

Supporting Information

Synthesis of Sulfonated Polyphenylene Block Copolymers via In Situ Generation of Ni(0)

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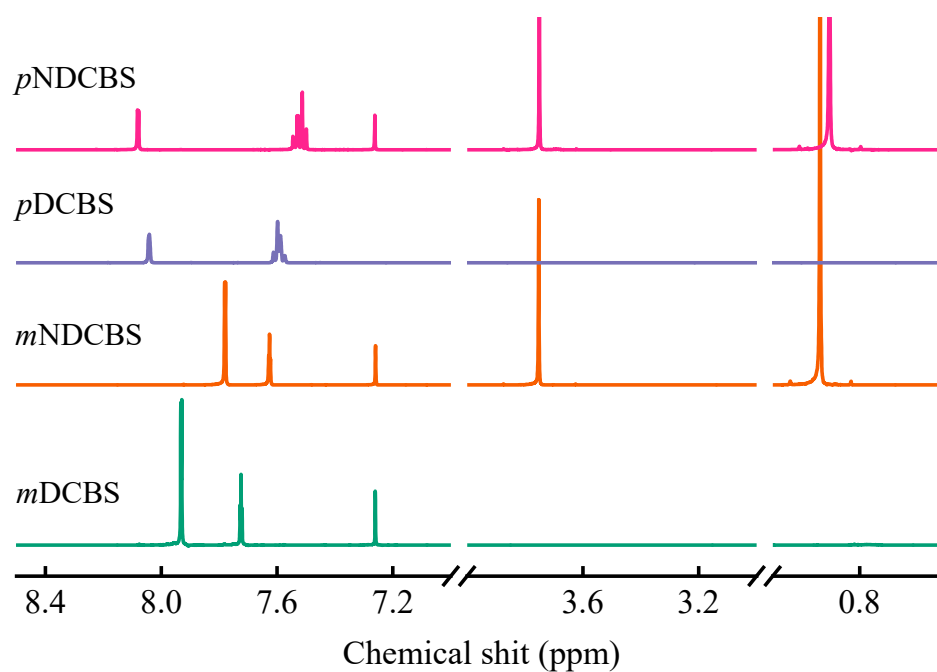


Figure S1. ¹H-NMR spectra of 3,5-dichlorobenzene sulfonyl chloride (*m*DCBS), 1-neopentylsulfonyl-3,5-dichlorobenzene (*m*NDCBS), 2,5-dichlorobenzene sulfonyl chloride (*p*DCBS), and 1-neopentylsulfonyl-2,5-dichlorobenzene (*p*NDCBS) recorded in CDCl₃ solution.

