

Supporting Information

Linear Phenolic Polymers with Amide Stabilized Catechol Moieties

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Experimental Section

Materials

1,6-Hexanedithiol (Aladdin), 3,4-Dihydroxybenzaldehyde (Aladdin), N-Acetylacetanilide (Macklin), N,N-Dimethylacetylacetamide (Macklin), N-Methylacetylacetamide (70% v/v water solution%, Macklin), Boron Trifluoride Dihydrate ($\text{BF}_3 \cdot 2\text{H}_2\text{O}$, Aladdin), Boron Trifluoride Etherate ($\text{BF}_3 \cdot \text{Ether}$, Aladdin), Trifluoroacetic Acid (TFA, Aladdin), Zirconium Tetrachloride (ZrCl_4 , Aladdin), 2,2-Diphenyl-1-picrylhydrazyl (DPPH, 96%, Macklin), and all solvents were purchased from Aladdin and used as received.

Characterization Methods

The NMR spectra of monomers and polymers were recorded using an Agilent DD2 600 MHz NMR spectrometer. Samples were dissolved in 0.5 mL DMSO- d_6 , and each sample was scanned 8 times. The structures of monomers and polymers were analyzed using a Bruker Tensor 27 spectrometer in attenuated total reflection (ATR) mode. The spectra were measured in the range of 4000–400 cm^{-1} . Molecular weight and molecular weight distribution of the polymers were determined using an Agilent 1260 gel permeation chromatography system with DMF as the mobile phase, using a PLgel 5 mm mixed-C column and DMF (containing 5 mM NH_4BF_4) as the eluent. The flow rate was 1.0 mL/min. DSC were recorded on TA Instruments DSC 250 to determine the glass transition temperature (T_g) of the polymers. Samples were heated at a rate of 20°C/min to 100°C and held for 5 minutes, cooled at 20°C/min to -70°C and held for 5 minutes, then reheated to 100°C at 10°C/min. The third heating cycle was used for T_g analysis. Thermogravimetric analysis was conducted on a METTLER TGA 2 (SF) instrument under a nitrogen atmosphere. Samples of approximately 8 mg were heated from 25°C to 650°C at a rate of

10°C/min. Jena AG UVS600 UV-Vis spectrophotometer was used to evaluate the antioxidant properties of the polymer and to monitor the accelerated thermal oxidation experiments. The absorption spectra were measured over a range of 200-800 nm, with a specific absorbance wavelength at 515 nm.

Free Radical Scavenging Assay: Prepared A 8×10^{-4} M DPPH methanol solution and a 0.06 mg/mL polymer solution in THF for the free radical scavenging assay. 10 mL of DPPH solution was mixed with 10 mL of polymer solution, and the absorbance was immediately measured using a UV-Vis spectrophotometer at 515 nm, over a range of 200–800 nm. The antioxidant activity of the polymer was calculated using the following equation:

$$\text{Antioxidant activity(\%)} = \left[1 - \frac{A_0 - A_i}{A_0} \right] \times 100$$

where A_0 represents the UV absorbance peak of the DPPH radical solution at 515 nm, and A_i represents the UV absorbance peak of the sample at 515 nm.

Accelerated Thermal Oxidation Experiment: The polymer and its DMF solution (2 mg/mL) were placed in an oven at 80°C. Samples were taken at intervals of 0 h, 24 h, 48 h, 72 h, and 96 h. After removal, the polymer was dissolved in DMF at a concentration of 1 mg/mL for analysis.

Preparation of amide modified phenolic polymers

N-methylacetoacetamide (K1, 5.94 g, 36.10 mmol) and 3,4-dihydroxybenzaldehyde (A, 4.99 g, 36.10 mmol) were dissolved in 40 mL THF. Subsequently, 1,6-hexanedithiol (T, 10.85 g, 72.20 mmol) was added. A solution of boron trifluoride in THF (0.2 g/mL) was prepared, and 7.5 mL of this solution was added to the mixture. The reaction mixture was stirred at room temperature for 48 hours. Afterward, the organic phase was washed with deionized water to remove boron trifluoride. The product was then dissolved in THF and precipitated from diethyl ether for three

times, to obtain a yellowish product PAK₁T. PAK₃T was similarly prepared, while PAK₂T was precipitated from ethyl acetate. The product was dried in a vacuum oven and then by freeze-drying.

