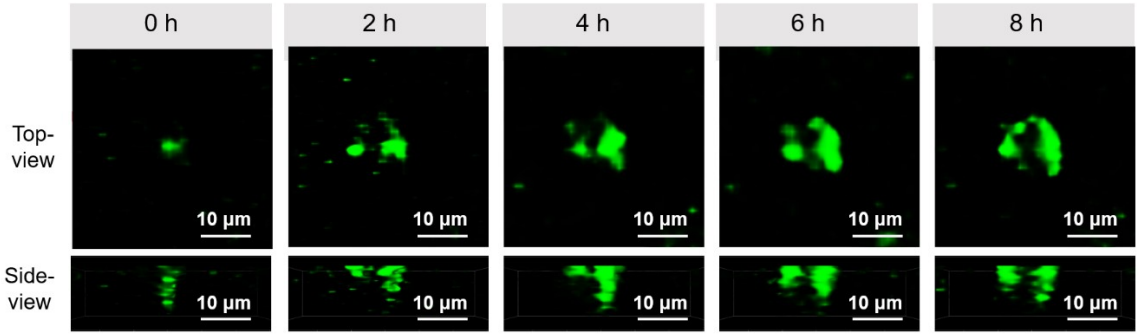


Fig. S8 Top-view (40 × 40 μm^2) and side-view (40 × 10 μm^2) fluorescent images of PBAT films after thermal treatment under 60 ºC for AF-labelled carbonyl groups (excitation of 488 nm and emission in the range 510 − 550 nm).

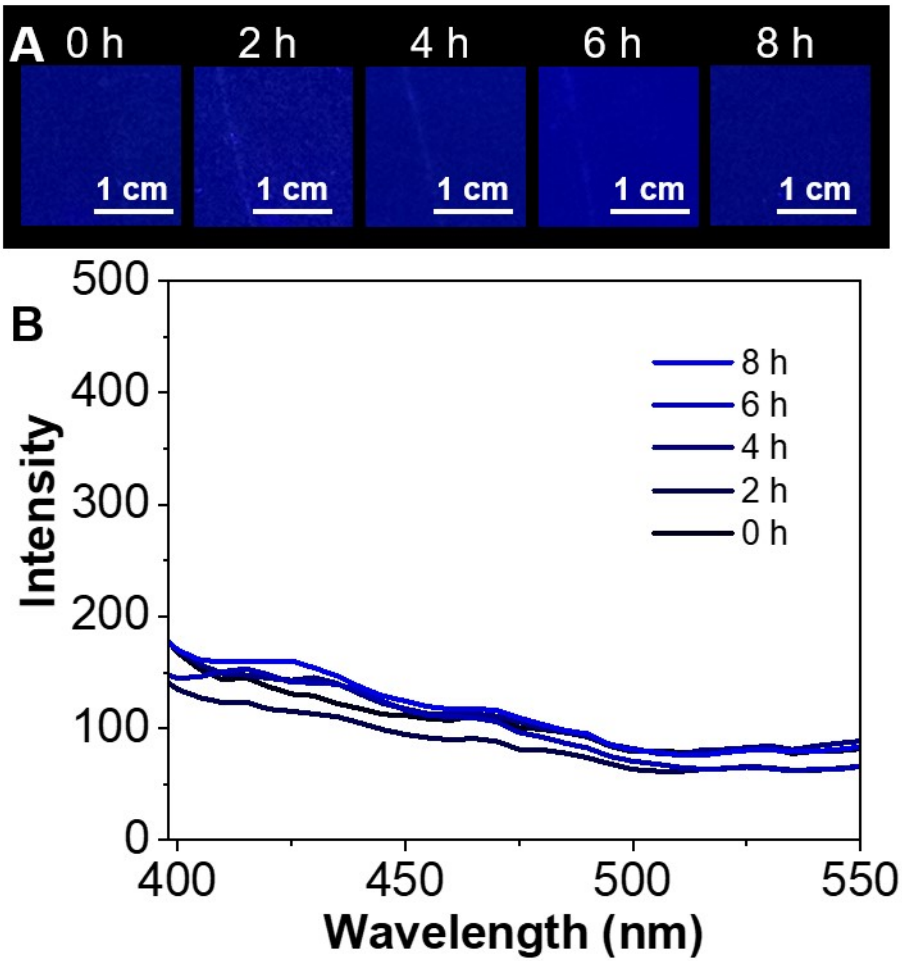


Fig. S9 (A) Digital photos (2 × 2 cm^2) and (B) fluorescent emission spectra of PBAT films after thermal treatment under 60 ºC for 0 h − 8 h.

