Electronic Supplementary Information

Multi-functionalization of Poly(vinylidene fluoride) Membranes via Combined "Grafting from" and "Grafting to" Approaches

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Experiment Section

Materials

Poly(vinylidene fluoride) (PVDF, Kynar® K-761 powders, M_w = 441 000 Da; from gel permeation chromatography (GPC) measurements, M_w = 360 000 Da and polydispersity index (PDI) = 1.34) were obtained from Elf Atochem of North America Inc. Propargyl methacrylate (PMA, 98%, Alfa Aesar) was passed through an inhibitor removal column prior to being stored under an argon atmosphere at -10 ºC. *N*-isopropylacrylamide (NIPAM, 97%), 4,4'-azobis(4-cyanopentanoic acid) (ACVA, ≥98%), *N*-methyl-2-pyrrolidone (NMP, reagent grade) and 1,4-dioxane (99.8%) were obtained from Sigma-Aldrich Chem. Co. and used as received without further purification. 2-(2-Bromoisobutyryloxy)ethyl methacrylate (BIEM)[1] and azide-functionalized chain transfer agent (CTA-N_3)[2,3] were prepared according to procedures described in the literature.

Thermally-Induced Graft Copolymerization of BIEM and PMA from the Ozone-Pretreated PVDF (PVDF-*g*-[PBIEM-*co*-PPMA] Copolymer)

The PVDF powder was first dissolved in NMP to form a 7 wt% solution. A continuous stream of O_3/O_2 mixture (generated from an Azcozon RMU16-04EM ozone generator) was bubbled through 30 ml of the NMP solution of PVDF at room temperature (~25 ºC). The inlet oxygen flow rate was adjusted to 300 l/h to result in an ozone concentration of about 0.027 g/l in the gaseous mixture. A treatment time of 15 min was used to achieve the desired content of peroxides in the PVDF chains since excessive ozone pretreatment could lead to over-oxidation and degradation of the polymer chains.[4] After ozone preactivation, the polymer solution was cooled in an ice bath. An argon stream was introduced for about 30 min to remove the dissolved ozone and oxygen. The BIEM monomer (1.5 g, 5.4 mmol), PMA monomer (1.5 g, 12.1 mmol) and NMP solvent (10 ml)

were then added into the reaction mixture. After an additional 15 min of argon purging, the temperature of the water bath was raised to 60 ºC to induce the decomposition of peroxide groups on the PVDF backbones and to initiate the graft copolymerization of BIEM and PMA. After the desired reaction time (6 h), the reactor flask was cooled in an ice bath, and the resultant PVDF-*g*-[PBIEM-*co*-PPMA] copolymer was precipitated in an excess amount of absolute ethanol. The copolymer was purified by re-dissolving in NMP and re-precipitation in ethanol. The copolymer was washed alternately with THF (a good solvent for PPMA and PBIEM homopolymers and a non-solvent for PVDF) and ethanol thrice and then dried by pumping under reduced pressure, before being subjected to further characterization and reaction. The processes of ozone preactivation of PVDF and thermally-induced graft copolymerization of BIEM and PMA are illustrated in Scheme 1.

