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Electronic Supplementary Information

A Facile Random Copolymer Strategy to Achieve Highly Conductive, Polymer Gel Electrolytes for Electrochemical Applications

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Synthesis of poly(styrene-*ran*-methyl methacrylate)

Poly(styrene-*ran*-methyl methacrylate) (PS-*r*-PMMA) copolymers in this work were prepared using one-pot reversible addition-fragmentation chain transfer (RAFT) polymerization with a RAFT agent of ethyl 2-(phenylcarbonothioylthio)-2-phenylacetate (Fig. S1a). A brief synthetic procedure is described for PS-*r*-PMMA-H. Both monomers (i.e., styrene and methyl methacrylate) were purified by passing through a column filled with basic alumina. Then, styrene (7.6 g, 72.9 mmol), methyl methacrylate (29.2 g, 291.8mmol), benzodithioate (0.0048 g, 0.015 mmol), and AIBN (0.0005 g, 0.00304 mmol) were mixed in a dried two-neck flask. The reaction mixture was purged with Ar gas at room temperature for 1 h. Then, the polymerization was carried out at 80 ºC for 18 h, followed by quenching with liquid nitrogen for termination. The solution was poured into a large amount of methanol for precipitation, which process was conducted three times. The resulting PS-*r*-PMMA was collected and dried at 50 ºC under reduced pressure. The adjustment of molecular weight of PS-*r*-PMMAs was achieved by controlling the polymerization time and feed ratio of monomer mixtures and the RAFT agent. For example, PS-*r*-PMMA-M was polymerized at a molar ratio of RAFT agent : monomer mixture ~ 5 : 60000 for 6 h. To further decrease molecular weight (namely, for PS-*r*-PMMA-L), the amount of monomer mixtures was reduced by half (i.e. mole ratio of RAFT agent : monomer mixture ~ 5: 30000), whereas the polymerization time (6 h) was fixed. It is noted that a molar ratio of AIBN : RAFT agent was 1: 5 for all cases. The control of PS-*r*-PMMA compositions was achieved by varying the feed monomer composition.