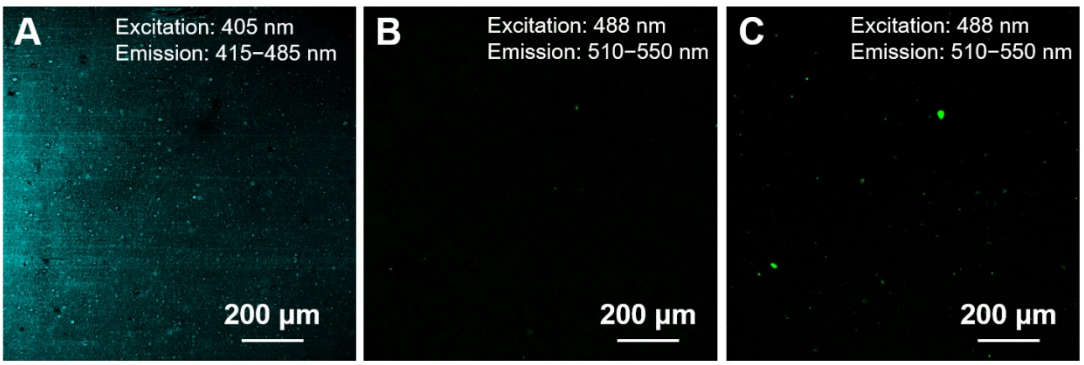


Fig. S10 Fluorescent images (1150 ×1150 μm^2) of PBAT films after photothermal treatment for 8 h: (A) excitation of 405 nm and emission in the range 415 − 485 nm, (B) excitation of 488 nm and emission in the range 510 − 550 nm before AF labelling, and (C) excitation of 488 nm and emission in the range 510 − 550 nm after labelling of AF molecules.

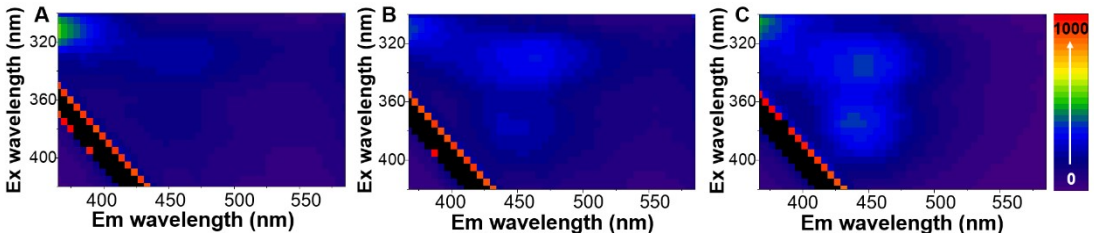


Fig. S11 3D excitation-emission fluorescent spectra of PBAT films after photothermal treatment for (A) 2 h, (B) 4 h, and (C) 6 h.

