Supplementary Information for:

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

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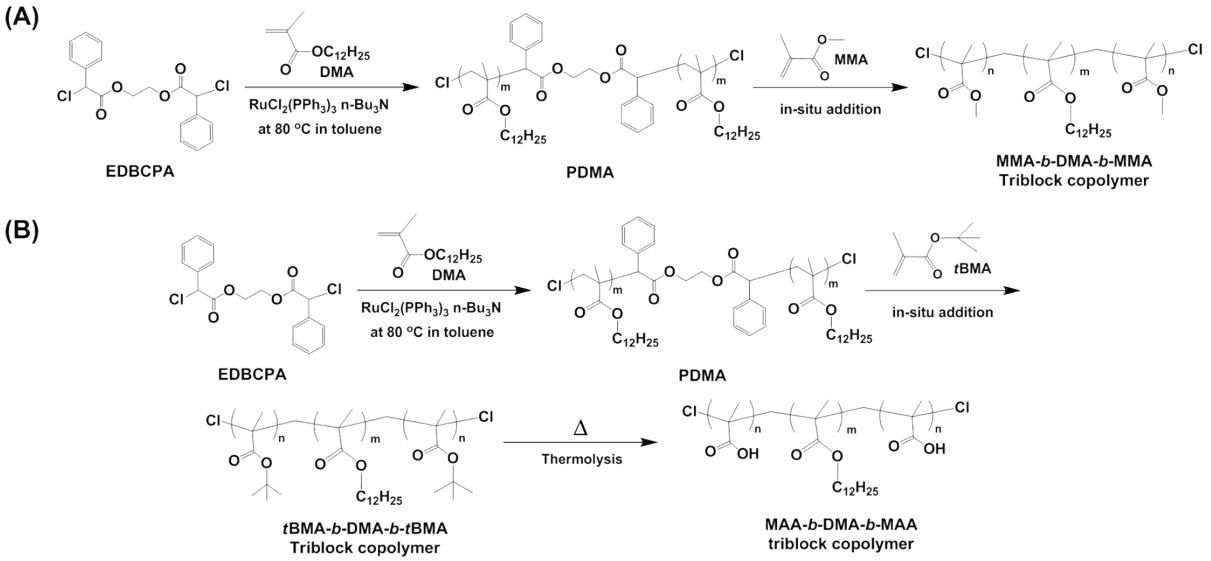

Scheme S1. Synthesis of (A) MMA-*b*-DMA-*b*-MMA (PMDM) and (B) *t*BMA-*b*-DMA-*b*-*t*BMA (PTDT) triblock copolymers by sequential living radical polymerization, employing EDBCPA difunctional initiator coupled with Ru-catalyst and Bu_3N. The thermolysis of PTDT at 200 ^oC introduces acid groups into the hard block segment of the triblock copolymer leading to MAA-*b*-DMA-*b*-MAA (PADA) in (B) bottom.

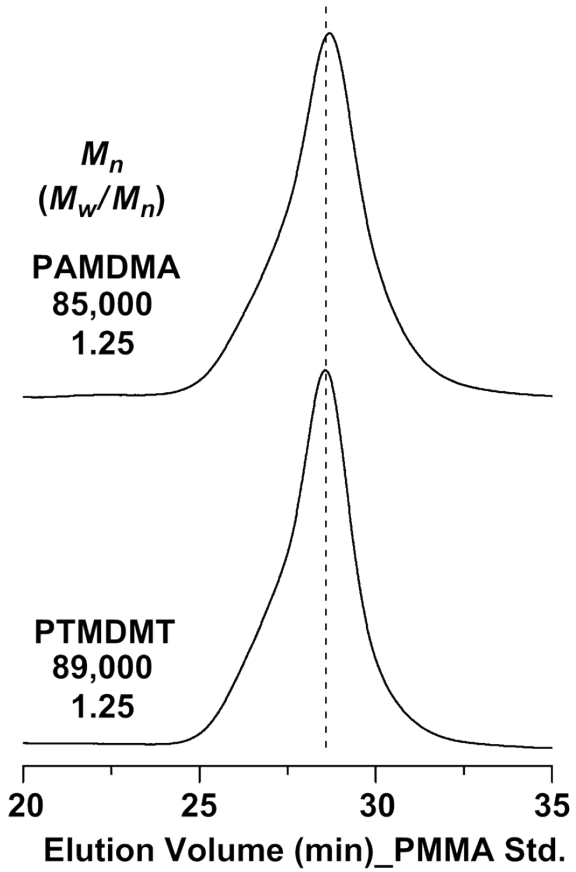

Fig. S1 SEC curves of PTMDMT and PAMDMA measured in THF eluent.