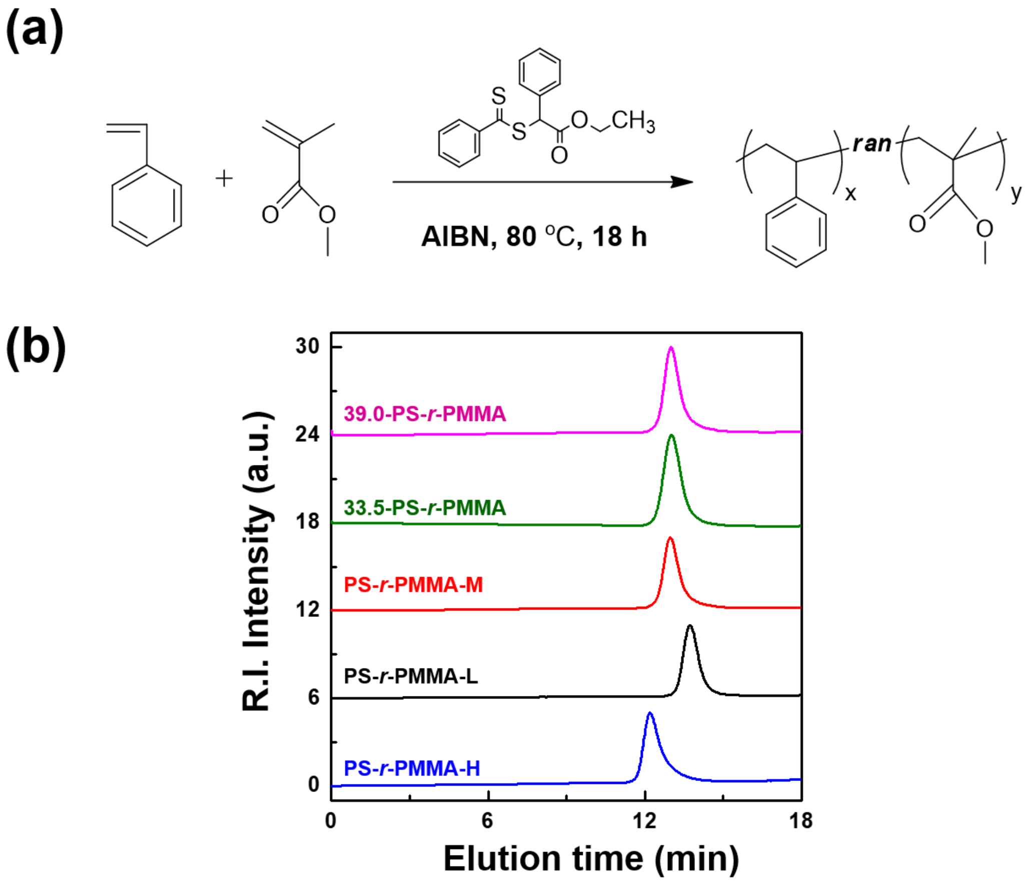

Fig. S1 (a) Synthetic route for PS-*r*-PMMAs. (b) SEC chromatograms of PS-*r*-PMMAs employed in this study.

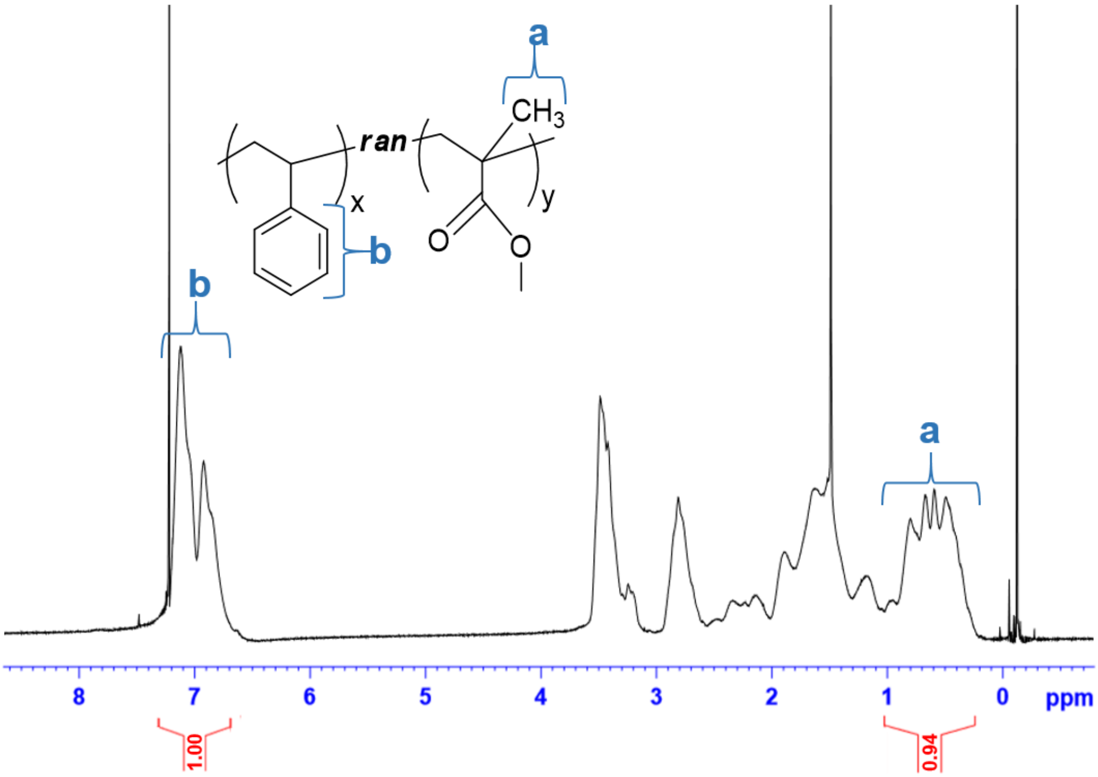

Fig. S2 ^{1}H NMR spectrum of 39.0-PS-*r*-PMMA.

