Electronic Supplementary Information

for

Micro-phase architectural design of fluorinated ethyl cellulose membranes: towards high permeation flux of pervaporation for gasoline desulfurization

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EXPERIMENTAL SECTION

1.1 Materials

Typical gasoline components, including thiophene, n-heptane, cyclohexane, cyclohexene and toluene, were selected as model compounds. All the above-mentioned chemicals used were of analytical reagent (A.R.) grade from Tianjin Chemical Reagent Corporation Ltd and used without further purification. 1, 6-hexanediol diacrylate (HDDA), benzoyl peroxide (BPO) and tetrahydrofuran (THF) were purchased from China National Medicines Corporation Ltd.

Two parameters of the copolymer structure on desulfurization performance are studied separately, namely (i) the length of grafted moieties and (ii) the number of grafted monomers on the main chain. Ethyl cellulose (EC, M_W= 20600 g/mol) was purchased from China National Medicines Corporation Ltd. Two types of fluorinated monomer, 1H,1H,2H,2H-perfluorooctyl acrylate (PFA, Mw = 418.15) and 1H,1H,2H,2H-heptadecafluorodecyl methacrylate (FMA, Mw =

532.19), were purchased from DuPont. Ethyl cellulose-graft-poly1H,1H,2H,2H-perfluorooctyl acrylate (EC-g-PFA) and series of ethyl cellulose-graft-poly1H,1H,2H,2H-heptadecafluorodecyl methacrylate (EC-g-FMA) with different F weight content were utilized as fluorinated ethyl cellulose copolymers. The element analysis of EC-g-FMA and EC-g-PFA was carried out by PANalytical Axios Petro wavelength dispersive X ray fluorescence spectrometer (Table S1). The F element content in EC-g-FMA was 14.45 wt%, which was similar with that of the EC-g-PFA of 14.32 wt%. The number of fluorinated monomer was calculated according to the content of fluorine element in the copolymers. The number of monomers on single EC chain of EC-g-FMA and EC-g-PFA were 121 and 158. The copolymers of EC-g-FMA with different F content were utilized to investigate the effect of grafted monomers number on desulfurization performance. The F content of EC-g-FMA series is 6.01 wt%, 8.63 wt%, 14.45 wt%, 16.67 wt%, 18.92 wt%, 21.53 wt% and 23.08 wt%.

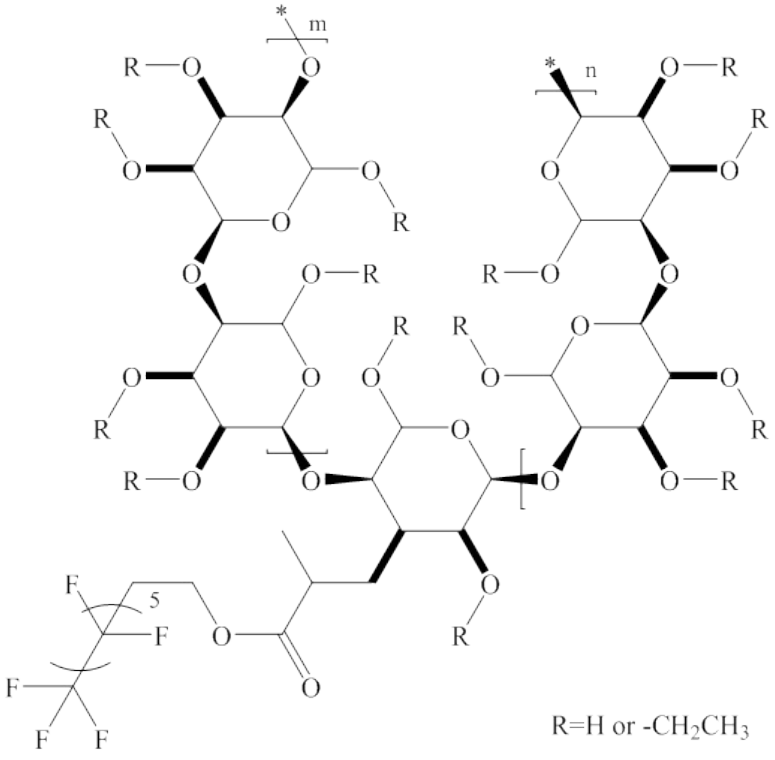

Fig.S1 Chemical structure of EC-g-PFA.

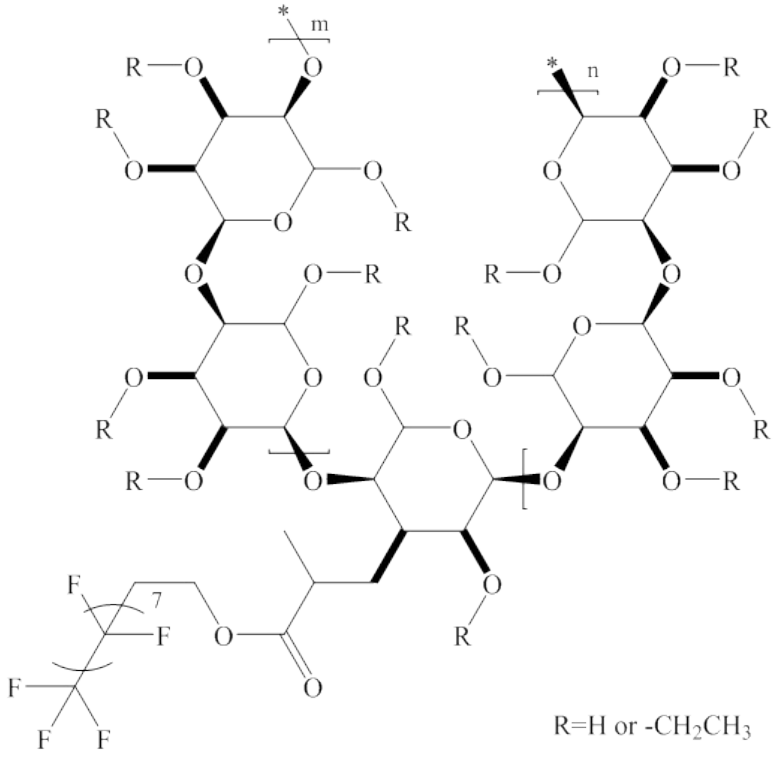

Fig.S2 Chemical structure of EC-g-FMA.