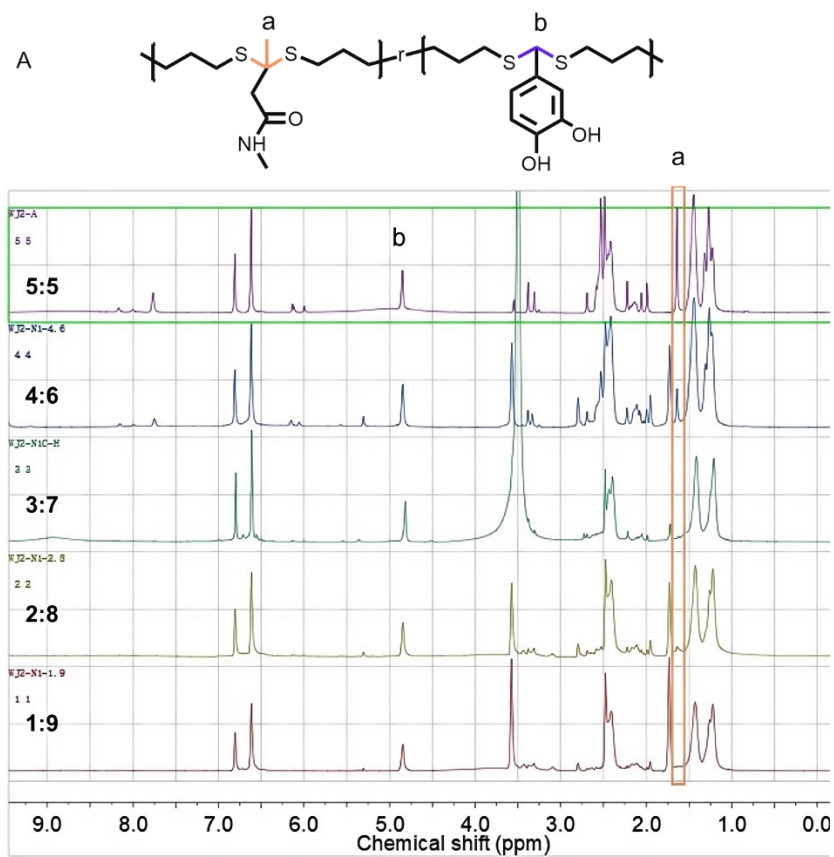


Fig. S1. ^1H NMR of copolymer crude of different A: K1: T ratios for calculating the monomer conversion of K1. The ratio on each spectrum is the charging ratio between K1 and A.

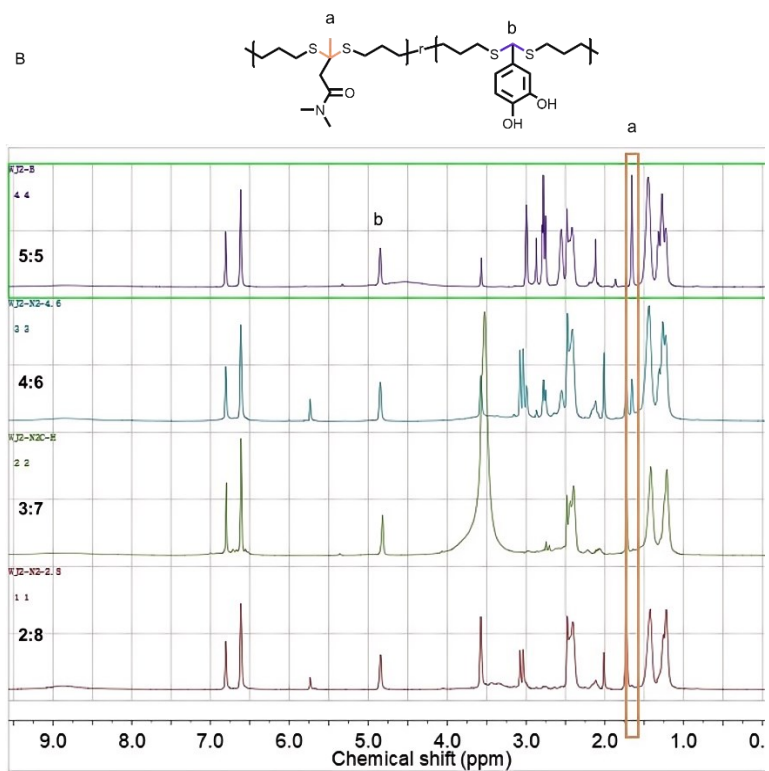


Fig. S2. ^1H NMR of copolymer crude of different A: K2: T ratios for calculating the conversion of monomer K2. The ratio on each spectrum is the charging ratio between K2 and A.