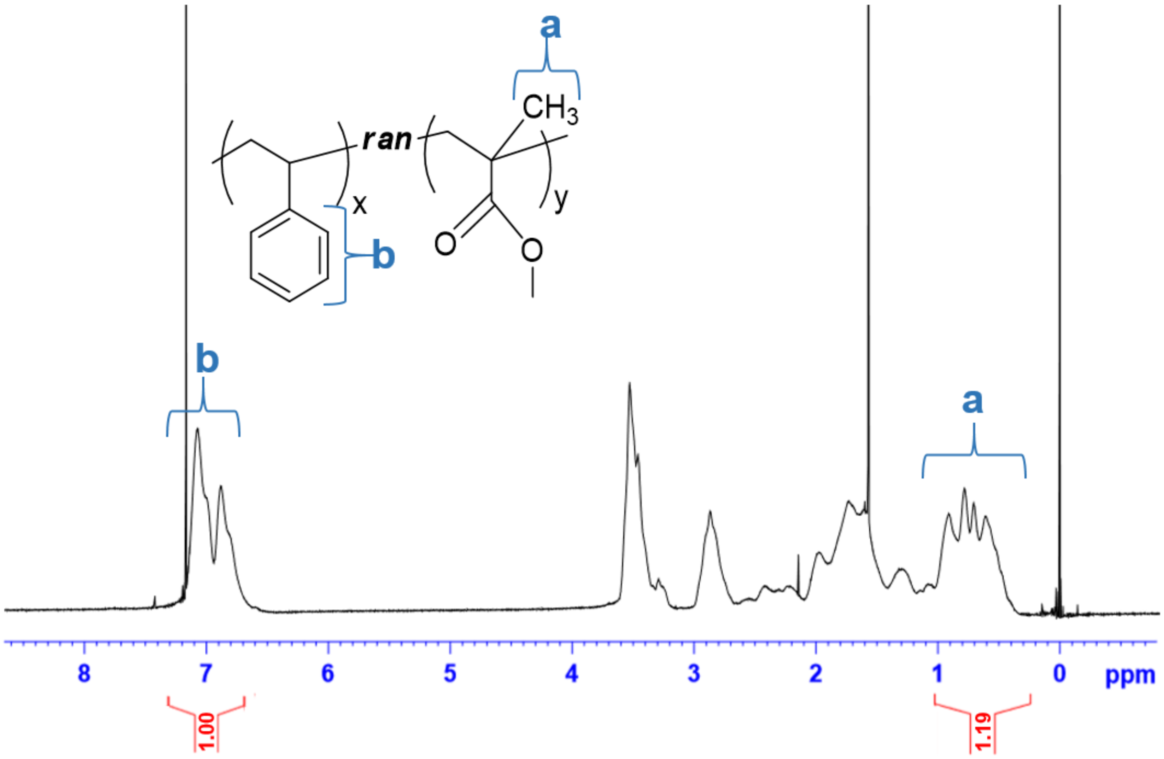

Fig. S3 ^{1}H NMR spectrum of 33.5-PS-*r*-PMMA.

