

Supporting information

Photo-crosslinked nanofibers of poly (ether amine) (PEA) for the fast separation of dyes through molecular filtration

Guangxia Fu, Zhilong Su, Xuesong Jiang*, Jie Yin

School of Chemistry & Chemical Engineering, State Key Laboratory for Metal Matrix

Composite Materials, Shanghai Jiao Tong University,

Shanghai 200240, People's Republic of China.

Tel.: +86-21-54743268; Fax: +86-21-54747445. E-mail: ponygle@sjtu.edu.cn

Experiment

Materials

MC-DE was synthesized according to our previous work¹. Polyethylene glycol diglycidyl ether (PEO-DE, Aldrich, $M_n=526\text{g}\cdot\text{mol}^{-1}$), phloroglucinol, acetacetic ether and piperazine anhydrous (Sinopharm Chemical Reagent Co Ltd.) were used as received. All water-soluble dyes Ponceau S (PS), Rose Bengal (RB), Bismarck Brown Y (BY), Rhodamine 6G (R6G), Calcein (Cal), Methylene Blue (MB), Ponceau SX (PSX), Orange G (OG) and Fluorescein (FR) were bought from Sinopharm Chemical.

Synthesis of PEA

PEA was synthesized according to Scheme S1. MC-DE (6.08 g, 0.02 mol), PEO-DE (1.74 g, 0.01 mol), piperazine anhydrous (2.58 g, 0.03 mol), DMF (30 mL) was added into three-necked round-bottomed flask. Then the mixture was stirred at 80°C for 24 h under nitrogen atmosphere. The mixture was poured into 300 mL ether and the precipitate was dried in vacuum to get pure PEA.

Synthesis of SA-PEA

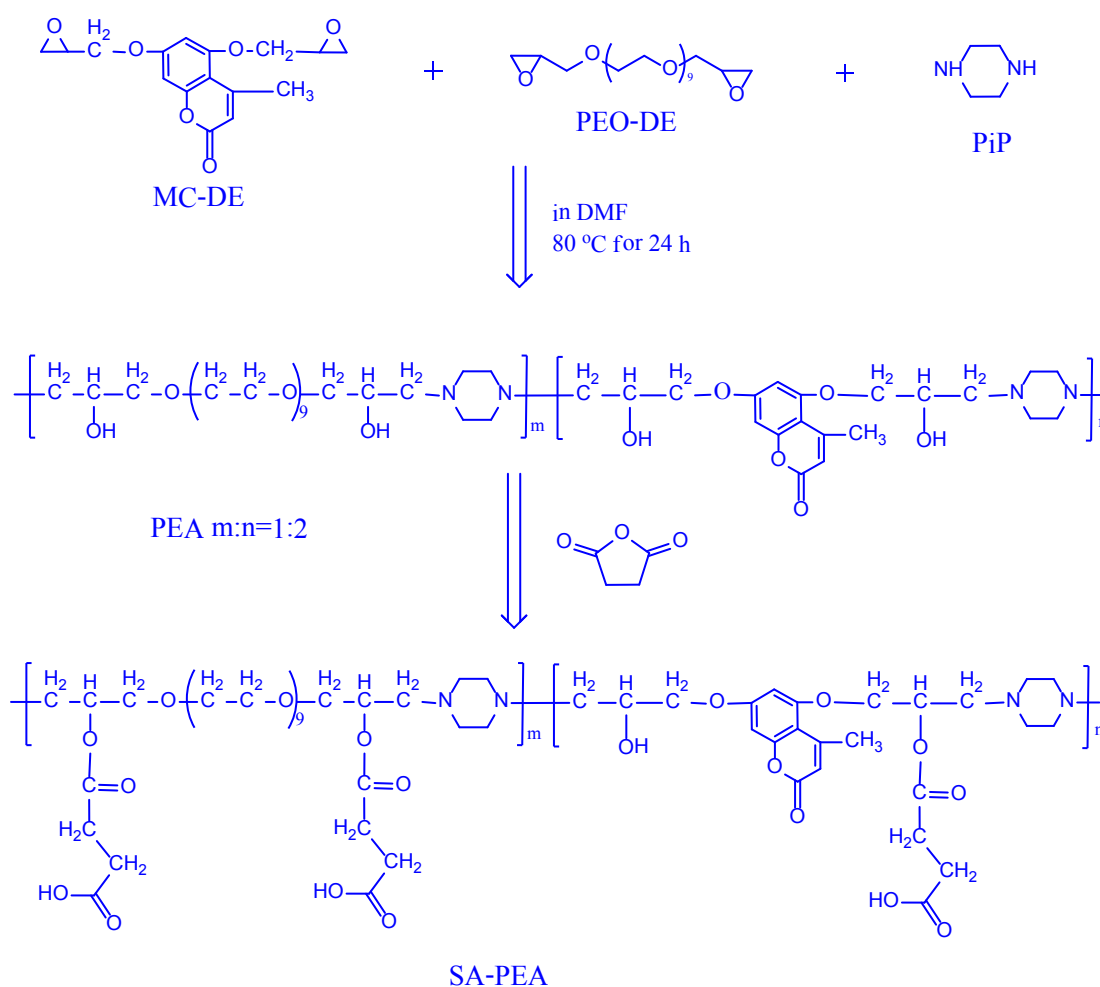
SA-PEA was synthesized via esterification of hydroxyl groups in PEA with SA.

