Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information

Polymerized Ionic Liquid Diblock Copolymers: Impact of Water/Ion Clustering on Ion Conductivity

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Density Estimation of PIL Homopolymer (poly(MUBIm-Br)). The density of the PIL homopolymer (poly(MUBIm-Br)) was estimated from an additive contribution of components to the molar volume, which is analogous to the group contribution method, were the polymer density is estimated from the additive contribution of functional groups.[1] In other words, the chemical structure of poly(MUBIm-Br) can be divided into two components: poly(decyl methacrylate) (PDMA) and tethered IL moiety (*i.e.*, 1-methyl-3-butylimidazolium bromide, MBIm-Br) (Figure S1).

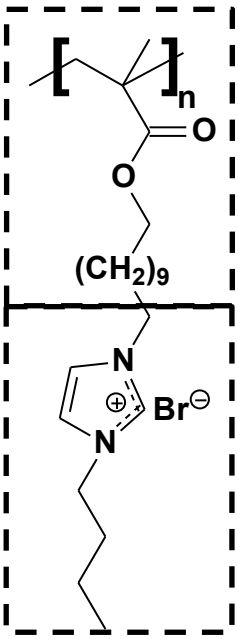

Figure S1. Chemical structure of poly(MUBIm-Br).

Thus, the molar volume (cm^3 mol^{-1}) of poly(MUBIm-Br) can be expressed as the additive of the molar volumes of these two components:

$$\frac{M}{\rho} = \frac{M_{PDMA}}{\rho_{PDMA}} + \frac{M_{IL}}{\rho_{IL}} \quad (1)$$

Where M, M_{PDMA}, M_{IL} and ρ, ρ_{PDMA}, ρ_{IL} are the molecular weights (g mol^{-1}) and densities (g cm^{-3}) of the PIL, PDMA and the MBIm-Br IL, respectively. Normalizing Eq. 1 by the total molecular weight yield:

$$\frac{1}{\rho} = \frac{w_{PDMA}}{\rho_{PDMA}} + \frac{w_{IL}}{\rho_{IL}} \quad (2)$$

From Eq. 1, the PIL density can be determined from the experimental density of MBIm-Br IL (ρ_{IL} = 1.29 g cm^{-3}) and the PDMA density was estimated using the known densities of poly(butyl methacrylate), poly(hexyl methacrylate), poly(octyl methacrylate), and poly(dodecyl methacrylate) (ρ_{PDMA} = 0.948 g cm^{-3}). The weight fractions of IL (w_{IL} = 0.48) and of PDMA (w_{PDMA} = 0.52) were calculated from the chemical structure (Figure S1). Thus, the calculated density for PIL poly(MUBIm-Br) is 1.09 g cm^{-3}. In this study, we also assume that the variation of volume fraction due to the density change at different temperatures is negligible for these PIL copolymers.

Calculation of Ion Exchange Capacity (IEC). Ion exchange capacity (IEC) [meq g^{-1}] was quantified as the moles of imidazolium cations per gram of polymer.

$$IEC = \frac{x_{IL} \times 1000}{MW_{cp}^{*}} \quad (3)$$

$$MW_{cp}^{*} = (1 - x_{IL})MW_{MMA} + x_{IL}MW_{MUBIm} \quad (4)$$

x_{IL} is the IL composition (mole fraction) and MW_{cp}^{*} is the molecular weight of the repeat unit of the copolymer (without counter anions). MW_{MMA} (100.12 g mol^{-1}) and $MW_{MUB\,\mathrm{Im}}$ (387.62 g mol^{-1}) are the molecular weights of MMA and MUBIm IL (or IL without counter anion), respectively. The counter anion was not considered in this calculation because IEC of the polymer is independent of the counter ion.