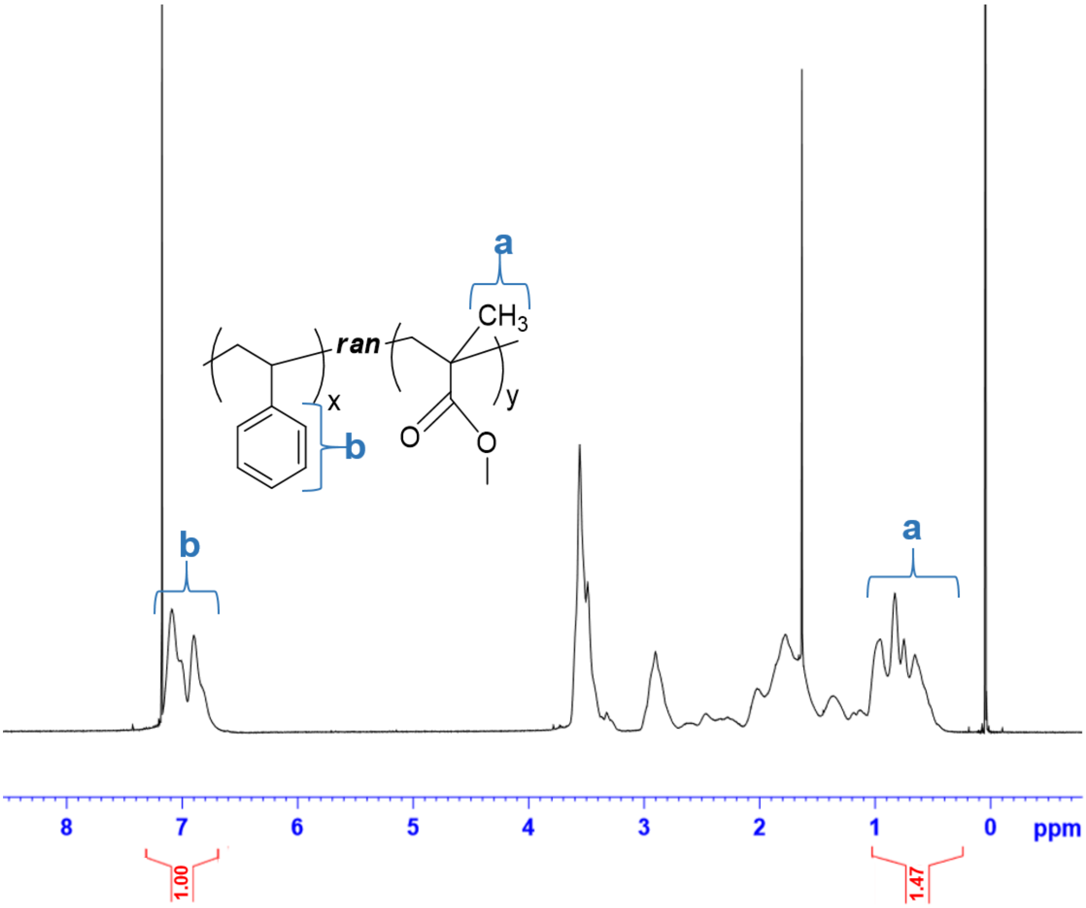

Fig. S4 ^{1}H NMR spectrum of PS-*r*-PMMA-M.

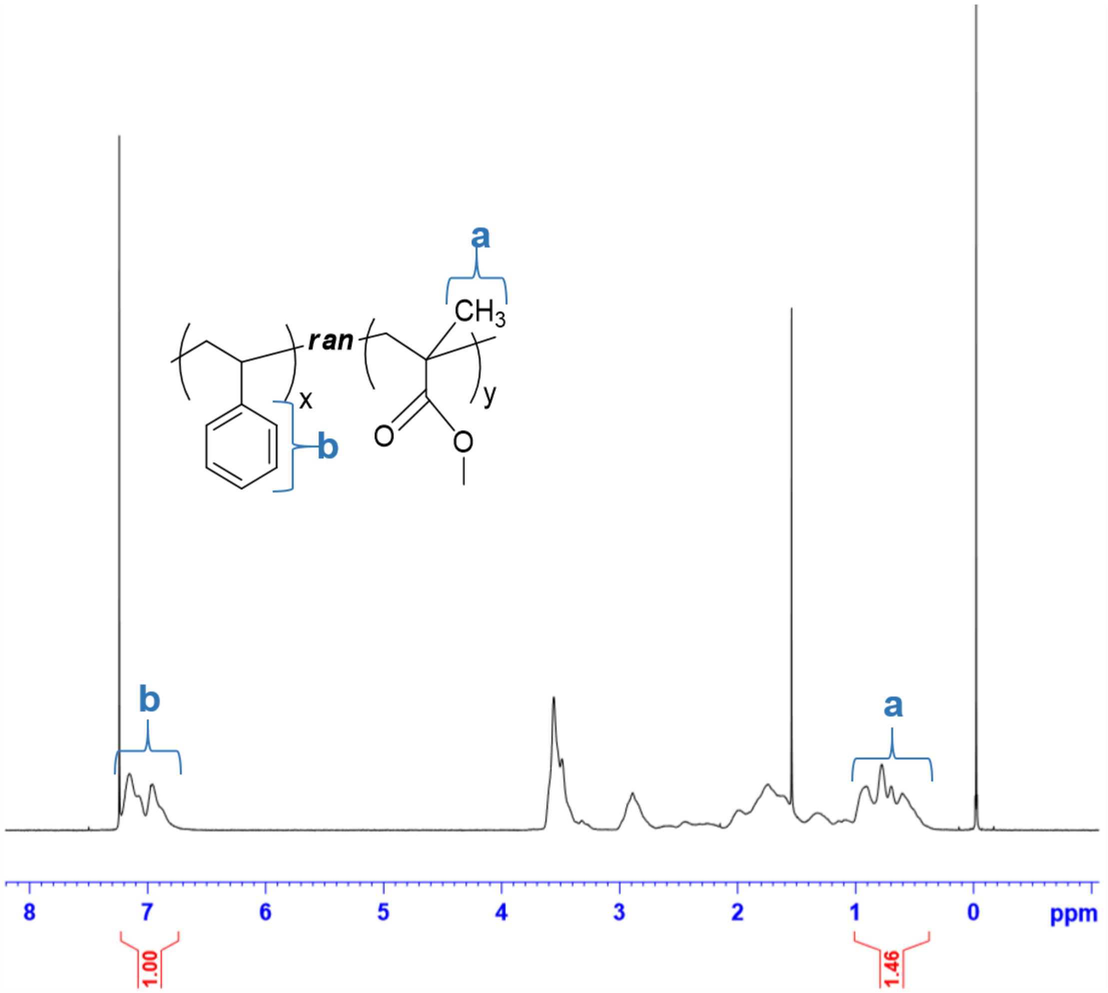

Fig. S5 ^{1}H NMR spectrum of PS-*r*-PMMA-L.

