

S1. Preparation and evaluation of the PP-HEMA membrane

To synthesize the PVDF-HEMA membrane, a fixed molar ratio of CuBr₂/PMDETA/L-Asc/EBIB was designed and experiments were performed to optimize the following parameters: 1) the molar ratio of HEMA/MBA (3:1, 2:1, 1:1, 1:2, 1:3); 2) the total concentration of monomers including HEMA and MBA (0.08 to 0.44 mM); 3) the reaction time (2 to 10 h). The following experiments were conducted: 500 μL of HSA (50 μg/mL in 12 mM PBS) was consecutively flowed through the membrane, and the eluate was collected for BCA assay for the recovery calculations.

S2. Preparation of the PVDF-HEMA-co-4-vinylpyridine membrane

To synthesize the PVDF-HEMA-co-4-vinylpyridine membrane, a fixed molar ratio of CuBr₂/PMDETA/L-Asc/EBIB was designed and experiments were performed to optimize the following parameters: 1) the amount of 4-vinylpyridine monomer (0.05 to 0.15 mM); 2) the reaction time (1 to 8 h). The evaluation of the indicators was mainly based on the recovery (%) of rituximab, calculated as $(1 - (\text{BCA value of analyte in eluent} / \text{BCA value of analyte in standard working solution})) \times 100\%$.

Table S1. Composition of the polymerization mixtures for preparing the PVDF-HEMA membrane.

No.	Monomers (%, w/w)		Modification reagent (%, w/w)			Reducing Agent (%)	Monomers/ Modification reagent (%, w/w)	Preparation Time (h)	CRP Recovery (%)
	HEMA	MBA	EBIB	CuBr ₂ and PMDETA	DMF	L-Asc			
1	76.69	28.31	2.53	0.69	84.82	47.32	17.65: 82.35	6	16.5
2	62.80	37.20	2.53	0.69	84.82	47.32	17.65:82.35	6	65.1
3	45.77	54.23	2.53	0.69	84.82	47.32	17.65:82.35	6	93.8
4	29.68	70.32	2.53	0.69	84.82	47.32	17.65:82.35	6	80.4
5	21.96	78.04	2.53	0.69	84.82	47.32	17.65:82.35	6	63.1
6	45.77	54.23	2.53	0.69	84.82	47.32	5.77:94.23	6	20.4
7	45.77	54.23	2.53	0.69	84.82	47.32	8.41:91.59	6	40.4
8	45.77	54.23	2.53	0.69	84.82	47.32	13.68:86.72	6	55.4
9	45.77	54.23	2.53	0.69	84.82	47.32	17.65:82.35	6	32.4
10	45.77	54.23	2.53	0.69	84.82	47.32	21.61:78.39	6	54.7
11	45.77	54.23	2.53	0.69	84.82	47.32	25.20:74.80	6	60.7
12	45.77	54.23	2.53	0.69	84.82	47.32	17.65:82.35	2	20.4
13	45.77	54.23	2.53	0.69	84.82	47.32	17.65:82.35	4	53.7
14*	45.77	54.23	2.53	0.69	84.82	47.32	17.65:82.35	6	94.7
15	45.77	54.23	2.53	0.69	84.82	47.32	17.65:82.35	8	86.4
16	45.77	54.23	2.53	0.69	84.82	47.32	17.65:82.35	10	91.1

*: the condition of No. 14 was considered as the optimum; w/w: weight to weight ratio.

Table S2. Composition of the polymerization mixtures for preparing the MPC polymer brush modified PVDF-HEMA-*co*-4-vinylpyridine membrane .

No.	Monomers (%)		Reducing agent (% w/w)		Preparation Time (h)	Rituximab Recovery (%)
	4-vinylpyridine	CuBr ₂ and PMDETA	DMF	L-Asc		
1	16.33	1.50	86.86	2.56	8	80.5
2*	16.33	1.50	96.74	2.56	8	93.5
3	16.33	1.50	80.65	2.56	8	76.5
4	5.45	1.50	96.74	1.26	8	38.6
5	10.24	1.50	96.74	1.26	8	64.2
6	16.33	1.50	96.74	2.56	8	92.5
7	20.08	1.50	96.74	1.26	8	79.6
8	16.33	1.50	96.74	1.26	8	94.6
9	16.33	1.50	96.74	1.26	4	75.6
10	16.33	1.50	96.74	1.26	6	64.6
11	16.33	1.50	96.74	1.26	8	70.6
12	16.33	1.50	96.74	1.26	10	77.6
13	16.33	1.50	96.74	1.26	12	89.6

*: the condition of No. 2 was considered as the optimum; w/w: weight to weight ratio; -: the membrane surface structure became too hard to be rolled.

Table S3. Comparison of XPS results for different membranes.

Atomic composition percentage (%)	C	O	N	Br
PVDF	98.15	1.68	0.17	-
PVDF-HEMA	70.04	29.64	0.22	0.10
PVDF-HEMA- <i>co</i> -4-vinylpyridine	72.73	22.86	4.34	0.07

-: cannot be detected