SAXS

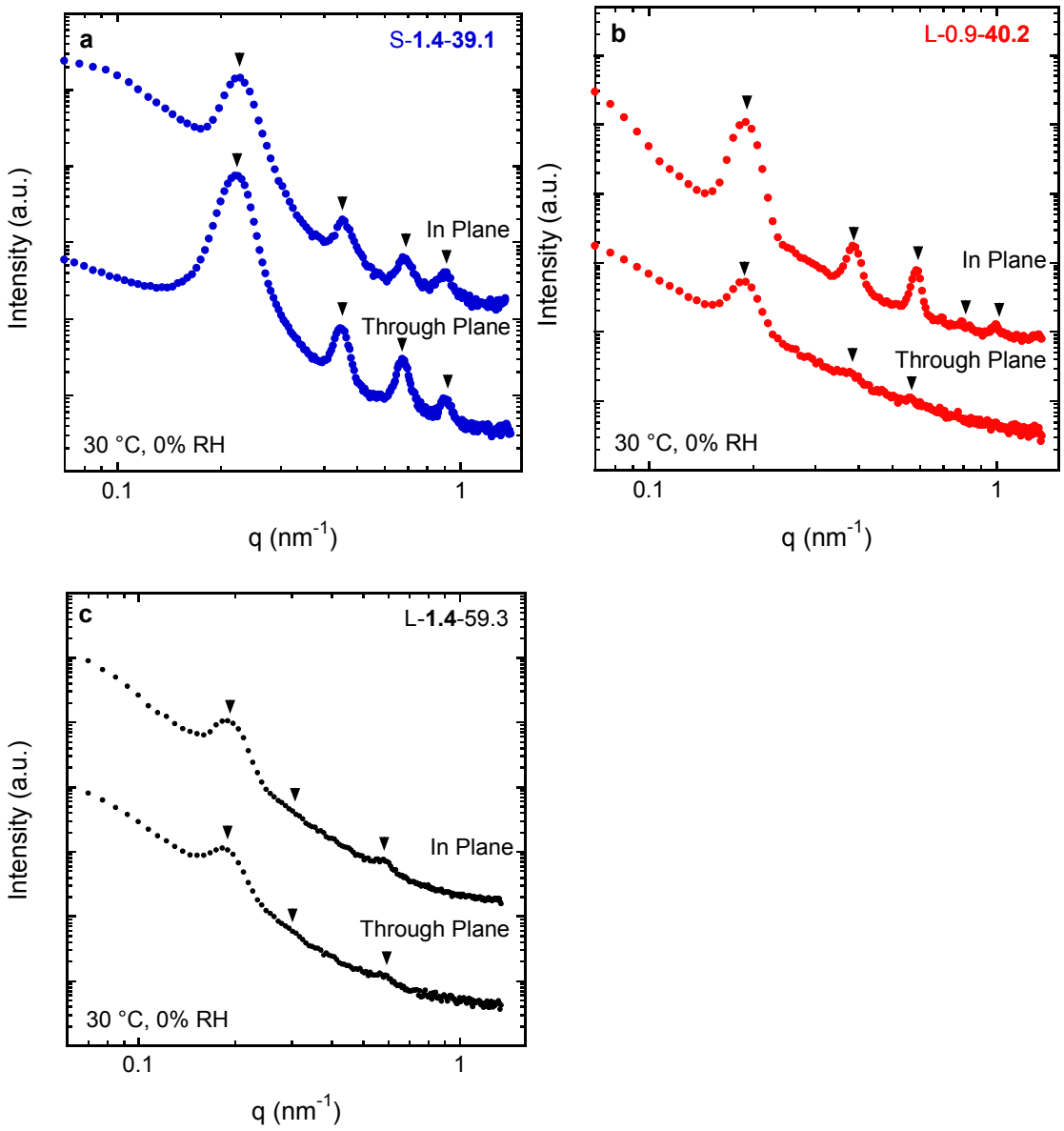

Figure S1. In-plane and through-plane SAXS at 30 °C under vacuum (0% RH): (a) S-1.4-39.1 (b) L-1.4-40.2 (c) L-1.4-59.3. Data are vertically offset for clarity.