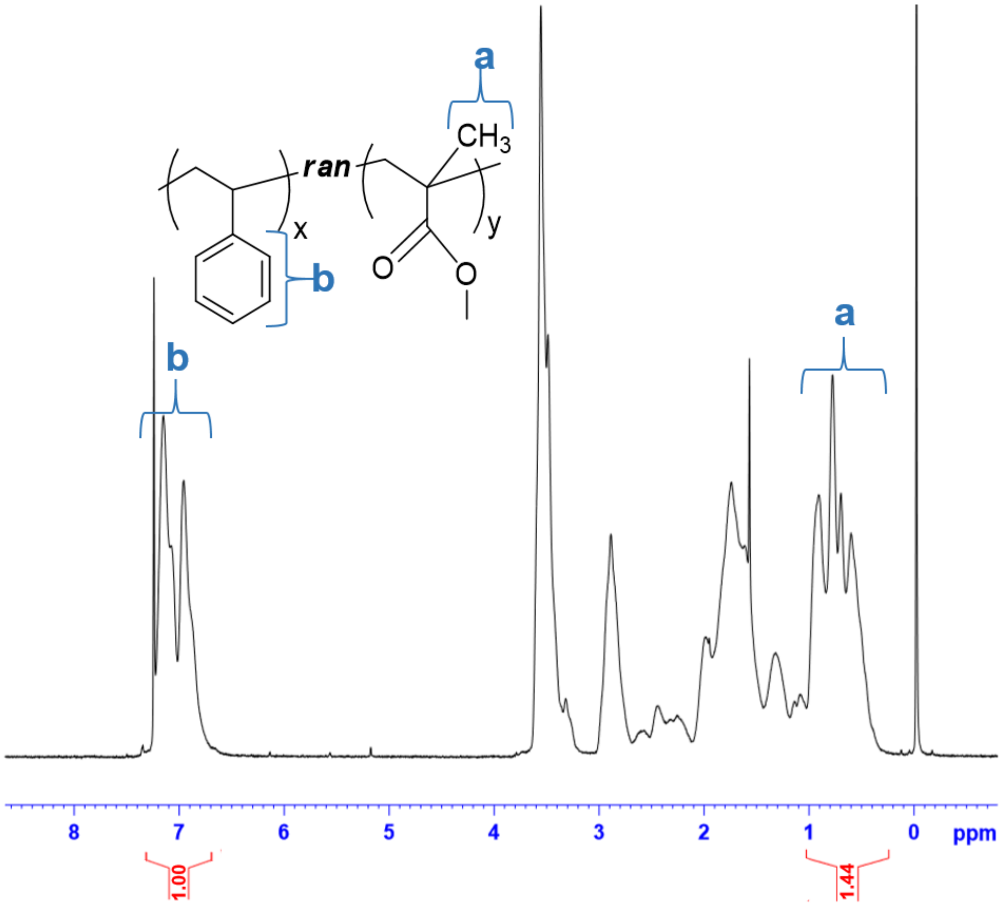

Fig. S6 ^{1}H NMR spectrum of PS-*r*-PMMA-H.