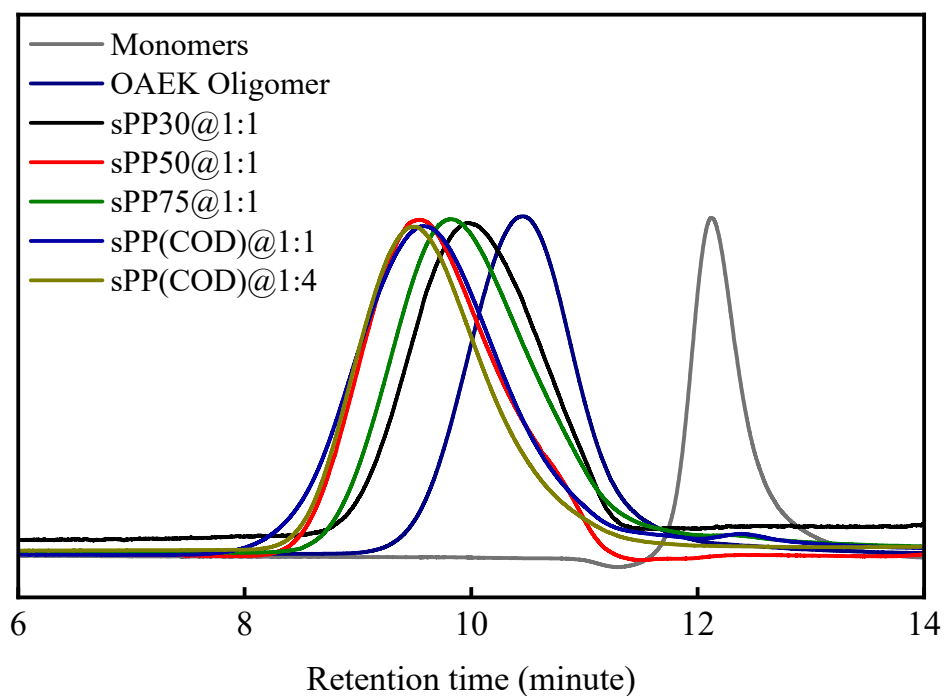


Figure S2. Gel permeation chromatography profiles of starting materials [pNDCBS, mNDCBS, and oligo(arylene ether ketone) (OAEK)] and sPP block copolymers catalyzed by different equivalents of $\text{NiBr}_2(\text{PPh}_3)_2$ [sPP30@1:1, sPP50@1:1, and sPP75@1:1] and $\text{Ni}(\text{COD})_2$ [sPP(COD)@1:1 and sPP(COD)@1:4] using different molar ratios of pNDCBS and mNDCBS; some properties of these copolymers are summarized in Table 1.

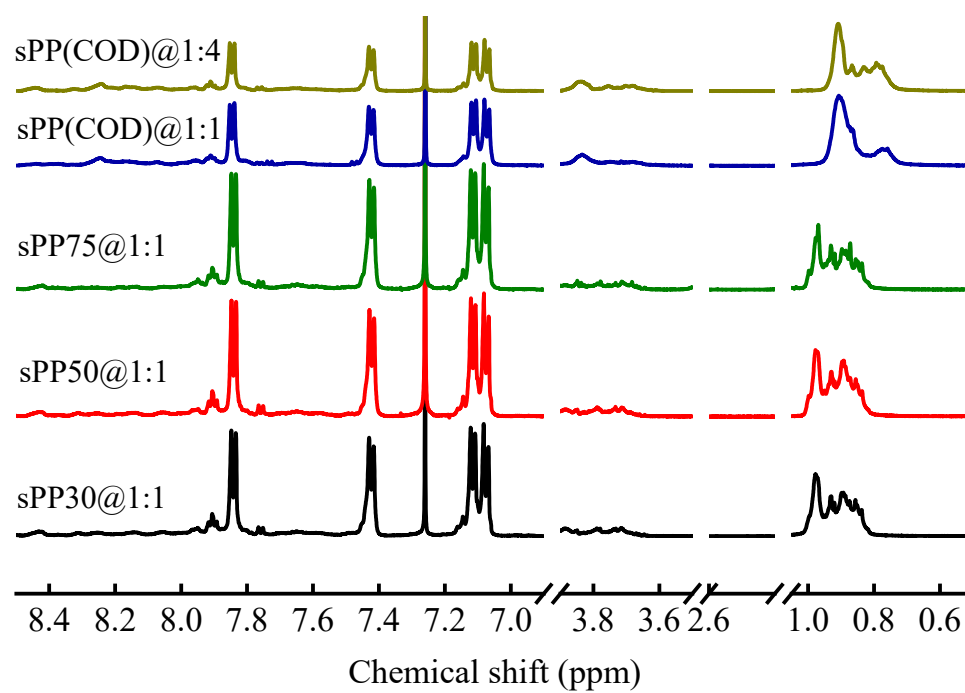


Figure S3. ^1H NMR spectra of block copolymers in their neopentyl protected forms recorded in CDCl_3 .

