Supporting Information

Influence of Rigid–Soft Domains on Proton Conduction and Microstructure in Block Copolymer Membranes

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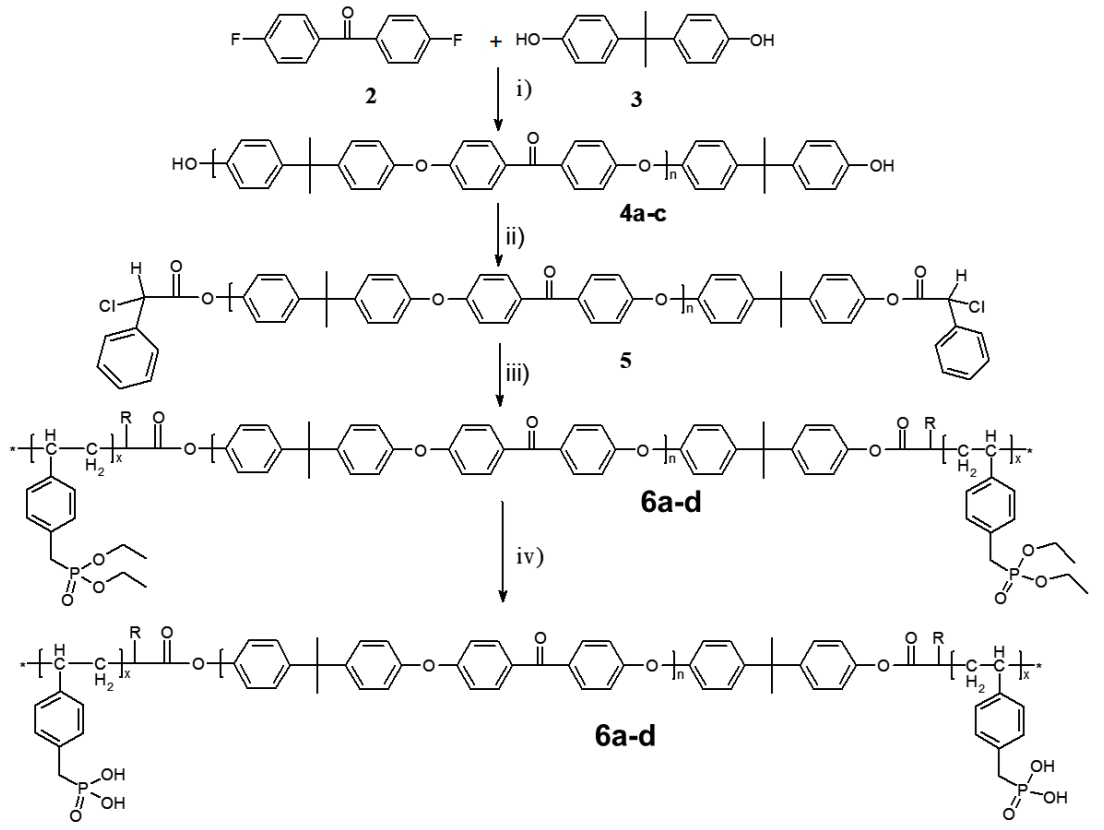
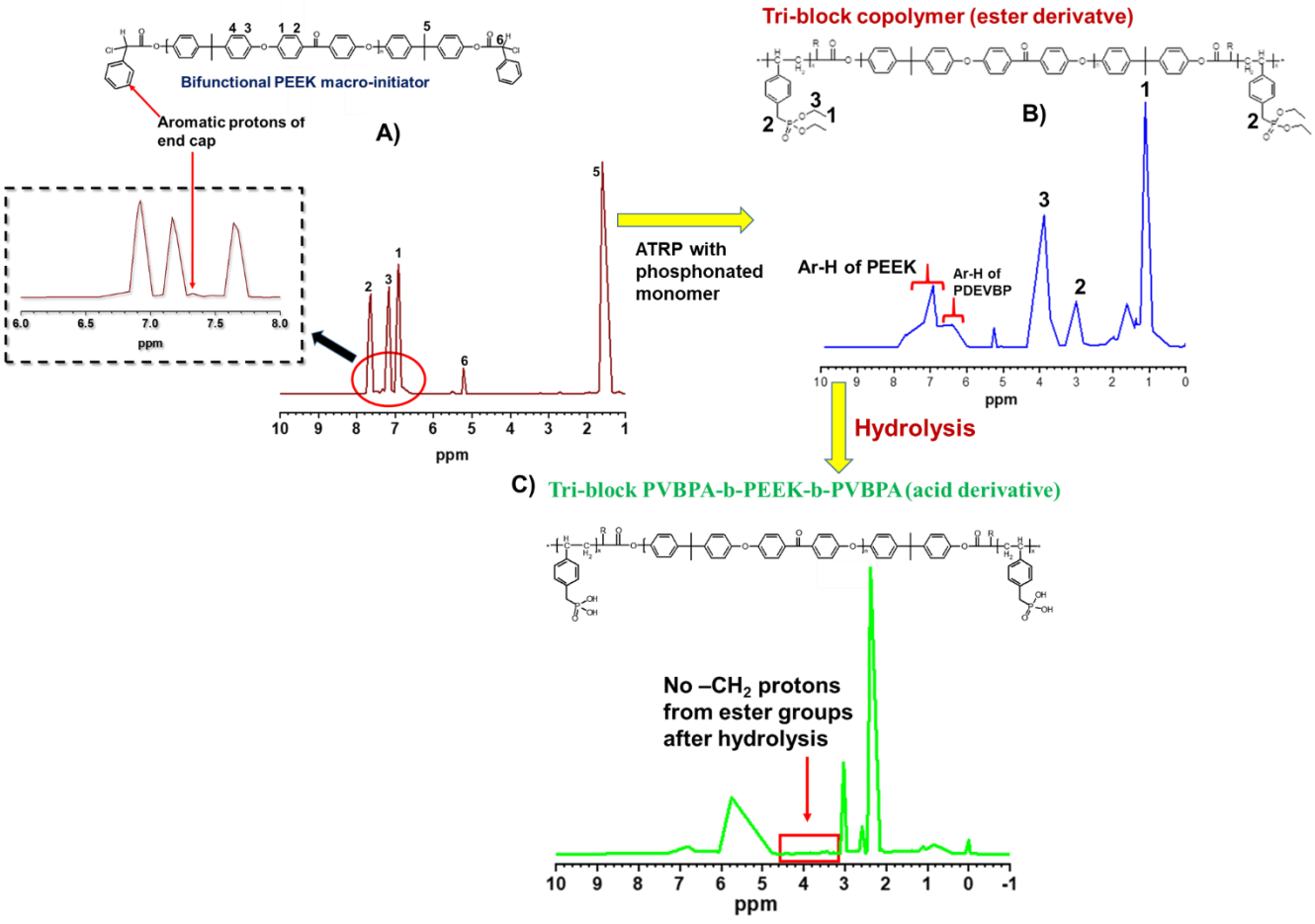
Synthesis and characterization