SA (0.18 mol) and PEA (0.06 mol) in term of its structure units were stirred in DMF (30 mL) for 12 h with nitrogen protect. The mixture was washed by ether and the precipitate was dried in vacuum to obtain SA-PEA.

Results

Synthesis and Characterization of polymer PEA and SA-PEA

The random PEA and SA-PEA containing coumarin units¹ whose structure and synthesis processes were shown in Scheme S1, were used to prepare photo-crosslinked nanofiber membrane. SA-PEA was synthesized via esterification of hydroxyl groups in PEA with SA. The structures of polymer PEA and SA-PEA were checked by ¹H-NMR spectrum (Figure S1).



Scheme S1. Process for Synthesis of PEA and SA-PEA

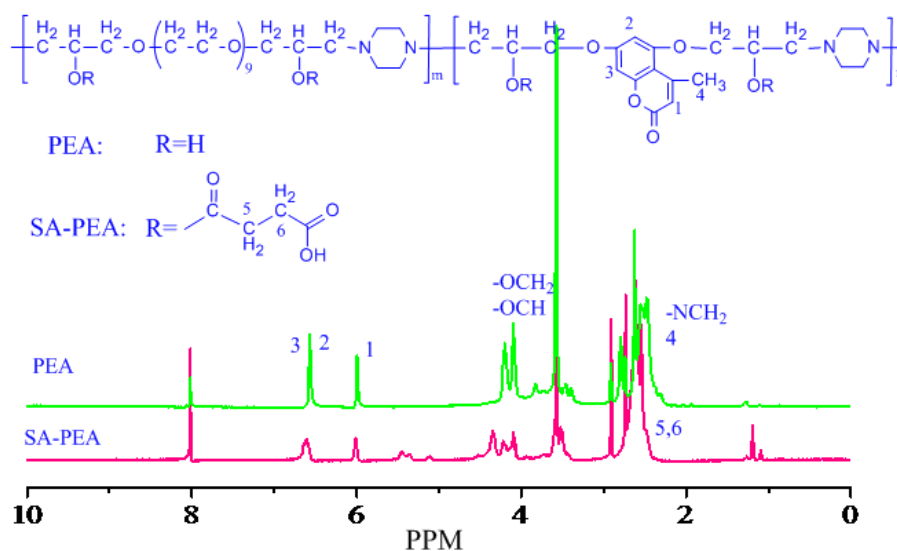


Figure S1. $^1\text{H-NMR}$ spectra of PEA and SA-PEA in DMF- d_6 .

The attribution of each signal was marked in Figure S1. Compared with PEA, the peak position of $-\text{OCH}_2$ and $-\text{OCH}$ was shifted to left, which indicates that the carboxyl groups (SA) was successfully introduced into PEA. According to integration of peaks at 2 ~ 3 ppm, respectively for PEA and SA-PEA, the percent of introduced SA was about 70 %.

