Electronic Supplementary Information for

Precise synthesis of amphiphilic diblock copolymers consisting of various ionic liquid-type segments and their influence on physical gelation behavior in water

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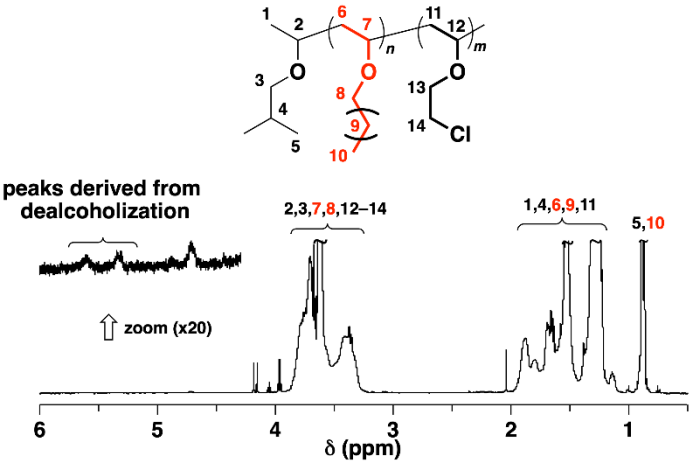

Figure S1. ^{1}H NMR spectrum of ODVE$_n$-*b*-CEVE$_m$: $[ODVE]_0$ = 0.20 M, $[CEVE]_{add}$ = 1.6 M, $[IBEA]_0$ = 4.0 mM, $[Et_{1.5}AlCl_{1.5}]_0$ = 20 mM, [ethyl acetate] = 1.0 M in toluene at 20 ºC. (in $CDCl_3$ at 30 ºC)

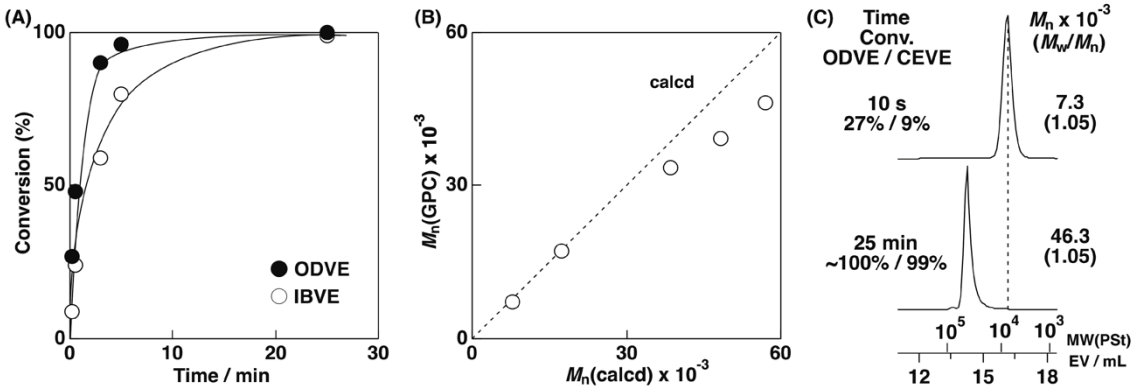

Figure S2. Synthesis of ODVE$_{50}$-*co*-CEVE$_{400}$ by living cationic copolymerization (entry 23, Table 1). (A) Time-conversion plots of the copolymerization, (B) the M_n values, and (C) MWD curves of the products obtained: $[ODVE]_0$ = 0.20 M, $[CEVE]_0$ = 1.6 M, $[IBEA]_0$ = 4.0 mM, $[Et_{1.5}AlCl_{1.5}]_0$ = 5.0 mM, $[SnCl_4]_0$ = 10 mM, $[DTBP]_0$ = 10 mM, [1,4-dioxane] = 1.2 M in toluene at 20 ºC.