S1. Synthesis of PEEK homopolymer 4a-c (Table 1), macro initiators 5, and block copolymers 6a-j and 7a-j i) K2CO3, Toluene, DMAc, 130 °C; ii) Chlorophenyl acetyl chloride, N3Et, toluene; iii) Diethyl vinyl benzyl phosphonate, Cu(I)Cl, ligand, anisole; iv) 1. TMSiBr, DCM rt 2. MeOH, rt.[1-3]

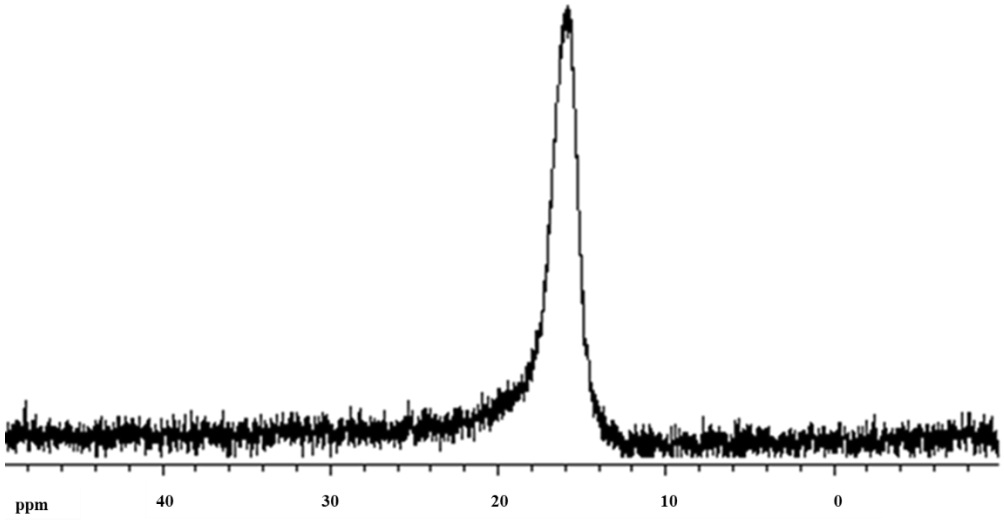
In the typical ^{1}H NMR spectrum of **4a-c (SI 1**), the signal at 1.63 ppm corresponds to 6 protons from the methyl groups of the repeating unit (5), and the signal at 1.57 ppm attributes to the methyl protons of the end group. A signal at 5.78 ppm is associated with the terminal OH-groups. In the region of 6.9-7.2 ppm there are signals assigned to the eight aromatic protons of the repeating unit (ortho to the ether junction, 2 and 3) (**S2**). The two doublets at 6.7 and 7.1 ppm represent the four aromatic protons of the end groups. The signal at 7.7 ppm results from absorption of the monomer unit (ortho to ketone junction, 1) (**S2**). The molecular weight of the PEEK 4a-c was calculated by comparison of the signals at 7.7 ppm and 6.7 ppm and gave Mn = 2000 g/mol.



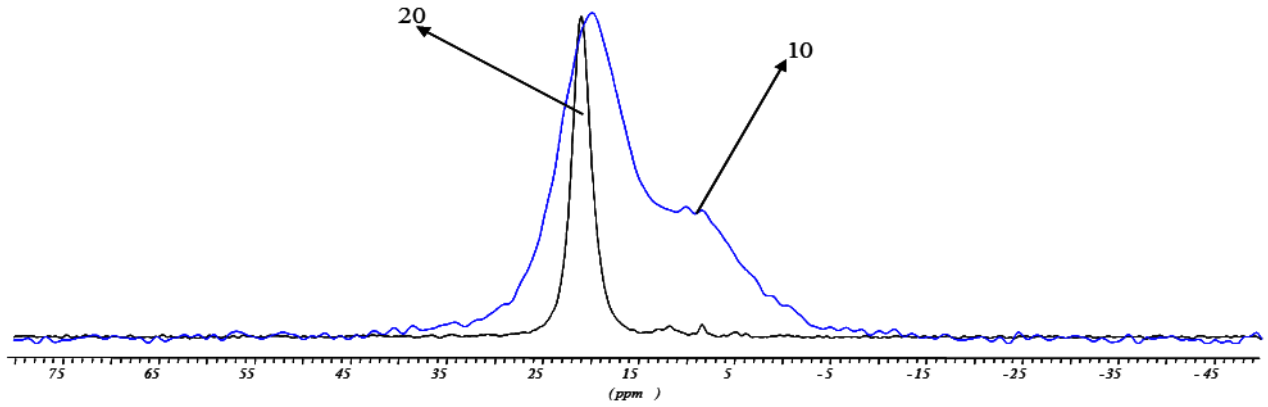
S2. Representative ^{1}H NMR spectrum (250 MHz) of A) PEEK-macroinitiator (B) tri-block

copolymer ester derivatives as obtained from ATRP by copolymerizing the monomer, and C) final acidic derivatives (with phosphonic acid) of tri-block copolymers after hydrolysis.

