Supplementary Information for:

Control of Hard Block Segments of Methacrylate-based Triblock Copolymers for Enhanced Electromechanical Performance

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Scheme S1. Synthesis of (A) MMA-b-DMA-b-MMA (PMDM) and (B) tBMA-b-DMA-b-tBMA (PTDT) triblock copolymers by sequential living radical polymerization, employing EDBCPA difunctional initiator coupled with Ru-catalyst and Bu$_3$N. The thermolysis of PTDT at 200 °C introduces acid groups into the hard block segment of the triblock copolymer leading to MAA-b-DMA-b-MAA (PADA) in (B) bottom.
Fig. S1 SEC curves of PTMDMT and PAMDMA measured in THF eluent.
Fig. S2 (A) SEC curves and (B) $^1$H NMR spectra of PDMA and PMDM, (C) SEC curves and (D) $^1$H NMR spectra of PDMA, PTDT, and PADA. SEC measurement is conducted in THF eluent. $^1$H NMR measurement is performed at room temperature in CDCl$_3$.

The PMDM and PTDT triblock copolymer with PDMA macroinitiator were investigated for its molecular weight and MWD by the use of SEC measurement in Fig. S2 (A) and (C). $^1$H NMR spectra of PMDM and PTDT were shown in Fig. S2 (B) and (D). The results from SEC curves and $^1$H NMR spectra demonstrated that this Ru based ATRP system properly suited for PMDM and PTDT copolymerization. Thermolysis of PTDT was performed at 200 $^\circ$C for 60 min to dissociate the tert-butyl group of tBMA units leading to generating PADA.
triblock copolymer. This result was evaluated by measuring SEC in Fig. S2 (C). The number averaged molecular weight of PADA ($M_n = 84,000$) was a little decreased in comparison to that of PTDT ($M_n = 92,000$) because of loss of tert-butyl groups. $^1$H NMR spectrum of PADA in Fig. S2 (D) exhibited clear peak disappearance at 1.35 ppm ($g$) originated from tert-butyl groups of PTDT indicating that thermolysis condition at 200 °C for 60 min was effective to generate PADA triblock copolymer.

![Fig. S3 DSC curves of PTMDMT3, PMDM, PTDT, PAMDMA3, and PADA measured in the temperature range from -70 °C to 150 °C (1st run curves).](image.png)
Fig. S4 Transverse strain changes as a function of electric field: PTMDMT, PMDM,\(^1\) and PDMS.\(^2\)

References