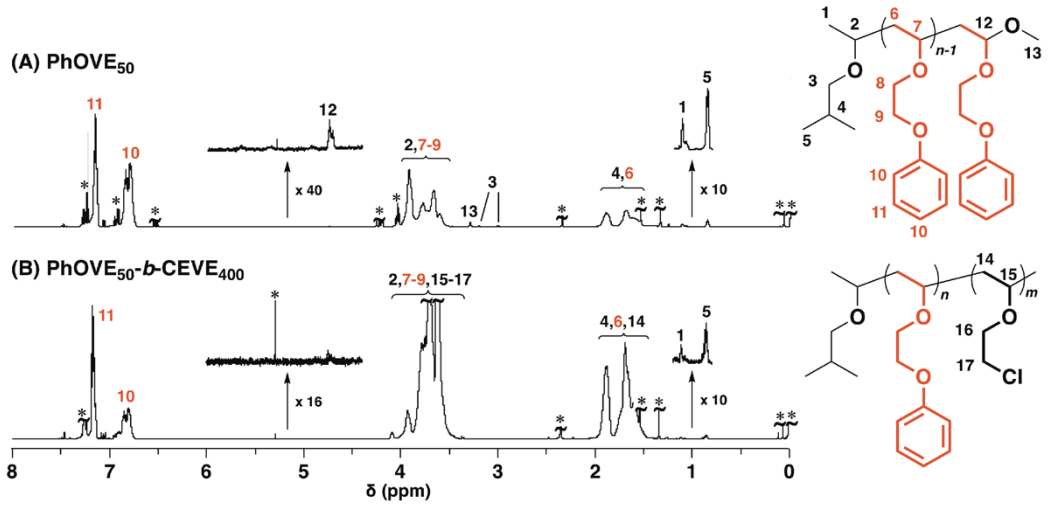

Figure S3. ^{1}H NMR spectra of (A) $PhOVE_{50}$ (the upper curve in Figure 4B) and (B) $PhOVE_{50}$-*b*-$CEVE_{400}$ (entry 25, Table 1; the lower curve in Figure 4B) (in $CDCl_3$ at 30 ºC; * monomer, solvent, toluene, water, grease, TMS).

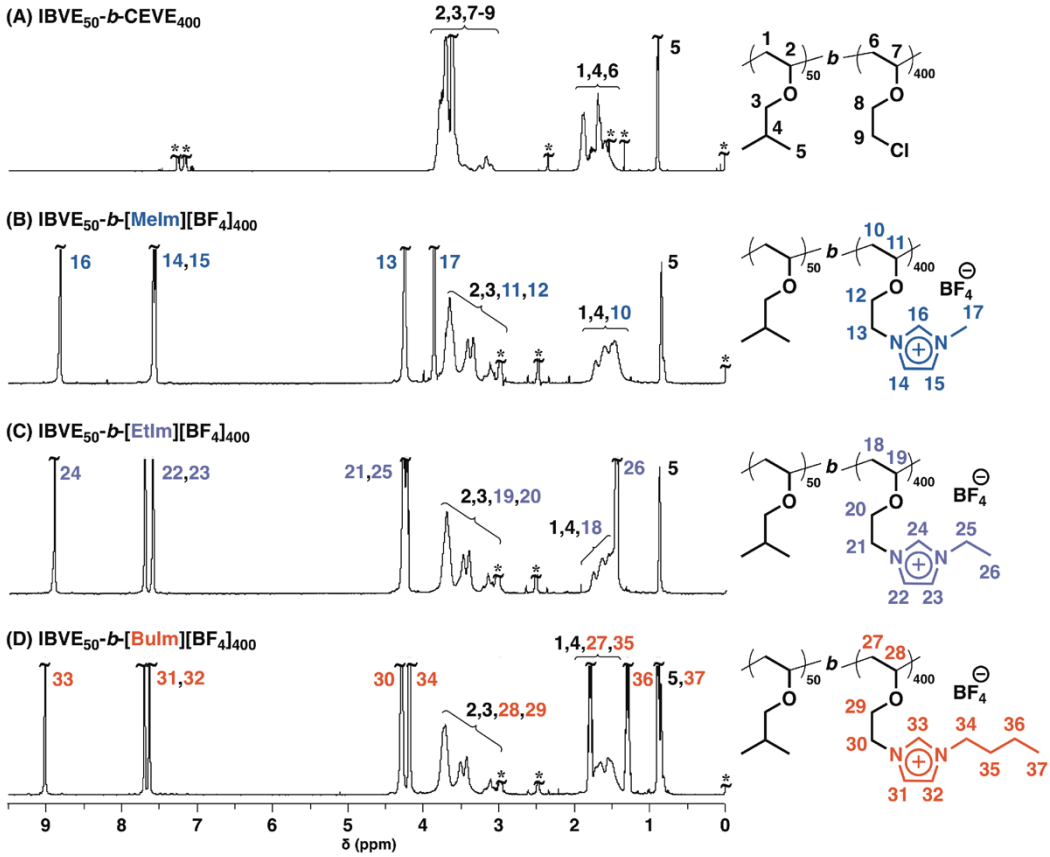

Figure S4. ^{1}H NMR spectra of (A) $IBVE_{50}$-*b*-$CEVE_{400}$ in $CDCl_3$ at 30 ºC, (B) $IBVE_{50}$-*b*-[MeIm][BF_4]$_{400}$, (C) $IBVE_{50}$-*b*-[EtIm][BF_4]$_{400}$, and (D) $IBVE_{50}$-*b*-[BuIm][BF_4]$_{400}$ in DMSO-d_6 at 100 ºC; *solvent, toluene, H_2O.