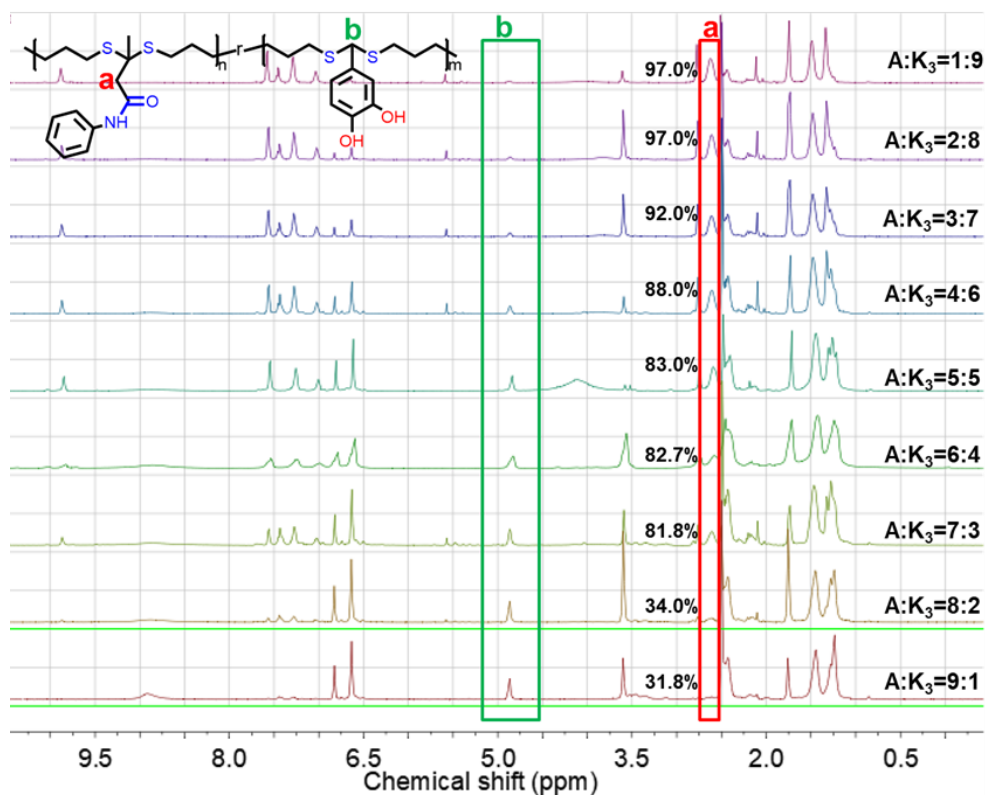


Fig. S3. ¹H NMR of copolymer crude of different A: K₃: T ratios for calculating the conversion of monomer K₃.

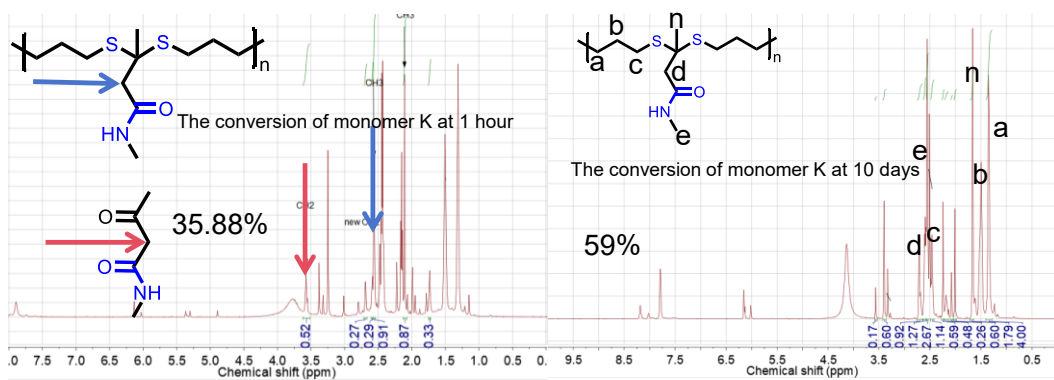


Fig. S4. ¹H NMR of two component copolymerization after 1h and 10 days between K1 and T.