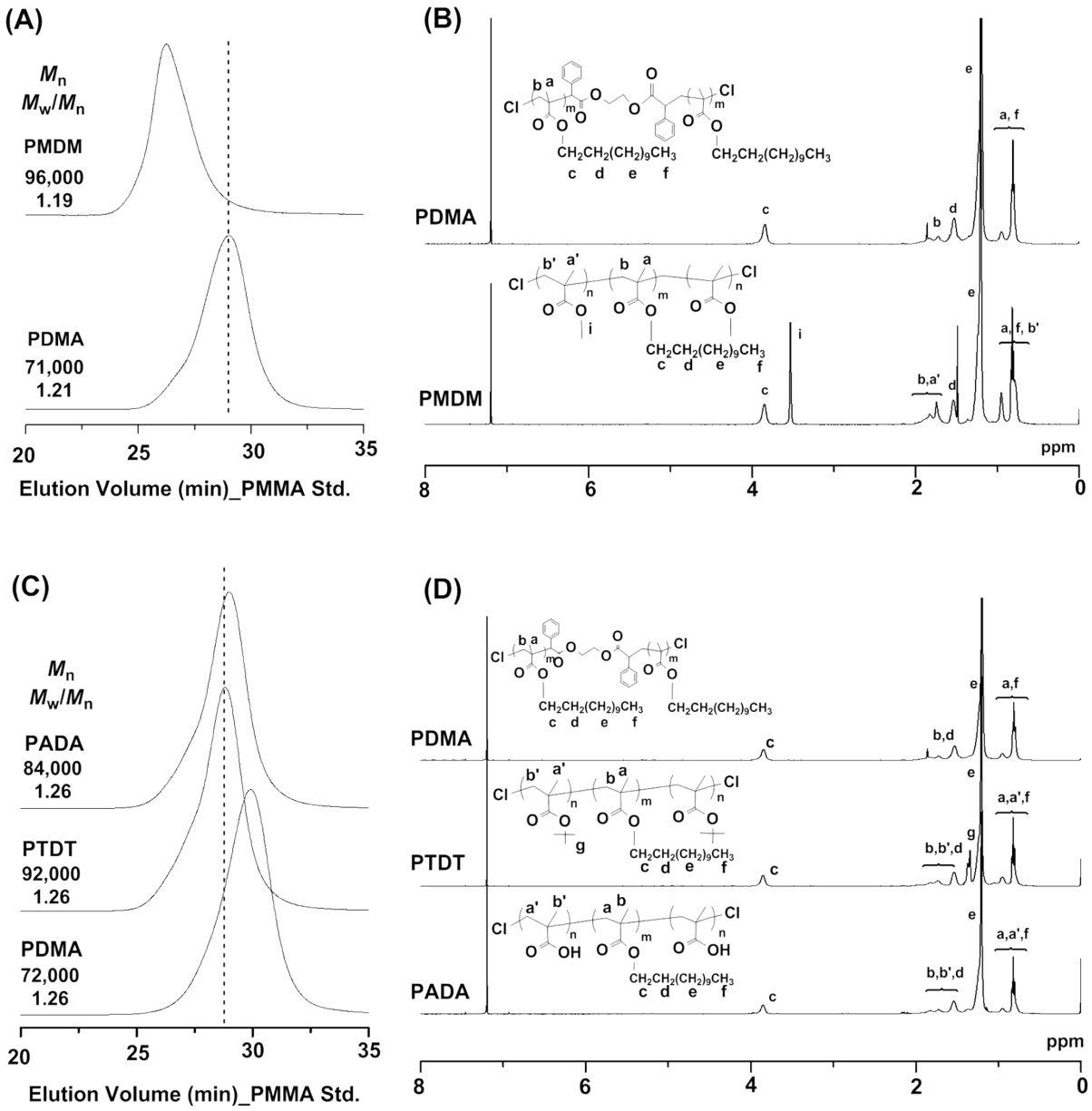

Fig. S2 (A) SEC curves and (B) ^{1}H NMR spectra of PDMA and PMDM, (C) SEC curves and (D) ^{1}H NMR spectra of PDMA, PTDT, and PADA. SEC measurement is conducted in THF eluent. ^{1}H NMR measurement is performed at room temperature in $CDCl_3$.

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 ^{o}C for 60 min to dissociate the *tert*-butyl group of *t*BMA 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.

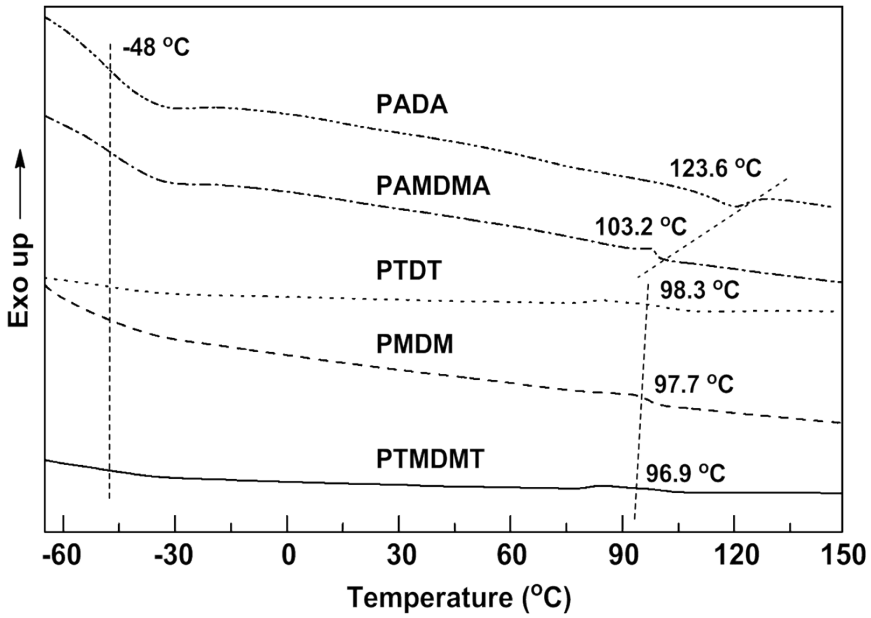