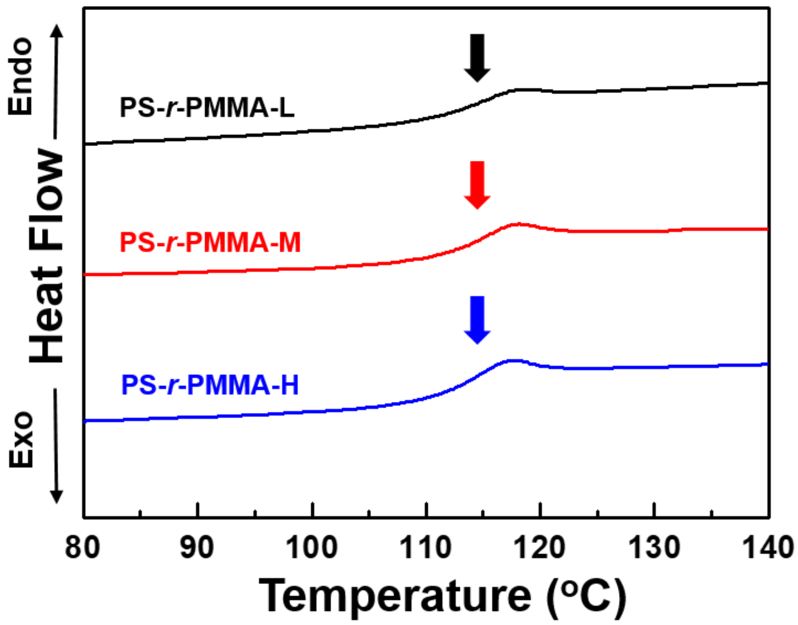

Fig. S7 DSC thermograms of PS-*r*-PMMA-L,-M,-H obtained during the second run at a heating rate of 10 ºC/min.

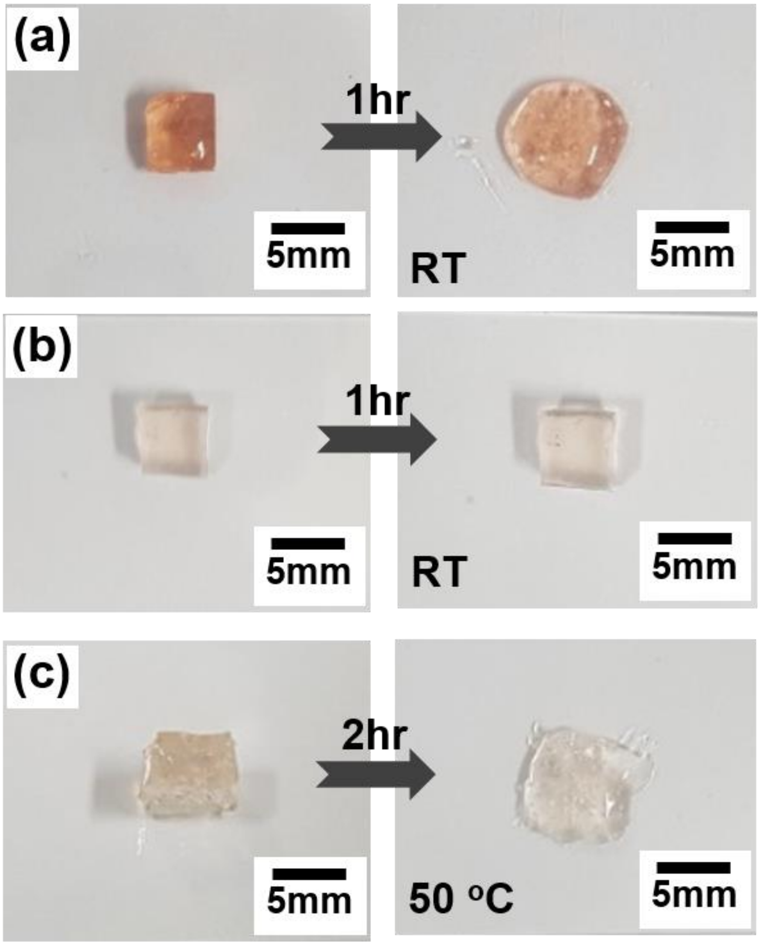

Fig. S8 Changes in a shape of PS-*r*-PMMA gels after 1 h: (a) PS-*r*-PMMA-L gel at RT, and PS-*r*-PMMA-M gel (b) at RT, and (c) 50 ºC, in which The 70 wt% ionic liquid ([EMI][TFSI]) was included in all gels. The shape of PS-*r*-PMMA-L gel having elastic modulus of ~2.3×10^4 Pa was deformed even after 1 h standing at RT, whereas the gel based on PS-*r*-PMMA-M having ~5.0×10^4 Pa at RT was maintained its original shape. However, the improvement of mechanical robustness is still necessary for higher dimensional stability even at elevated temperature (e.g. 50 ºC), so we adjusted the total molecular weight of PS-*r*-PMMA.