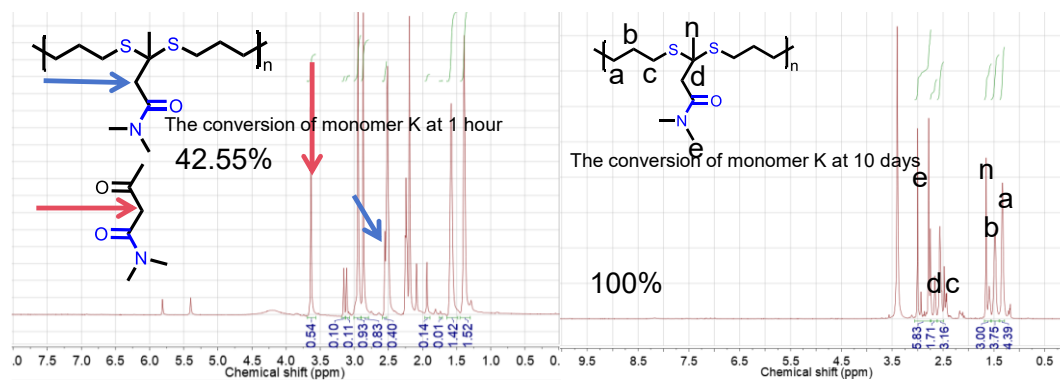


Fig. S5. ¹H NMR of two component copolymerization after 1h and 10 days between K2 and T.

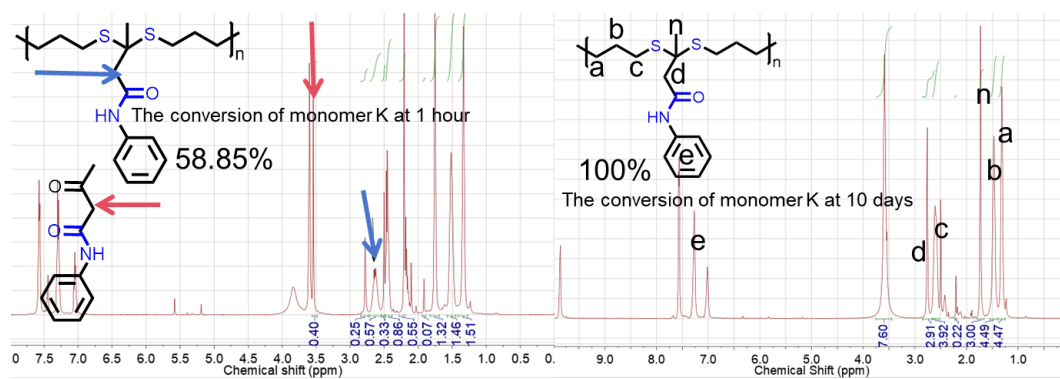


Fig. S6. ¹H NMR of two component copolymerization after 1h and 10 days between K3 and T.



Fig. S7. Photo of PAT prepared with ZrCl₄ right after the polymerization.

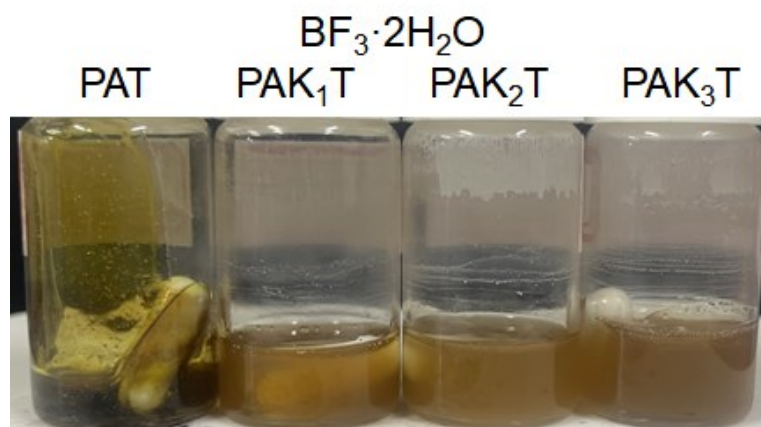


Fig. S8. Photo of PAT, PAK₁T, PAK₂T, PAK₃T solution right after finishing the polymerization.