Fig. S3 DSC curves of PTMDMT3, PMDM, PTDT, PAMDMA3, and PADA measured in the temperature range from -70 °C to 150 °C (1st run curves).

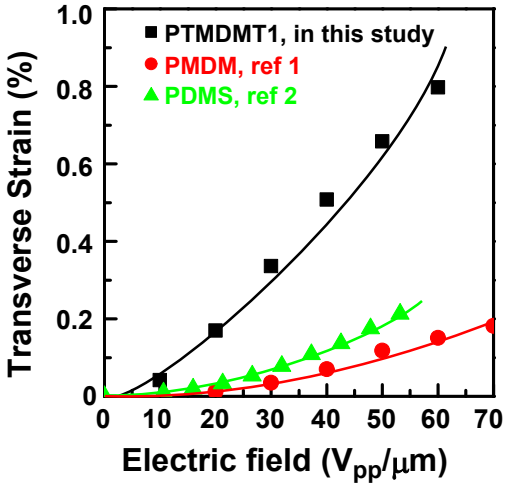

Fig. S4 Transverse strain changes as a function of electric field: PTMDMT, PMDM,[1] and PDMS.[2]

References

1 K. Y. Cho, S. S. Hwang, H. G. Yoon and K. –Y. Baek, *J. Polym. Sci., Part A: Polym. Chem.,* 2013, **51**, 1924.

2 I. J. Kim, K. Min, H. Park, S. M. Hong, W. N. Kim, S. H. Kang and C. M. Koo, *J. Appl. Polym. Sci.*, 2014, **131**, 40030.