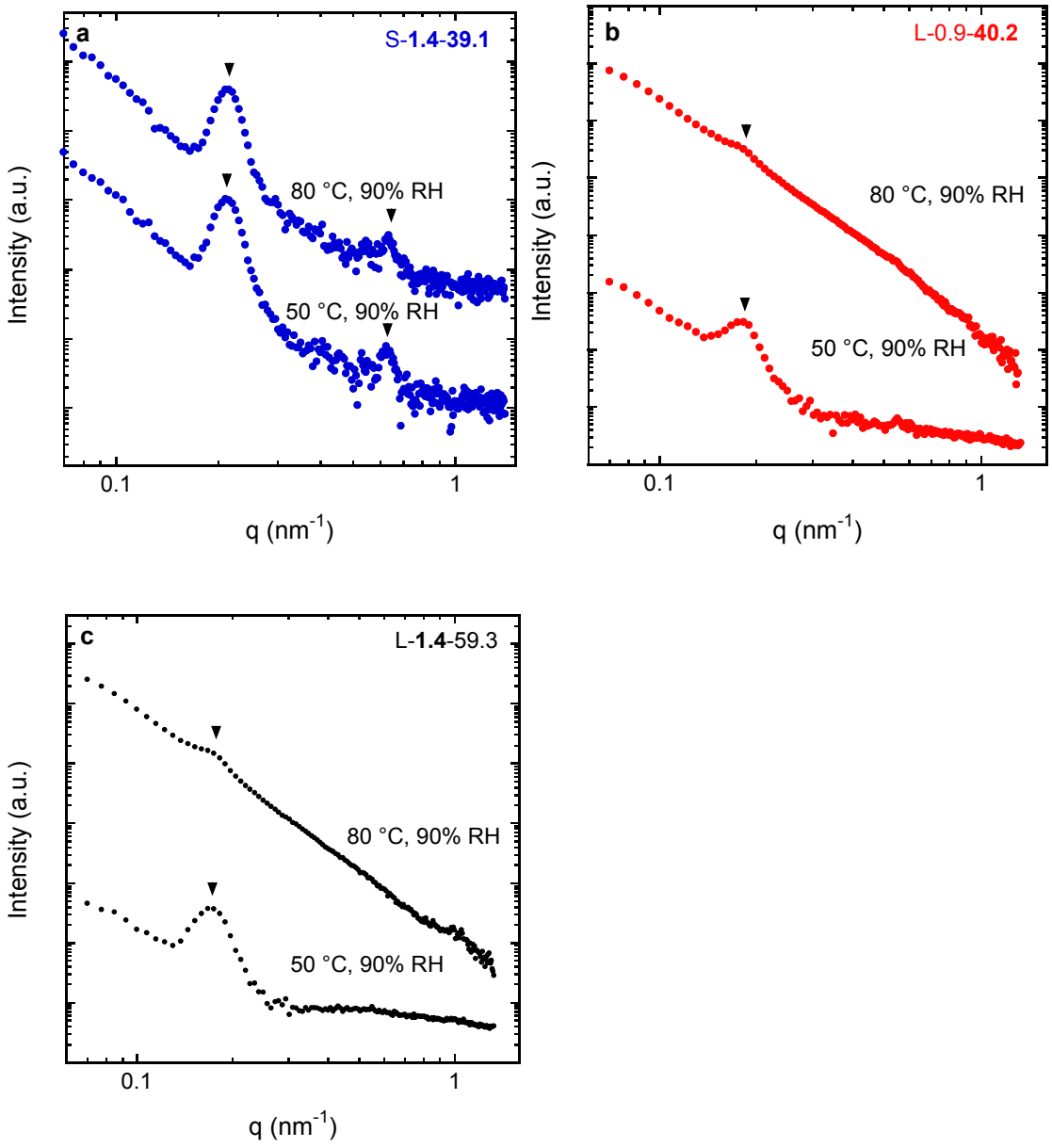

Figure S2. Through-plane SAXS at 90% RH and 50 and 80 °C for (a) S-1.4-39.1, (b) L-0.9-40.2, and (c) L-1.4-59.3. Arrows indicate peak positions. Data are offset for clarity. Graph (a) is reproduced from ref [2].

Table S1. Small-Angle X-ray Scattering Results.

Sample	Temp. (°C)	Humidity (%)	q^* (nm^{-1})	d^* (nm)[a]
S-1.4-39.1	30	0	0.25	25.1
	50	90	0.21	30.0
	80	90	0.215	29.2
L-0.9-40.2	30	0	0.225	27.9
	50	90	0.183	34.4
	80	90	0.175	35.9
L-1.4-59.3	30	0	0.225	27.9
	50	90	0.17	37.0
	80	90	0.17	37.0

[a]Correlation distance calculated by $d^* = 2\pi/q^*$, where q^* is the position of the primary peak obtained from 1-D SAXS data.

Notes and References

1. J. Fedderly, E. Compton and B. Hartmann, *Polymer Engineering and Science*, 1998, **38**, 2072-2076.
2. Y. Ye, S. Sharick, E. M. Davis, K. I. Winey and Y. A. Elabd, *ACS Macro Letters*, 2013, **2**, 575-580.