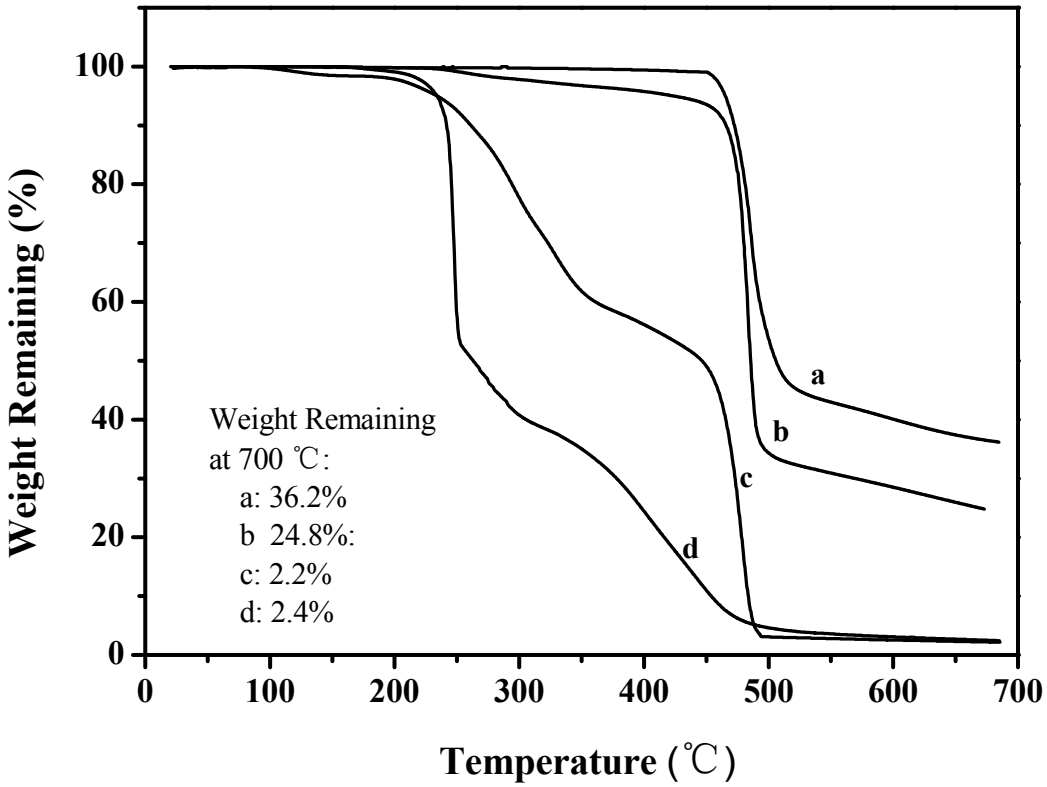

Figure S1. Thermogravimetric analysis (TGA) curves of the (a) PVDF homopolymer, (b) PVDF-*g*-[PBIEM-*co*-PPMA] copolymer with a $([\text{-BIEM-}]:[\text{-PMA-}]:[\text{-}CH_2CF_2\text{-}])_{bulk}$ molar ratio of 0.05:0.12:1.00, (c) PBIEM homopolymer and (d) PPMA homopolymer.

Synthesis of PNIPAM-N_3 Homopolymers

The azido-terminated poly(*N*-isopropylacrylamide) (PNIPAM-N_3) chains were first prepared via reversible addition-fragmentation chain-transfer (RAFT) polymerization of the NIPAM monomer using CTA-N_3 as the RAFT agent.[5] In a typical reaction, NIPAM (2.5 g, 22.1 mmol), ACVA (12.4 mg, 0.044 mmol), CTA-N_3 (88 mg, 0.22 mmol), and 10 ml of 1,4-dioxane were introduced into a 25 ml reaction flask. The light yellow homogeneous solution was purged with argon for about 20 min to remove the dissolved oxygen. The reaction flask was then sealed and placed in an oil bath at 70 ºC to initiate the polymerization. At the end of the reaction (4 h), the reaction flask was quenched in cold water and opened, diluted with THF, and precipitated into a large volume (200 ml) of hexane. The product was redissolved in THF and precipitated into cold diethyl ether to remove the residual monomers. The dissolution-reprecipitation cycle was repeated twice. The resulting polymer, PNIPAM-N_3, was dried under reduced pressure at room temperature for at least 24 h until a constant weight was obtained. The PNIPAM-N_3 yield was about 1.8 g, and the conversion of NIPAM was about 72%. ($M_{n,NMR}$ = 8900 g/mol, as determined by ^{1}H NMR spectroscopy)

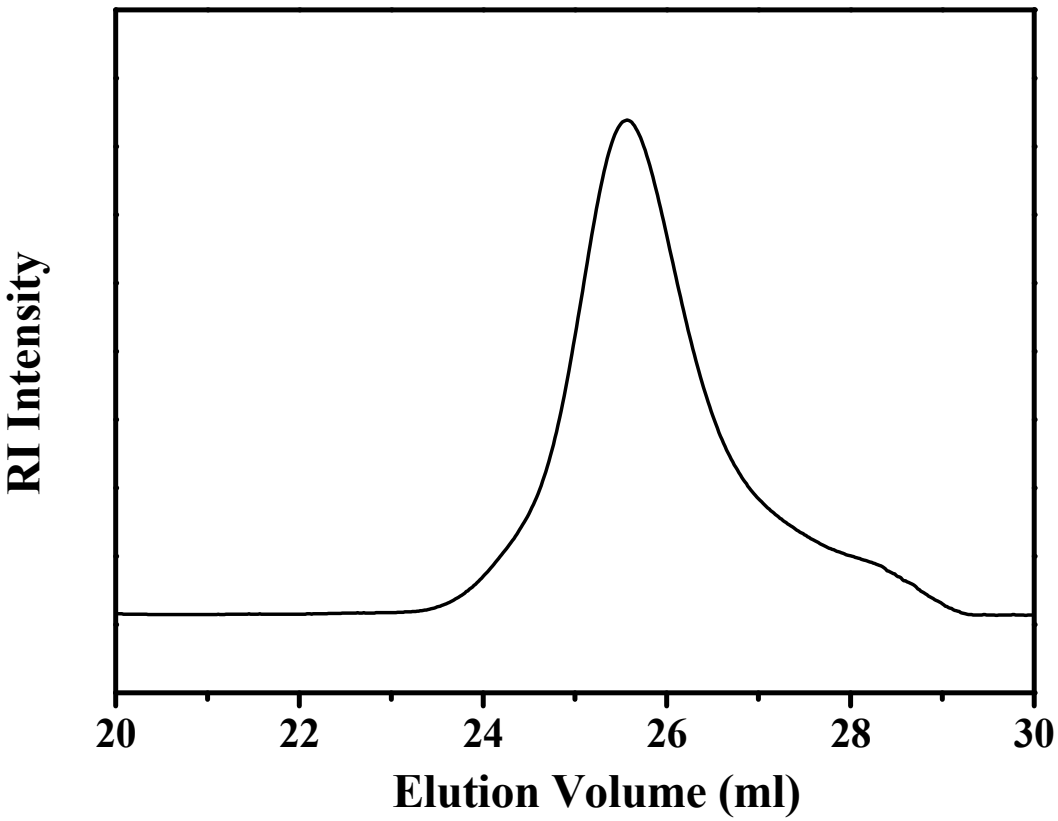

Figure S2. Gel permeation chromatography (GPC) elution curve of azido-terminated poly(*N*-isopropylacrylamide) (PNIPAM-N_3) chains in *N,N*-dimethylformamide (DMF) at an elution rate of 1.0 ml/min.

References

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