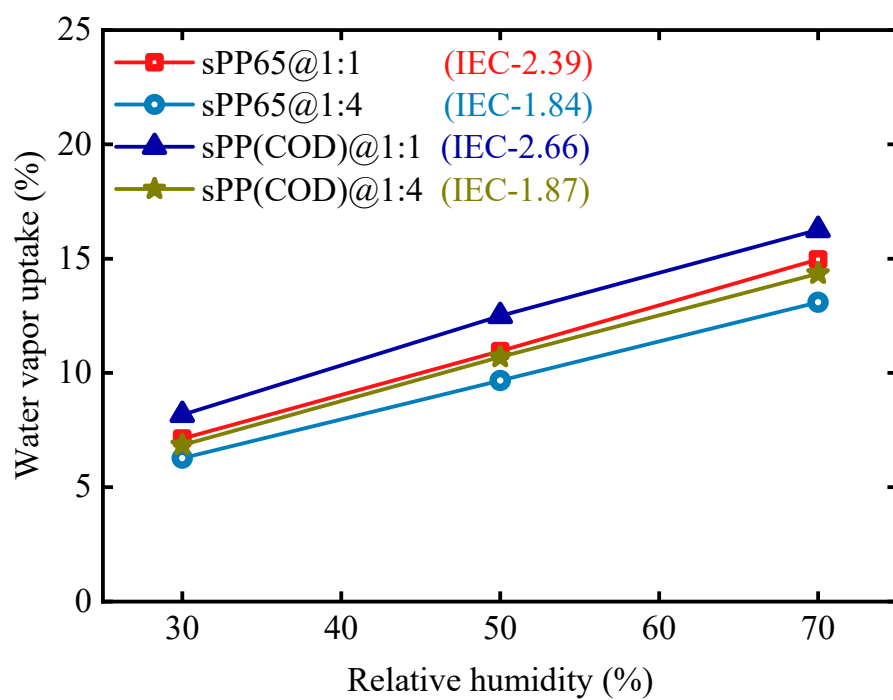


Figure S4. Dependence of water vapor uptake of the sPP membranes on the relative humidity measured at 70 °C.

Table S1. Summary of Ni(II)-salt-catalyzed polymerization in previous studies and current work

Poly(phenylene)s	Catalyst	Catalyst equivalents	Ligand used	Ligand equivalents	References
SFPP	NiCl ₂ (PPh ₃) ₂	0.030	PPh ₃	13	1
PBP-Z	NiCl ₂ (PPh ₃) ₂	0.030	PPh ₃	12	7
sPP-b-PES	NiBr ₂	0.070	PPh ₃	07	8
sPP-b-PKS	NiBr ₂	0.070	PPh ₃	07	8
sPP-b-PPSU	NiBr ₂	0.070	PPh ₃	07	8
sPP-b-PPES	NiBr ₂	0.070	PPh ₃	07	8
PTSP-b-PAESs	NiBr ₂	0.200	PPh ₃	10	9
PPBPs	NiCl ₂ (PPh ₃) ₂	0.033	PPh ₃	12	12
PES	NiCl ₂	0.050	PPh ₃	24	21
PEEK	NiCl ₂	0.050	PPh ₃	02	26
PAPO	NiCl ₂	0.050	PPh ₃	02	27
sPP65@1:1	NiBr ₂ (PPh ₃) ₂	0.065	PPh ₃	10	This work
sPP65@1:4	NiBr ₂ (PPh ₃) ₂	0.065	PPh ₃	10	This work

SFPP - Poly(4-phenoxybenzoyl-1,4-phenylene) with 1,1,2,2-tetrafluoro-2-oxyethane-1-sulfonic acid; PBP-Z - poly(2,5-benzophenone-co-4'-fluorine-2,5-benzophenone); sPP-b-PES – No abbreviation provided; sPP-b-PKS - No abbreviation provided; sPP-b-PPSU - No abbreviation provided; sPP-b-PPES - No abbreviation provided; PTSP-b-PAESs - poly(tri-sulfonated phenylene)-block-poly(arylene ether sulfone) copolymers; PPBPs - poly(4-phenoxybenzoyl-1,4-phenylene)s; PES – poly(ether sulfone)s; PEEK - poly(ether ketone)s; PAPO - poly(arylene phosphine oxide).