Adsorption experiments

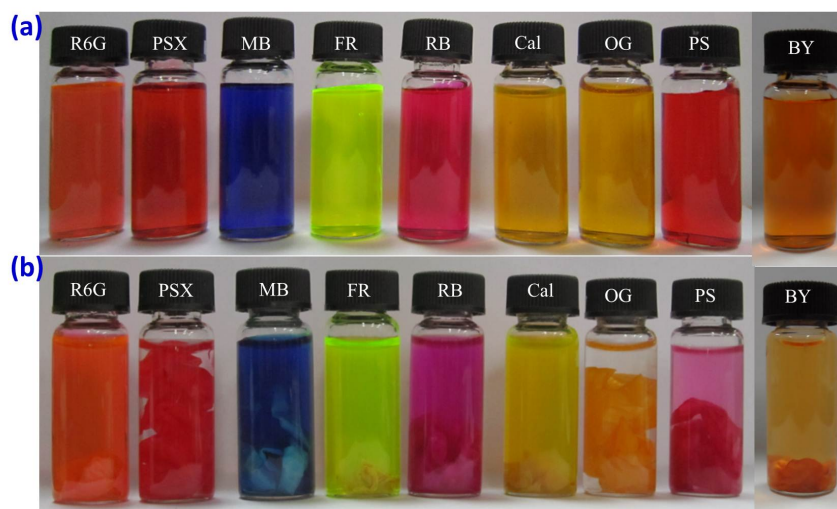


Figure S2. Photos of solution of dyes (a) before and (b) after adsorption by PEA-NF. Initial dye concentration is 200 μM .

The adsorption kinetics

Pseudo-second-order equation was used to analyze the adsorption kinetics to investigate the adsorption mechanism of dyes onto PEA-NF. The equation is shown below.

$$\frac{dQ_t}{dt} = k(Q_{eq} - Q_t)^2 \quad (1)$$

Calculating the integration of eq (1) with the condition $Q_t=0$, $T=0$ and $Q_t=Q_t$, $T=t$ to get the equation (2) shown as follows.

$$\frac{t}{Q_t} = \frac{1}{k \cdot Q_{eq}^2} + \frac{t}{Q_{eq}} \quad (2)$$

On the basis of eq(2), we studied the Pseudo-second-order adsorption behavior onto PEA-NF. In eq(2), k is Pseudo-second-order adsorption constant. Q_{eq} and k can be calculated according to the slope and intercept of plots of t/Q_t versus t . The plot of t/Q_t versus t is shown in Figure S4. The value of k and Q_{eq} are summarized in Table S1, where R^2 is correlation coefficient. From the Figure S4, the Pseudo-second-order equation fitted well to the whole range of contact time and the high value of R^2 in Table S1 also supports that. The value of $Q_{eq, cal}$ is approximate the value of $Q_{eq, exp}$, further indicating the adsorption behavior corresponding with Pseudo-second-order adsorption.

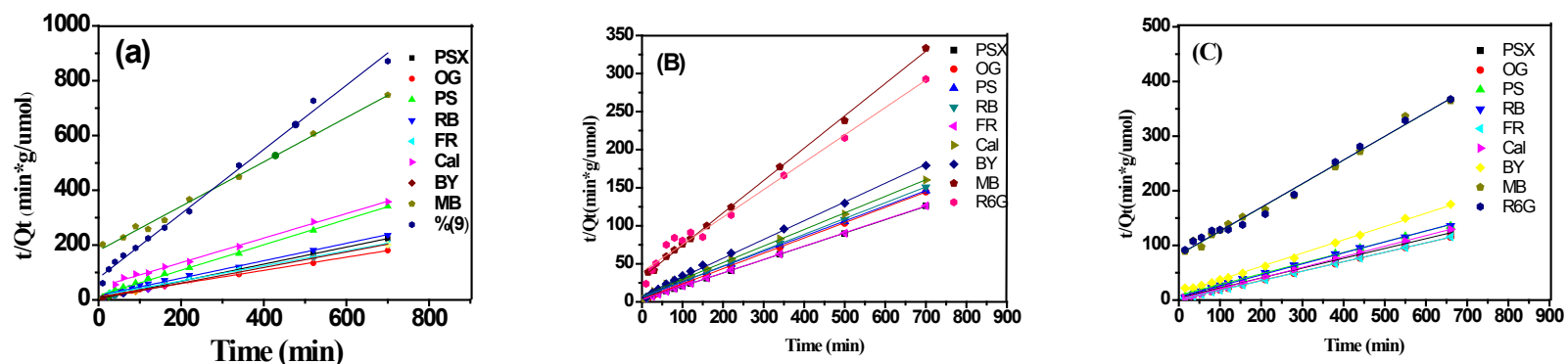


Figure S3. Pseudo-second adsorption kinetics of dyes onto (A) PEA-Gel, (B) PEA-NF, (C) SA-PEA-NF at 25 °C.