In the ^{1}H NMR spectra of 5 (**S2**), three new signals of the end-capper are observed: one at 5.48 ppm corresponding to a methyne proton (CH) and at two at 7.3 and 7.5 ppm related to the five aromatic protons from the end-group. In the ^{1}H NMR spectra of 5 the signal for the OH-groups disappeared and a new signal at 2.01 ppm was observed, corresponding to 6 protons from the two methyl groups of the end-capper (**S2A**). The degree of polymerization (DP) of DEVBP and the molecular weight of the products were calculated by evaluating the relative signal intensities of the aromatic protons of PEEK (7.7 ppm 4H from the repeating unit) and the aromatic protons from PDEVBP (6.3 ppm). The values obtained were combined with the GPC data of the corresponding PEEK macroinitiator in order to determine the exact molecular weight of the polymer (**Table 2**). In a representative spectrum, the methyl and methylene protons of the ethyl ester group were observed at 1.1 and 3.9 ppm respectively. At 3.0 ppm the signal of the methylene protons at the benzyl position was observed, while in the region 1.1-2 ppm there was a broad signal for the protons of the PDEVBP main chain. The signal at 6.3-6.9 ppm was assigned to the aromatic protons of the PDEVBP block. All these signals exist in the ^{1}H NMR spectra of the BAB block copolymer in conjunction with the characteristic signals of the PEEK.



S3. The typical solution ^{31}P NMR spectrum of PVBPA-b-PEEK-b-PVBPA (acid derivative) in DMSO-d6



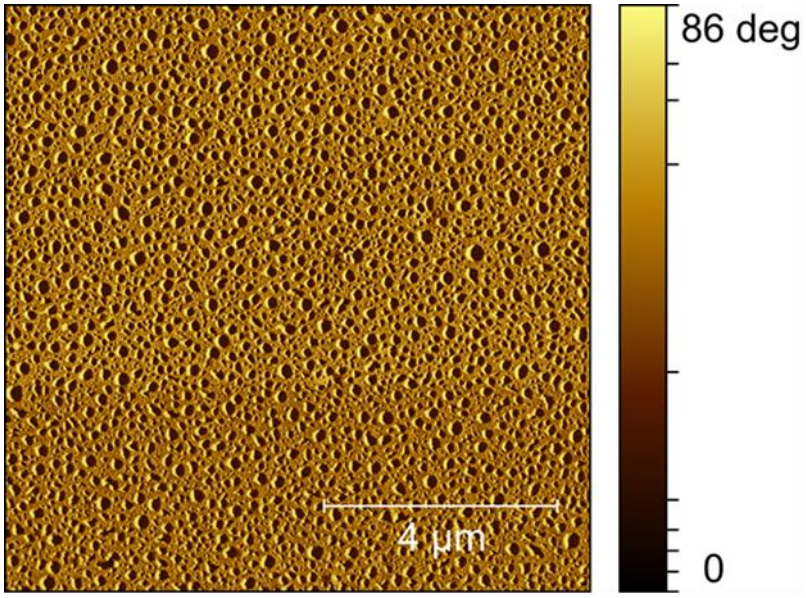
S4. Solid state ^{31}P NMR of poly(vinyl benzyl phosphonic acid) homopolymer recorded at room temperature and above 130 ℃. The black curve represents the signal from P-(OH) at room temperature and the blue curve corresponds to the signal from P-(OH) and P-O-P bond above 130 ℃.