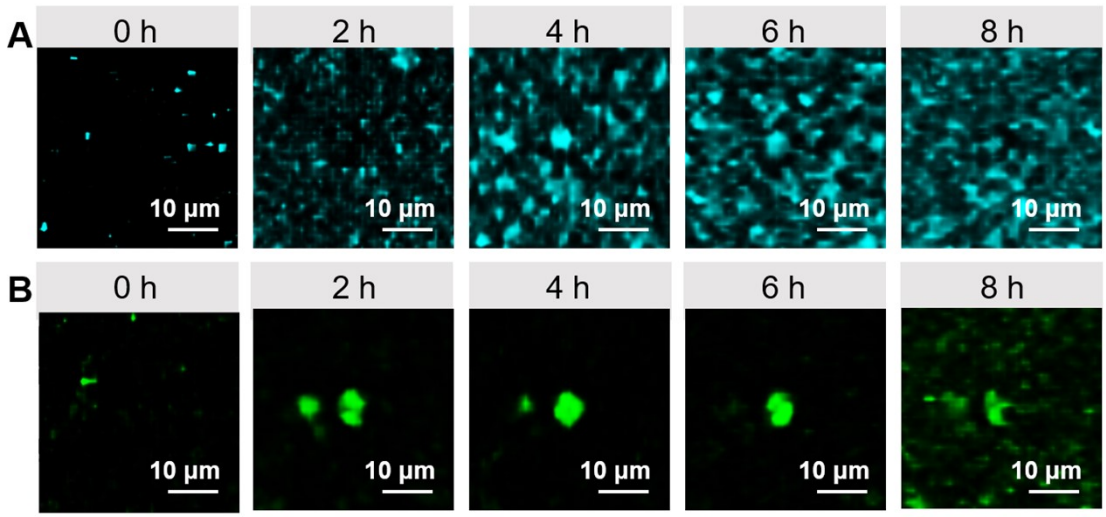


Fig. S12 Fluorescent images (40 × 40 μm^2) of PBAT films after photothermal treatment under 60 ºC for (A) intrinsic emission (excitation of 405 nm and emission in the range 415 − 485 nm) and (B) AF-labelled carbonyl groups (excitation of 488 nm and emission in the range 510 − 550 nm).

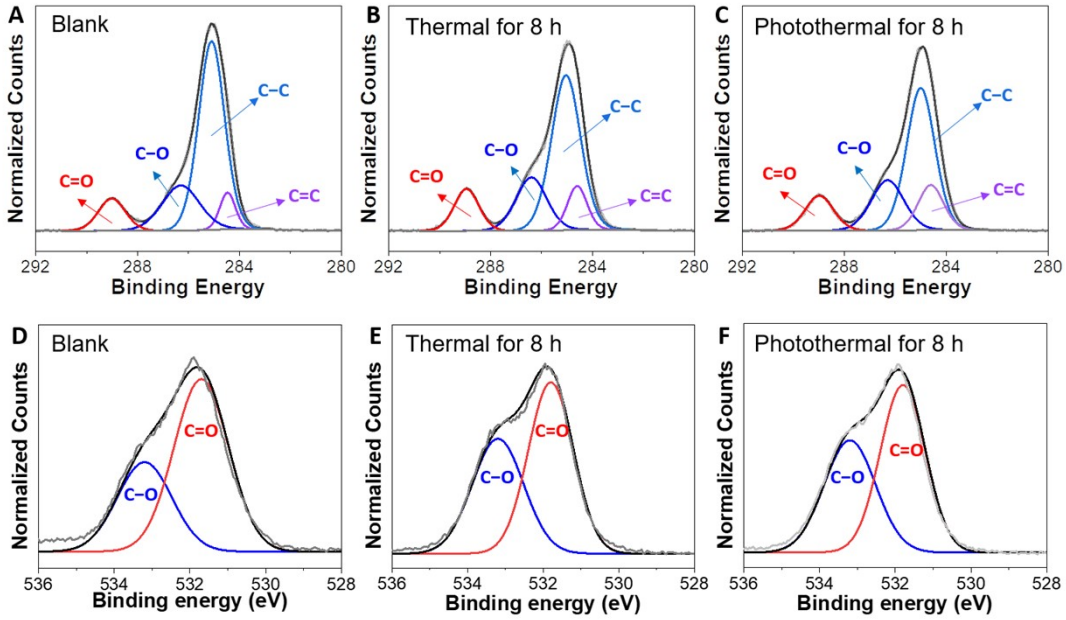


Fig. S13 XPS spectra of (A–C) C 1s and (D–F) O 1s for (A and D) blank PBAT films, (B and E) PBAT films after thermal treatment for 8 h and (C and F) PBAT films after photothermal treatment for 8 h, respectively.