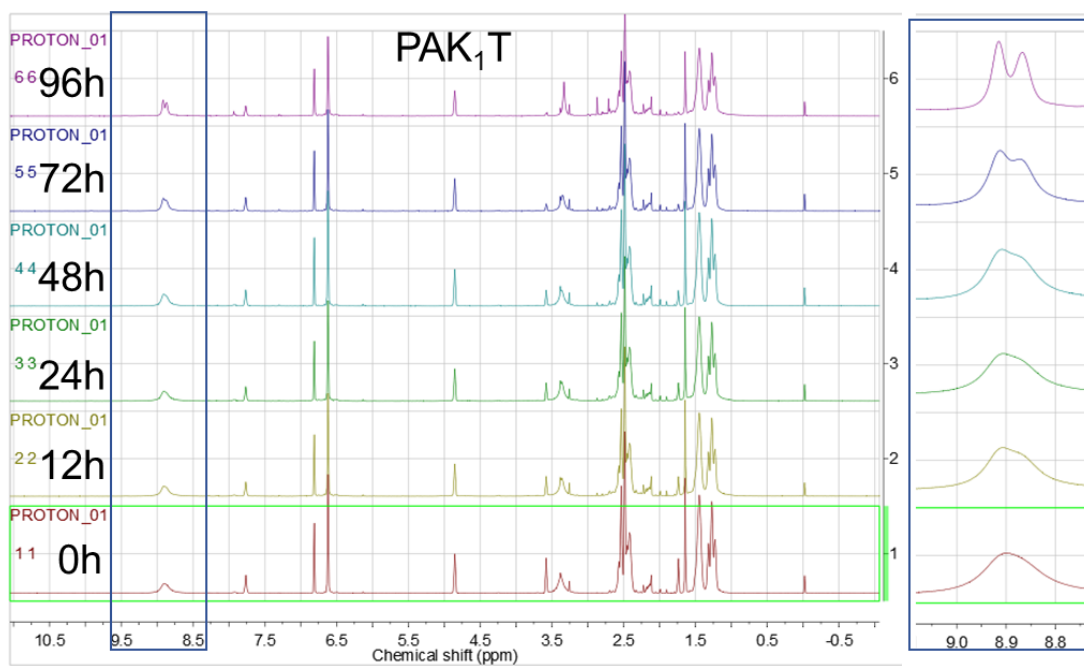


Fig. S9. ^1H NMR of copolymer PAK_1T after storage at 80°C .