Table S1. Pseudo-second adsorption kinetics parameters describing the adsorption of dyes onto PEA-NF, SA-PEA-NF and PEA-Gel.

	PEA-NF				SA-PEA-NF				PEA-Gel			
	$Q_{eq,exp}$ ($\mu\text{mol/g}$)	k ($\text{g/min}\cdot\mu\text{mol}$)	$Q_{eq,cal}$ ($\mu\text{mol/g}$)	R^2	$Q_{eq,exp}$ ($\mu\text{mol/g}$)	k ($\text{g/min}\cdot\mu\text{mol}$)	$Q_{eq,cal}$ ($\mu\text{mol/g}$)	R^2	$Q_{eq,exp}$ ($\mu\text{mol/g}$)	k ($\text{g/min}\cdot\mu\text{mol}$)	$Q_{eq,cal}$ ($\mu\text{mol/g}$)	R^2
PSX	5.55	1.01E-02	5.72	0.999	5.34	7.34E-03	5.56	0.999	3.14	1.61E-02	3.21	0.999
OG	4.84	1.18E-02	4.92	0.997	5.72	2.42E-02	5.80	0.999	3.88	5.02E-03	4.16	0.997
PS	4.80	5.85E-03	5.03	0.998	4.87	4.32E-03	5.11	0.997	2.05	1.35E-02	2.16	0.997
RB	4.64	7.60E-03	4.82	0.997	4.86	6.92E-03	4.97	0.997	2.97	6.45E-03	3.14	0.993
FR	5.55	1.10E-02	5.68	0.999	5.71	5.17E-02	5.76	0.999	3.43	5.17E-03	3.65	0.998
CAL	4.37	5.93E-03	4.59	0.997	5.11	2.39E-02	5.16	0.999	1.95	4.30E-03	2.23	0.996
BY	3.90	7.47E-03	4.06	0.997	3.77	4.56E-03	4.11	0.997	3.47	1.75E-02	3.52	0.999
MB	2.10	5.66E-03	2.35	0.998	1.81	2.29E-03	2.30	0.992	0.94	2.93E-03	1.31	0.975
R6G	2.39	3.28E-03	2.78	0.982	1.80	2.26E-03	2.31	0.989	0.80	1.71E-02	0.85	0.993

Molecular filtration separation of mixed dyes

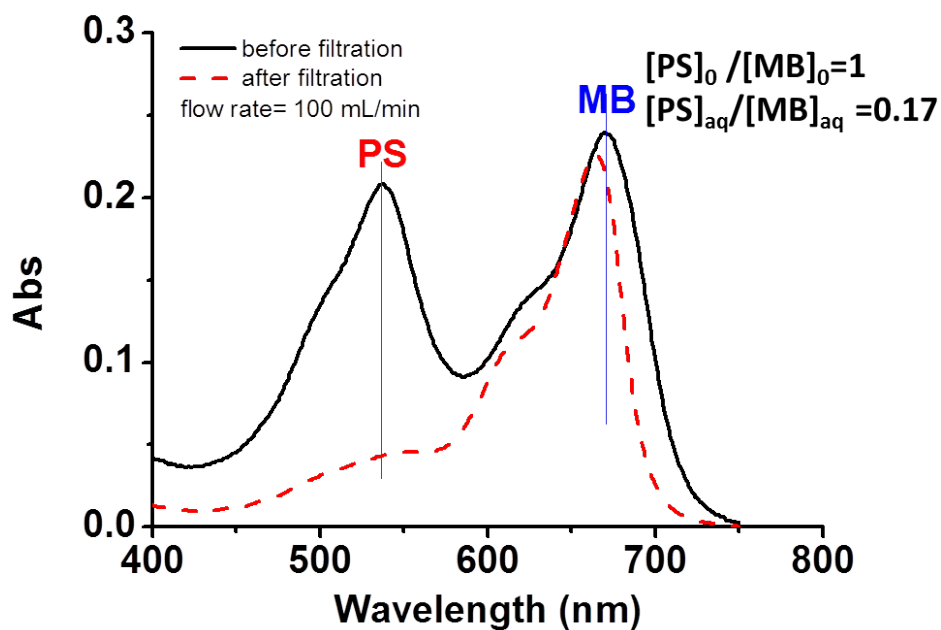


Figure S4. UV-vis spectra of PS/MB solution before and after filtration at 100 mL/min onto PEA-NF membrane. Original concentration of PS and MB is 5.5 μ M.