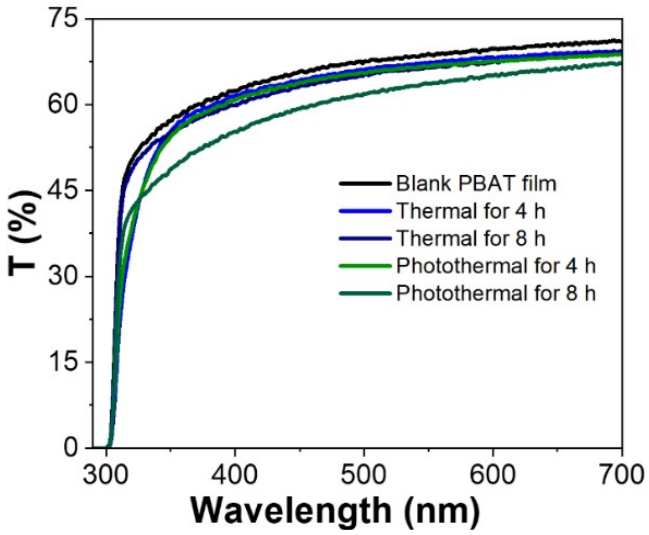


Fig. S14 UV-Vis spectra of PBAT films before and after thermal/photothermal treatment.

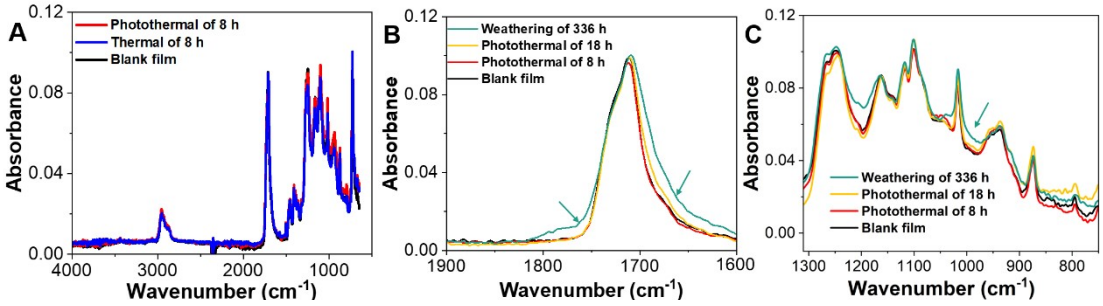
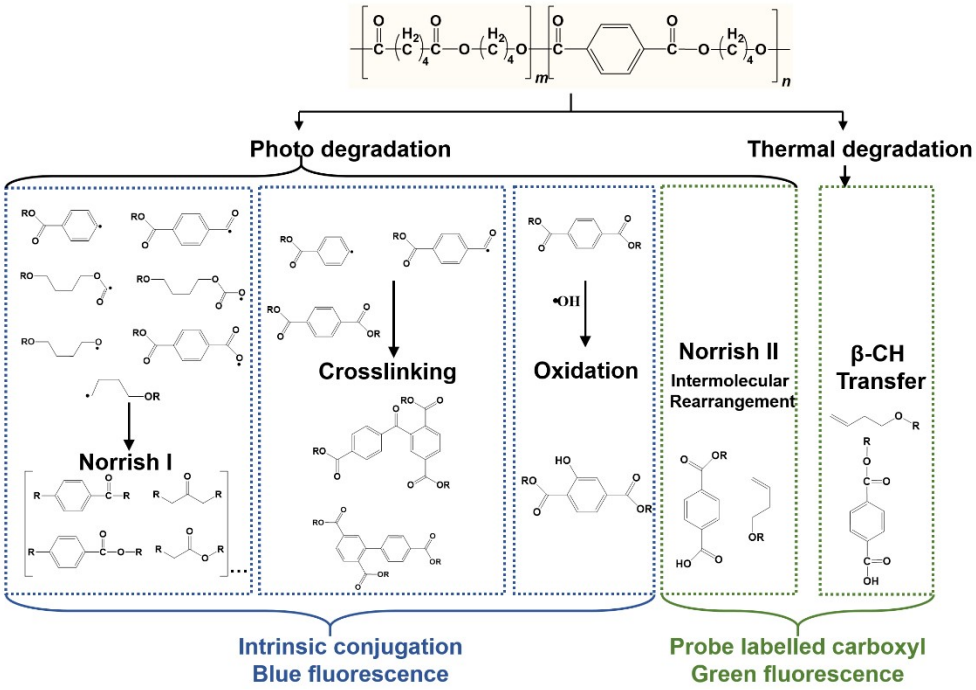


Fig. S15 FT-IR absorbance spectra of PBAT films for (A) photothermal or thermal treatments for 8 h, and enlarged spectra after photothermal for 8 h, 18 h and weathering for 336 h in the range of (B) 1600–1900 cm^{-1} and (C) 750–1350 cm^{-1}.