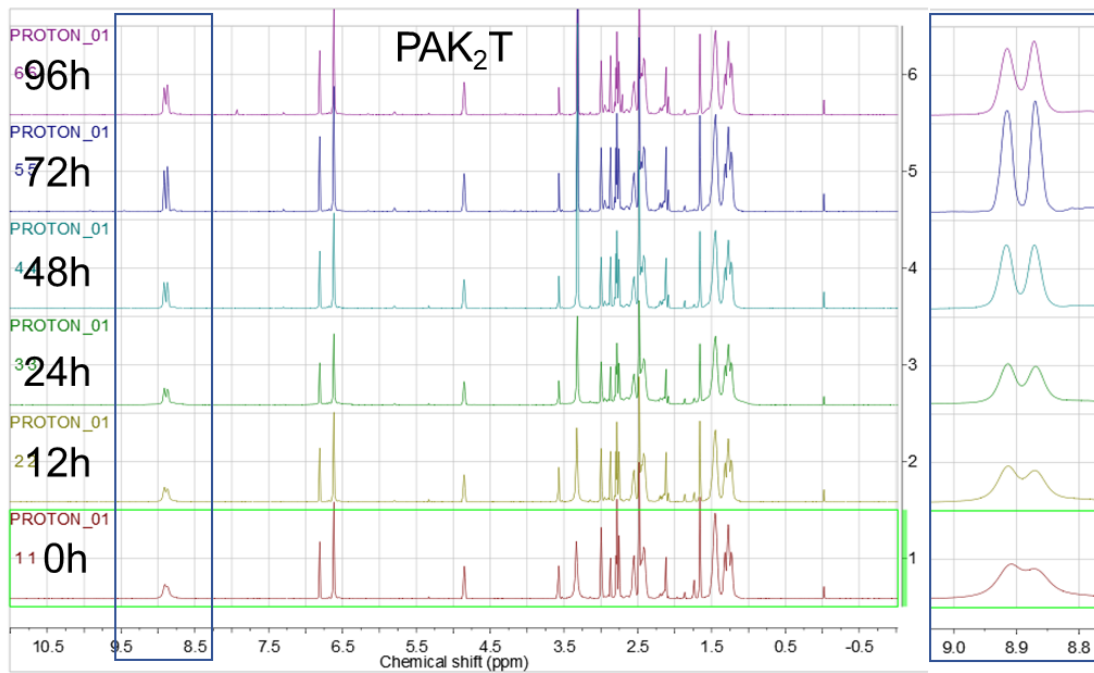


Fig. S10. ¹H NMR of copolymer PAK₂T after storage at 80°C.

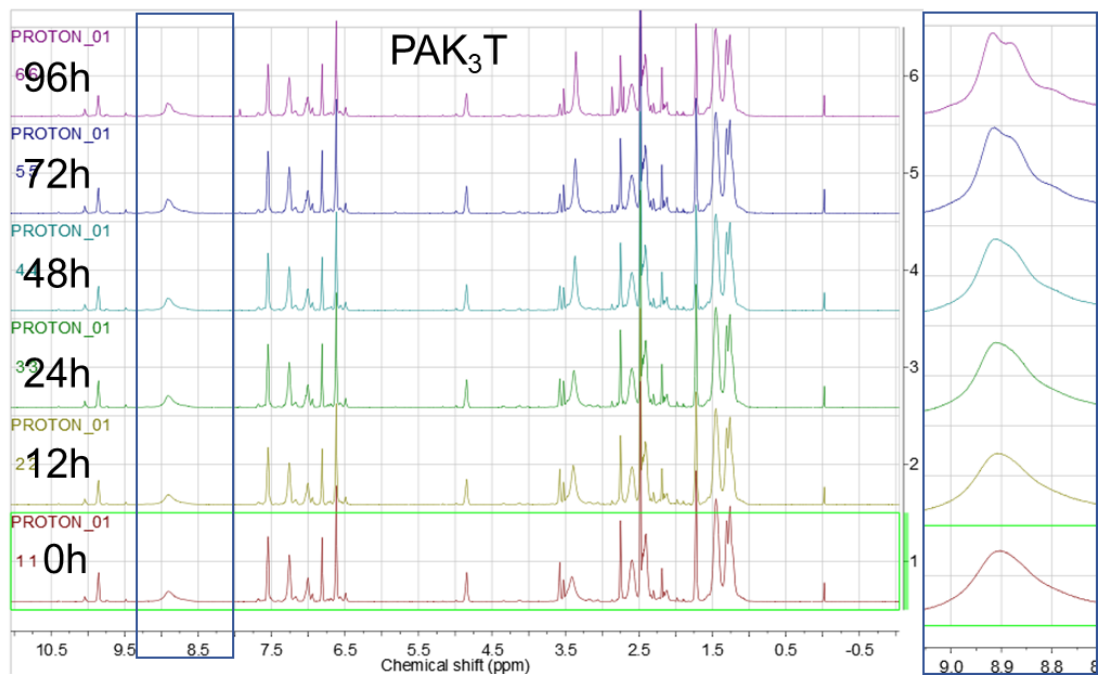


Fig. S11. ¹H NMR of copolymer PAK₃T after storage at 80°C.