Table S1. The side chain information of the fluorinated ethyl cellulose copolymers

Sample	Fluorinated monomer	Element composition (wt %)			Number of Fluorinated monomers on single EC chain
		C	H	F	
EC	--	69.84	30.16	0	0
EC-g-FMA	FMA	67.93	17.62	14.45	121
EC-g-PFA	PFA	61.27	23.33	14.32	158

1.2 Characterization

The FT-IR spectra of the copolymers were obtained on a Nicolet Avatar 370 Fourier Transform Infrared (FT-IR) spectrometer. Differential scanning calorimetry (DSC) measurements were performed using NETZSCH DSC under nitrogen atmosphere heating from room temperature up to 250 °C with a rate of 20 °C/min. The morphology of the fluorinated ethyl cellulose copolymers were determined by transmission electron microscopy (TEM) (H-600A, Hitachi, Tokyo, Japan).

Two types of the fluorinated ethyl cellulose copolymers, which were prepared in THF solution with the content of 0.1 wt%, were observed.

1.3 Membranes preparation

Since the fluorine parts caused poor mechanical strength of the copolymer membranes, the membranes should be crosslinked to enhance the mechanical properties of the membranes. The copolymer, crosslinker HDDA and initiator BPO were dissolved in THF to form a homogenous solution of 12 wt% polymer at room temperature. Mass ratio of crosslinker and polymers was kept constant at 20 wt%. After degassing under vacuum, the solution was cast onto the glass plate with a scraper. The cast film was placed in an oven at 80 °C for 24 h to evaporate the solvent, and induced by ultraviolet rays (UV) irradiation for some time to crosslink. The thickness of obtained membranes was about 12 μm. All membrane samples were stored in dust-free and dry environment before used in the PV experiments.

1.4 PV tests

The model gasoline was composed of thiophene, n-heptane (35 wt%), cyclohexane (10 wt%), cyclohexene (40 wt%) and toluene (15 wt%).[1] The sulfur content was 1000 $\mu g \cdot g^{-1}$ by adjusting the content of thiophene. Pervaporation experiments were conducted on the similar equipment as reported previously.[2] The permeation flux (J, $kg \cdot \mu m \cdot m^{-2} \cdot h^{-1}$) was obtained by equation (1).

$$J = Q \cdot h \cdot A^{-1} \cdot t^{-1} \tag{1}$$

where Q is the total amount permeated during the experimental time interval (kg), h is the thickness of the membranes (μm), t is the operating time (s) and A is the effective membrane area (m^2).

The total sulfur content of feed and permeation was analyzed by Micro-Coulometric Analysis

Instrument (Taizhou, China). The sulfur enrichment factor, E, is defined as equation (2).

$$E = C_P / C_F \tag{2}$$

where C_f and C_p are the total sulfur content of feed and permeation samples, respectively.

DSC analysis results

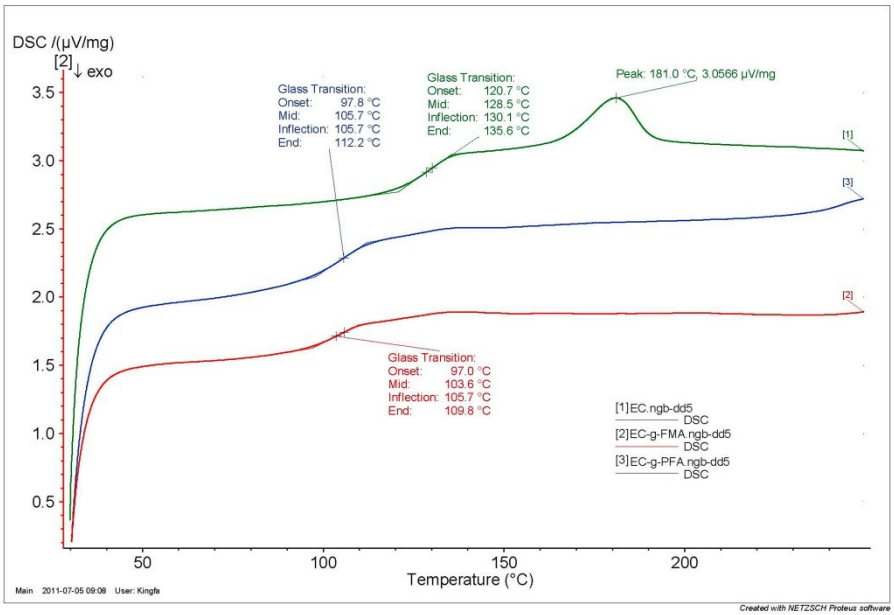

Fig. S3 DSC curves of [1] EC; [2] EC-g-FMA; [3] EC-g-PFA.

References

1 Y. Kong, L. Lin, J. Yang, D. Shi, H. Qu, K. Xie and L. Li. *J. Membr. Sci.*, 2007, **293**, 36-43.

2 Y. Kong, L. Lin, Y. Zhang, F. Lu, K. Xie, R. Liu, L. Guo, S. Shao, J. Yang and D. Shi. *Eur. Polym. J.*, 2008, **44**, 3335-3343.