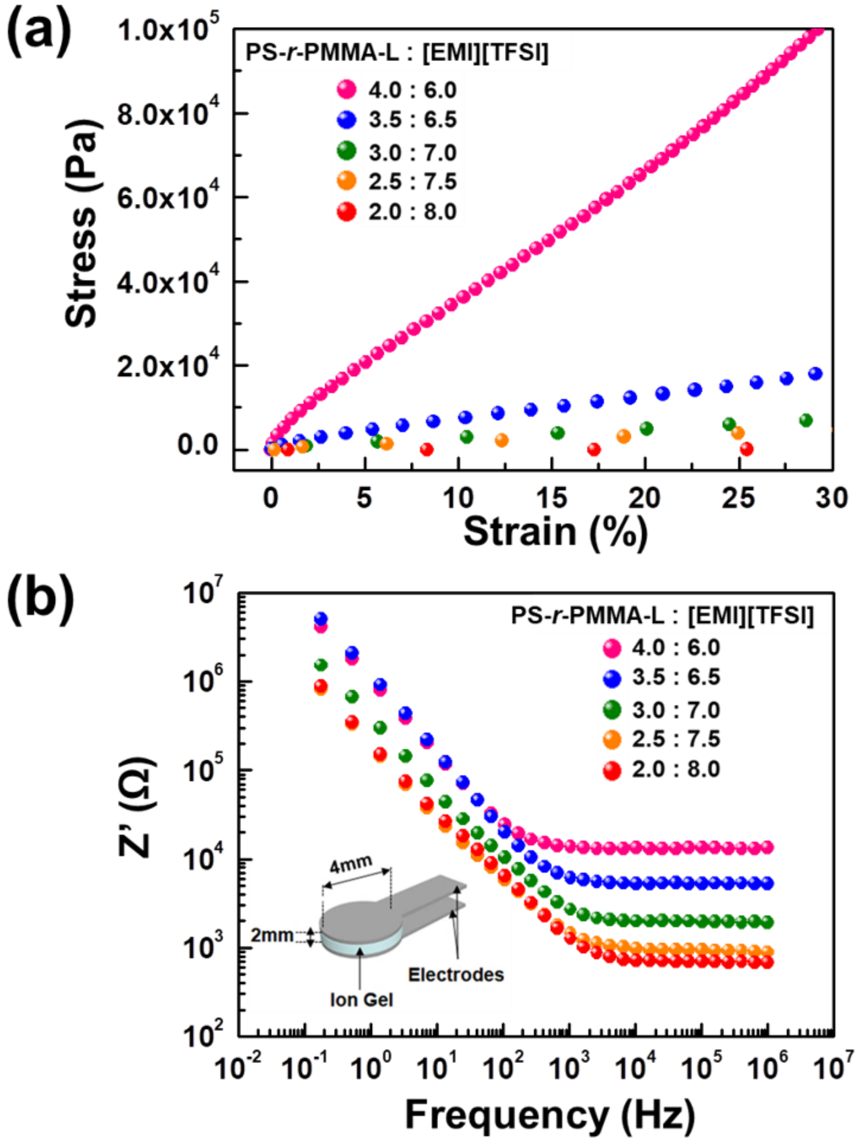

Fig. S9 (a) Stress-strain curves, and (b) frequency dependence of the resistance (Z') for ion gels, in which five different weight ratios of PS-*r*-PMMA-L and [EMI][TFSI] were tested.