AFM Experiments

In AFM, a probe with sharp tip (nominal tip radius on the order of 10 nm) located near the end of a cantilever beam is scanned across the sample surface using piezoelectric scanners. And. an optical lever detection system with laser monitors the changes in the tip sample interactions by reflecting laser off of the cantilever and onto a position-sensitive photodiode. During scanning, a specific operating parameter is maintained at a constant level, and images are generated through a feedback loop between the optical detection system and the piezoelectric scanners. There are three different imaging modes to generate a topographic view of sample surfaces, contact mode, noncontact mode and tapping made. Tapping-mode AFM was used to obtain height and phase imaging data simultaneously on a Nanoscope IIIa AFM from Microfabricated cantilevers or silicon probes (Nanoprobes, Digital Instruments) with 125 μm long cantilevers used at their fundamental resonance frequencies which typically varied from 270 to 350 kHz depending on the cantilever.

Table S1. Various factors and values obtained for the film of copolymer

Factor	
1. Root mean square roughness (Rq)	5.42116 nm
2. Skewness (Rsk)	-1.32621
3. Kurtosis (Rku)	3.98035
4. Maximum height of the profile (Pt)	30.7517 nm



S5 AFM phase image of PVBPA29-b-PEEK5-b-PVBPA29 scanned at a scale of 4 µm.

Table S2. Activation energy for various proton conductors

Entry	Proton conductor	[1]E_a	
1.	perfluorinated covalent triazine framework	0.22-0.37 eV	Ref. 3
2.	cationic molecular aggregates	0.22-0.36 eV	Ref. 4
3.	Free-Standing Serum Albumin Mats	0.29 ± 0.02 eV	Ref. 5
4.	PS-bPVBPA/PPO	0.19 eV	Ref. 6
5.	2m-2Be-4Cp	0.26 eV	Ref. 6
6.	PA33@PEM2.200	0.1 eV	Ref. 6
7.	Nafion hybrid membrane	0.29 eV	Ref. 7

[1]Grotthuss-type hopping mechanism

References

[1] Kumar, A., Pisula, W., Markova, D., Klapper, M., Müllen, K., Proton-Conducting Poly(phenylene oxide)–Poly(vinyl benzyl phosphonic acid) Block Copolymers via Atom Transfer Radical Polymerization, 2012, Macromolecualr Chem. & Phy., 213, 489-499
[2] Kumar, A., Self Assemblies of Poly (ether ether ketone) Block Copolymers for Biomedical Applications, 2021, ChemistrySelect, 6, 9060-9068
[3] Markova, D., Kumar, A., Pisula, W., Klapper, M., Müllen, K., Phosphonic acid-containing homo-, AB and BAB block copolymers via ATRP designed for fuel cell applications, 2009, Polymer, 50, 3411
[4] Guan, L., Guo, Z., Zhou, Q., Jhang, J., Cheng, C., Wang, S., Zhu, Z., Dai, S., Jin, S., A highly proton conductive perfluorinated covalent triazine framework via low-temperature synthesis, 2023, *Nature Communications*, 14, Article number: 8114

[5] Samanta, D., Mukherjee, P. S., Self-assembled multicomponent Pd_6 aggregates showing low-humidity proton conduction, 2014, *Chem. Commun.*, 50, 1595-1598
[6] Amdursky, N., Wang, X., Meredith, P., Bradely, D. C. D., Stevends, M. M., Long-Range Proton Conduction across Free-Standing Serum Albumin Mats, 2016, Ad. Mat., 14, 2692-2698
[7] Gilbert, P., Stankovic, J., Galaffu, N., Abrahams, I., Sullivan, A. C., Covalently attached phosphonic acid-Si_2O_3-PEO polymer membranes for PEMFC applications, 2024, Journal of Applied Polymer Science, 39, e56001
[8] Wang, H., Zhao, Y., Shao, Z., Xu, W., Wu, Q., Ding, X., Hou, H., Proton Conduction of Nafion Hybrid Membranes Promoted by NH_3-Modified Zn-MOF with Host–Guest Collaborative Hydrogen Bonds for H_2/O_2 Fuel Cell Applications, 2021, *ACS Appl. Mater. Interfaces*, 6, 7485–7497