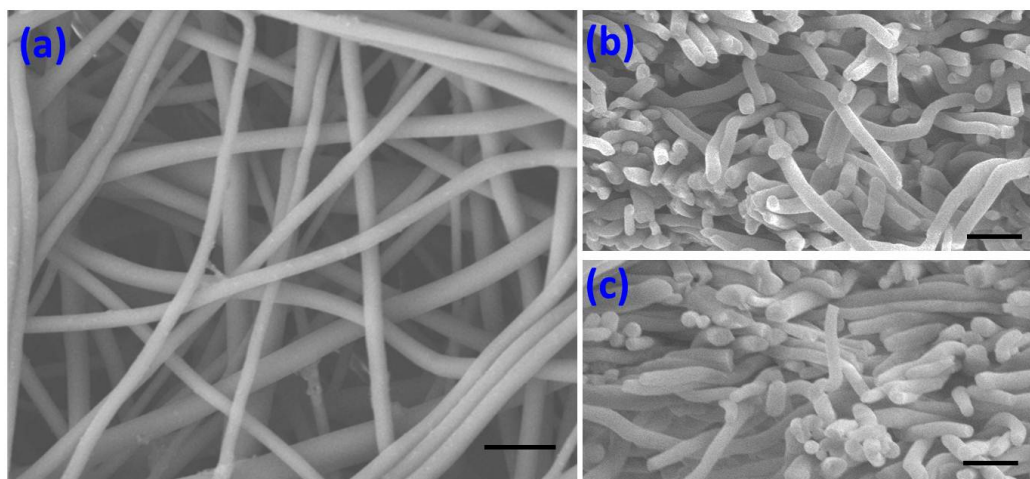


Figure S5. SEM image of PEA-NF membrane (a) cross-section (b) after adsorbing PS through PS/MB filtration separation; (c) SEM cross-sectional image of PEA-NF membrane after 10 continuous filtration separation experiments.

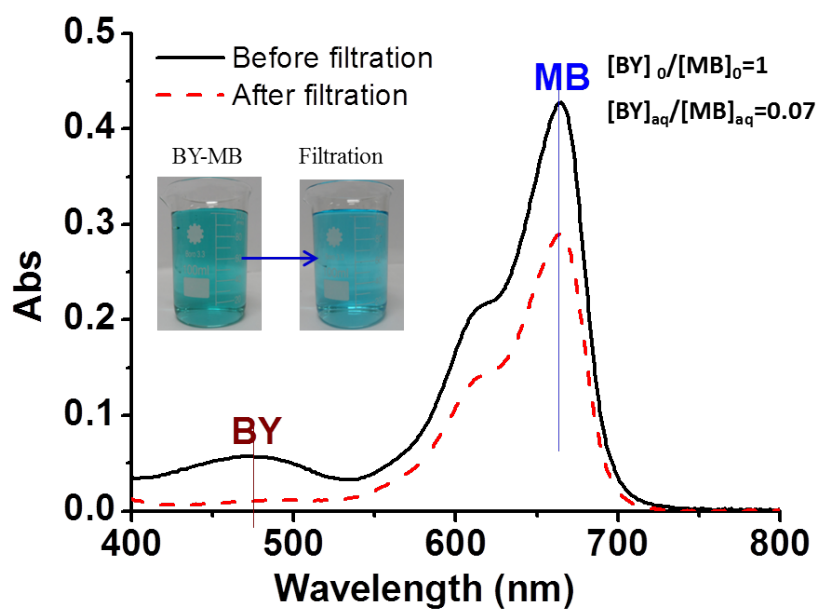


Figure S6. UV-vis spectra of BY/MB solution before and after filtration at 60 mL/min onto PEA-NF membrane. Original concentration of BY and MB is 5.5 μ M. Inset: photos of BY/MB solution before and after filtration.

References

1. X. Jiang, R. Wang, Y. Ren and J. Yin, *Langmuir*, 2009, **25**, 9629-9632.