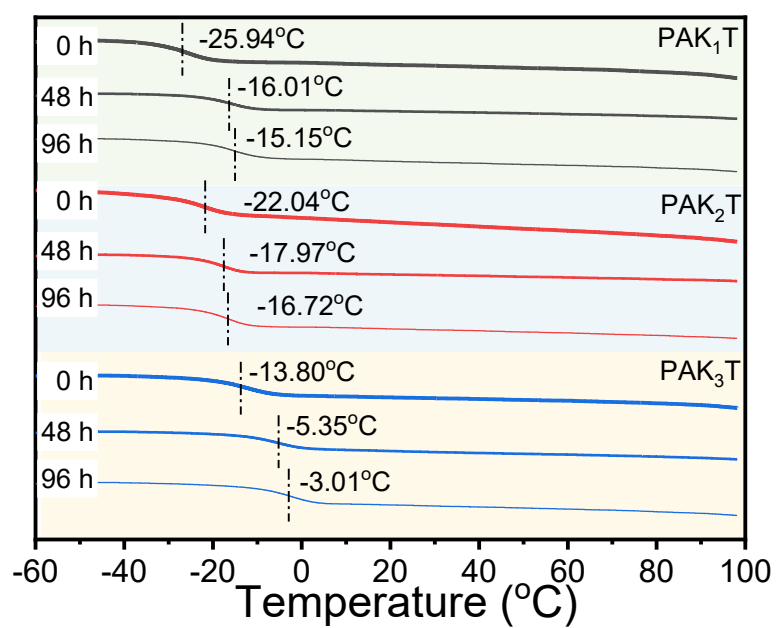


Fig. S12. DSC curves of copolymers after storage at 80°C

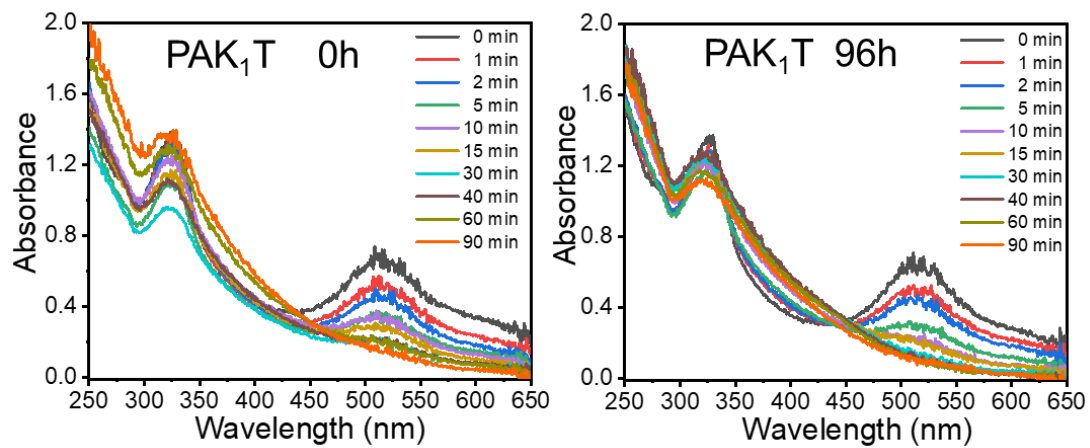


Fig. S13. Antioxidation test of copolymer PAK₁T before and after storage at 80°C for 96h.