Table S1. Critical gelation concentration and physical gelation temperature of IBVE$_n$-*b*-[Me$_2$Im][BF$_4$]$_{400}$ in 1 wt% aqueous solution.

Entry	IBVE$_n$-*b*-[Me$_2$Im][BF$_4$]$_{400}$ *n* =	Critical Gelation Concentration[b]
1	10	3 wt%
2	20	0.4 wt%
3	30	0.6 wt%
4	40	0.6 wt%
5	50	0.7 wt%
6	100	1 wt%
7	200	Insoluble

[a] Determined by ^{1}H NMR spectra of copolymers before and after chemical modifications. [b] Status of solution at 60 ºC.

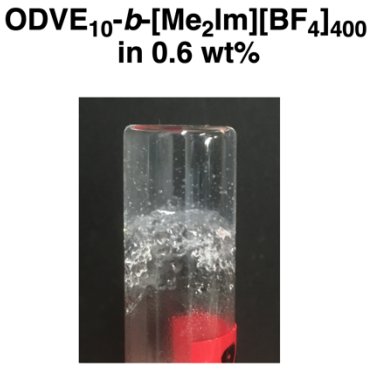

Figure S5. Photograph of physical gelation behavior of ODVE$_{10}$-*b*-[Me$_2$Im][BF$_4$]$_{400}$ in 0.6 wt% aqueous solution

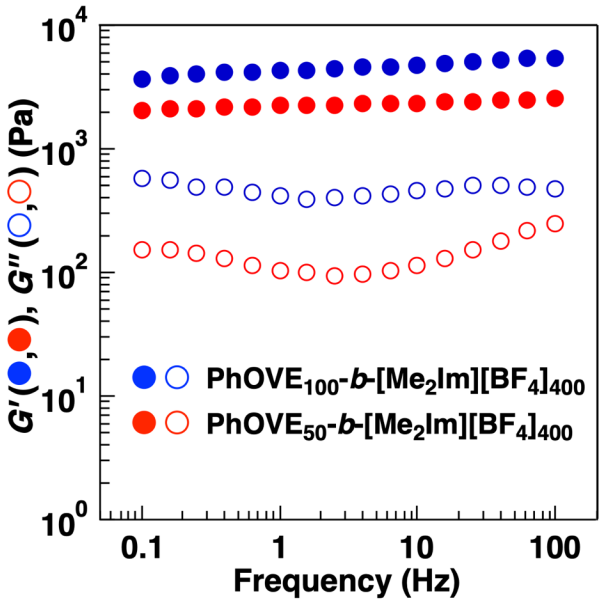

Figure S6. Frequency dependence of dynamic moduli, storage modulus *G*' (filled symbols) and loss modulus *G*" (open symbols) of PhOVE$_n$-*b*-[Me_2Im][BF_4]$_{400}$ (n = 50 and 100) in 10 wt% aqueous solutions at 55 ºC.

Table S2. Status of aqueous solutions of various amphiphilic block copolymers at different concentrations.

Entry	Hydrophobic	Unit	Cation	Anion	Unit	Conc. (wt%)			
						1	0.4	0.2	0.1
1	PhOVE	50	Me_2Im	BF_4	400	Gel	Sol	Sol	Sol
2	IBVE	20	MeIm	Cl	800	Gel	Sol	–	–
3	ODVE	10	Me_2Im	BF_4	400	Gel	Sol	–	–
4	ODVE	10	MeIm	BF_4	800	Gel	Sol	–	–
5	ODVE	10	MeIm	Cl	800	Gel	Gel	Gel	Sol
6	ODVE	10	MeIm	BF_4	1200	Gel	Sol	–	–
7	ODVE	10	MeIm	Cl	1200	Gel	Sol	–	–
8	ODVE	20	Me_2Im	BF_4	400	Sol	–	–	–
9	ODVE	20	Me_2Im	BF_4	800	Gel	Sol	–	–
10	ODVE	20	Me_2Im	Cl	800	Gel	Gel	Sol	–
11	ODVE	20	MeIm	BF_4	800	Sol	–	–	–
12	ODVE	20	MeIm	Cl	800	Gel	Sol	–	–
13	ODVE	20	MeIm	BF_4	1200	Sol	–	–	–
14	ODVE	20	MeIm	Cl	1200	Gel	Sol	–	–

[a] Determined using the test-tube inversion method (gel: retention, sol: flow) at 50 ºC.