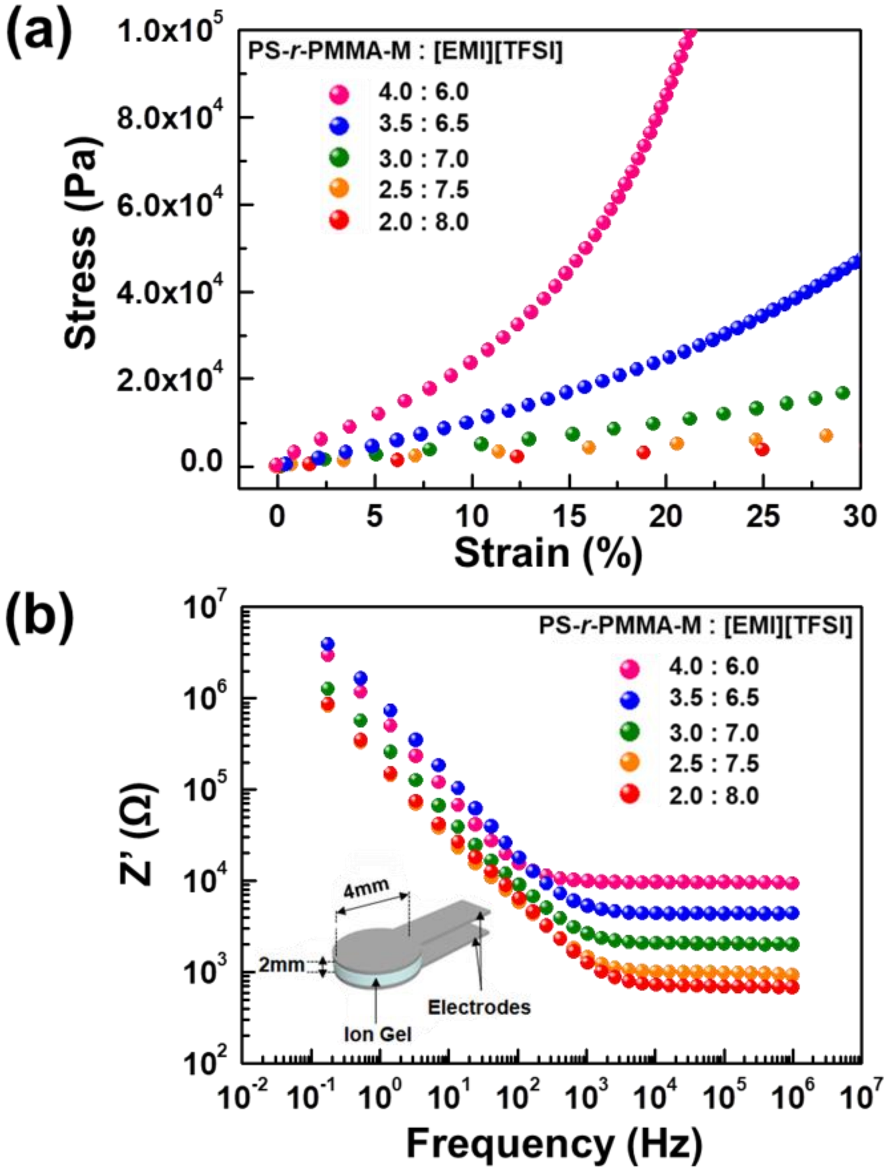

Fig. S10 (a) Stress-strain curves, and (b) frequency dependence of the resistance (Z’) for ion gels, in which five different weight ratios of PS-*r*-PMMA-M and [EMI][TFSI] were tested.

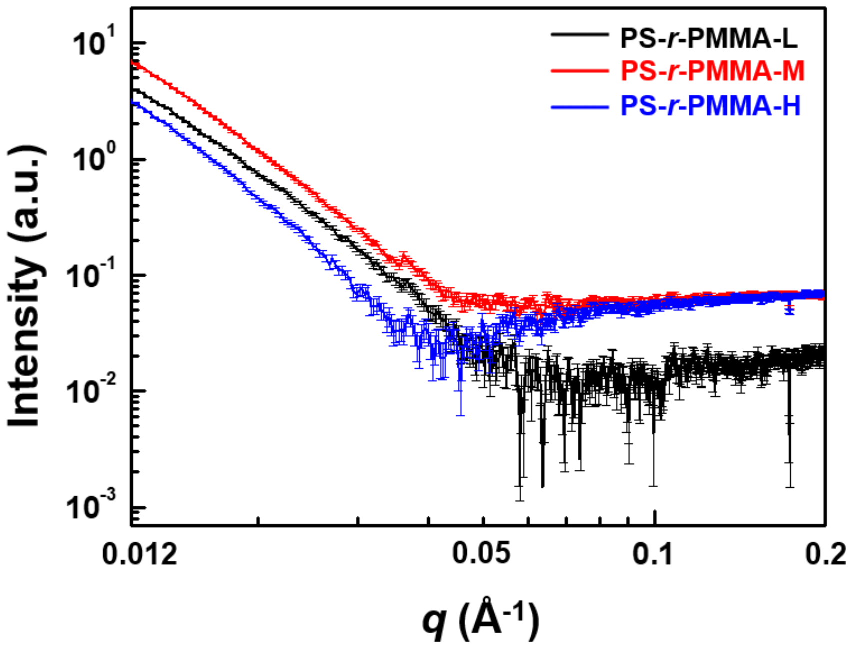

Fig. S11 Small angle x-ray scattering (SAXS) profiles of neat PS-*r*-PMMAs, in which any characteristic scatterings were not observed, indicating homogeneous phase of random copolymers.