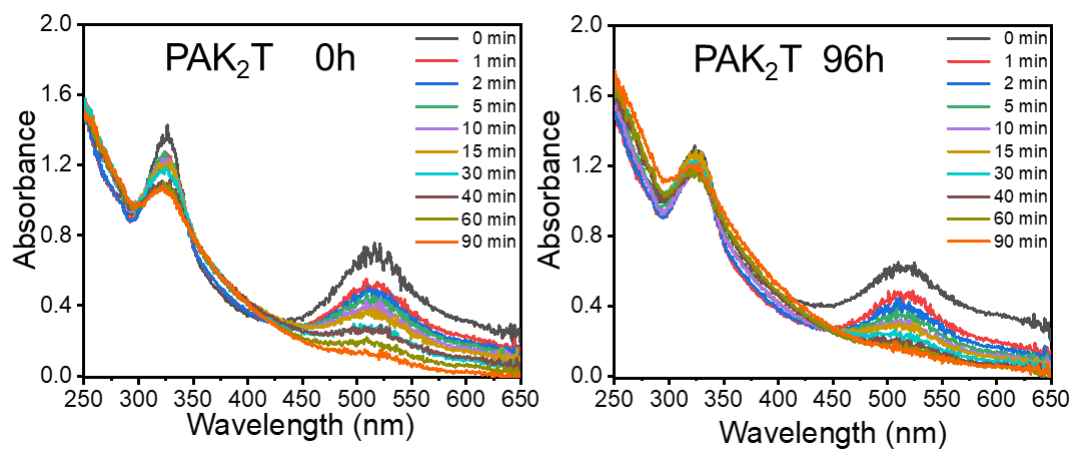


Fig. S14. Antioxidation test of copolymer PAK₂T before and after storage at 80°C for 96 h.

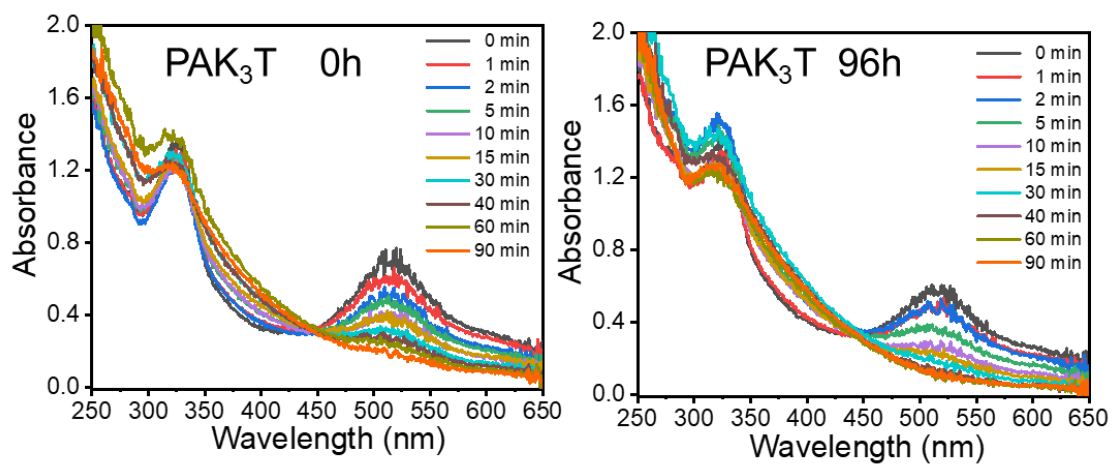


Fig. S15. Antioxidation test of copolymer PAK₃T before and after storage at 80°C for 96 h.

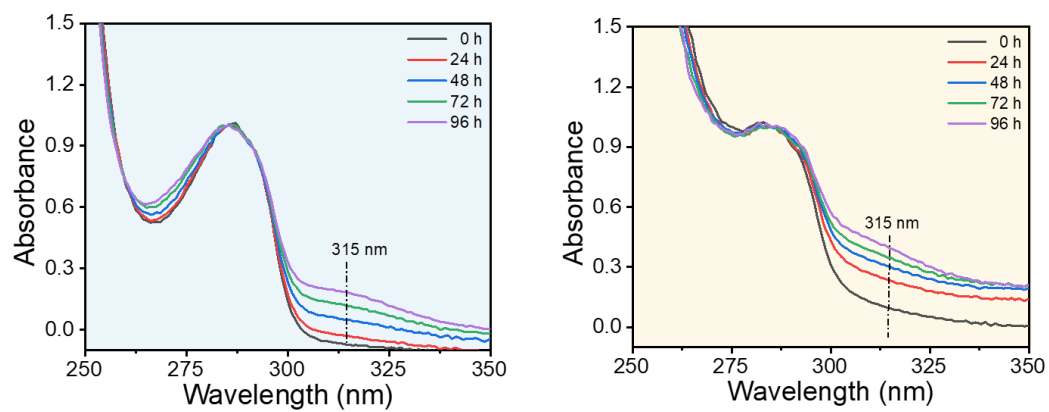


Fig. S16. UV-vis spectra of copolymers PAK₂T (left) and PAK₃T (right) after storage at 80°C.