Scheme S2. The degradation reactions of PBAT occurred under thermal and photo treatment.

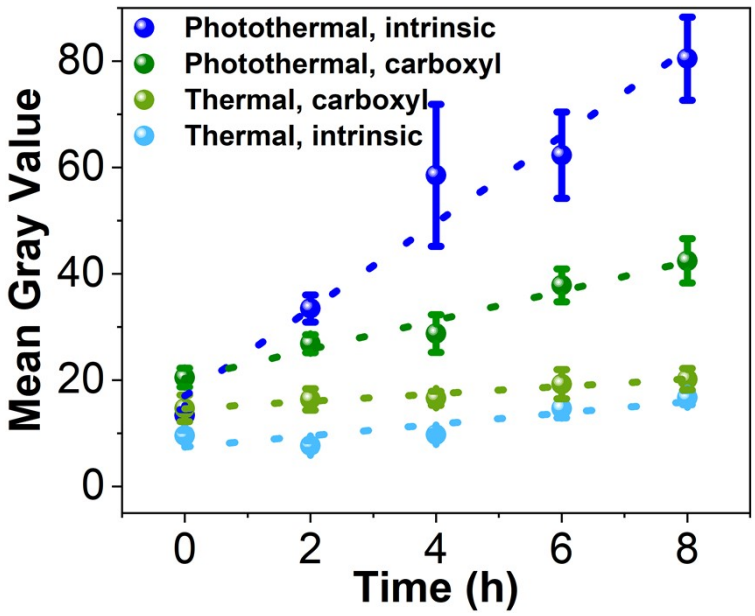


Fig. S16 Quantitative calculation of the mean value for the fluorescence in the PBAT films in a section of 200 × 200 μm^2 after thermal and photothermal treatment, respectively; blue dots represented the intrinsic emission exited by 405 nm and green ones stood for the probe-labelled fluorescence exited by 488 nm.

Table S1. Titration results for the concentration of carboxyl groups in PMAA.

Theoretical values/M	Titration results/M
0.025	0.02311
0.050	0.04454
0.075	0.06637
0.100	0.08870
0.125	0.1109

Table S2. Depth variations of PBAT films after thermal treatment for different time.

Time/h	Depth/μm
0	0
2	4.9
4	6.2
6	7.6
8	8.3

Table S3. Titration results in the leaching solutions for the different PBAT films.

PBAT samples	Consumption of KOH /mL	Titration results/mM
Pristine	＜0.11	/
Photothermal 8 h	＜0.11	/
Photothermal 18 h	0.16	0.08
Weathering 336 h	0.51	0.26

Table S4. XPS peak analysis of C 1*s* in blank PBAT films and PBAT films after thermal/photothermal treatment for 8 h.

Sample	Area ratio of C=C	Area ratio of C–C	Area ratio of C–O	Area ratio of C=O
Blank film	0.07	0.61	0.21	0.11
Thermal 8 h	0.11	0.57	0.20	0.12
Photothermal 8 h	0.14	0.53	0.20	0.13

Table S5. Comparisons on the grey value (y) variations as a function of time (x) for PBAT films under thermal and photothermal treatments in a section of 40 × 40 μm^2.

Treatment	Fluorescence origin	Fitting slope k	Expressions
Photothermal	Intrinsic	8.04	$y = 8.04\,x + 17.56$
Photothermal	Carboxyl	2.77	$y = 2.77\,x + 21.57$
Thermal	Intrinsic	1.13	$y = 1.13\,x + 7.65$
Thermal	Carboxyl	0.71	$y = 0.72\,x + 15.11$

Table S6. Comparisons on the grey value (y) variations as a function of time (x) for PBAT films under thermal and photothermal treatments in a section of 200 × 200 μm^2.

Treatment	Fluorescence origin	Fitting slope k	Expressions
Photothermal	Intrinsic	8.15	$y = 8.15\,x + 17.03$
Photothermal	Carboxyl	2.75	$y = 2.75\,x + 20.29$
Thermal	Intrinsic	1.06	$y = 1.06\,x + 7.42$
Thermal	Carboxyl	0.69	$y = 0.69\,x + 14.63$