Supporting Information

Amphiphilic Triblock Phospholipid Copolymers Bearing Phenylboronic Acid Groups for Spontaneous Formation of Hydrogels with Tunable Mechanical Properties

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Supporting Information S1

MPC Monomer Conversion Rate

Conversion rate of MPC monomer during polymerization of PMPC middle chain by ARGET ATRP was performed by collecting the polymerizing mixture in every 30 minutes with continuously flow of argon gas to prevent leak-in of the air. The collected solutions were immediately frozen by liquid nitrogen to stop reaction. After allowed to melt at room temperature, the mixture was diluted in methanol-*d4* and examined by NMR.

The conversion rate was examined by observing the change in monomer's vinyl signals at δ 5.5 and 6.0 compared to characteristic peak of phosphorylcholine in MPC monomer at δ 3.2. In this experiment, three types of most used ATRP catalysts, *i.e.* 2,2'-bipyridine (bpy), *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMEDTA), and tris(2-pyridylmethyl)amine (TPMA) were compared.
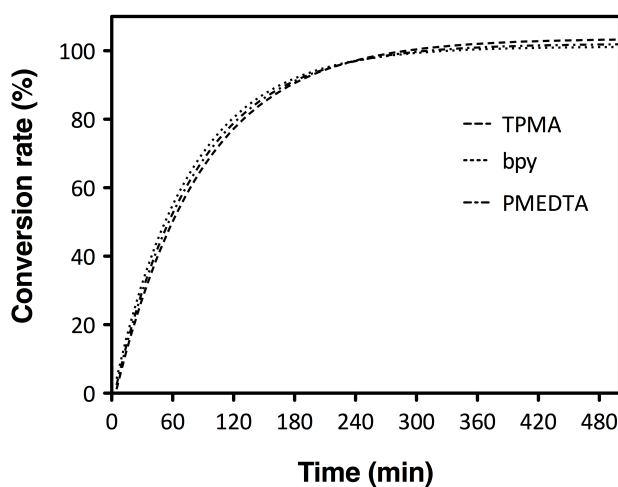

Figure S1 Time-dependence MPC monomer conversion when synthesized PMPC homopolymer by ARGET ATRP technique with different catalysts

Figure S1 shows the comparison of each catalyst by plotting the conversion rate versus time and performed the nonlinear regression curve-fit with 95% confidence. The conversion rates from all catalysts were almost identical, which more than 98% conversion could be achieved after 4h. However, TPMA was chosen for the rest of experiments as it allowed GMA to polymerize as an extended chain of PMPC with highest efficiency (data not showed).

Supporting Information S2

¹H-NMR Charts of Synthesized Triblock Polymers

Successful of ABA-type triblock polymerization and modification, including final chemical composition of polymers were analyzed by NMR. To examine monomer composition, ethanol-*d6* was chosen as deuterated solvent because it could dissolve all polymers available in this research, and the characteristics peaks of ethanol-*d6* (δ 5.19 and 3.56) do not overlap with characteristics peaks from each units available in triblock copolymers (MPC (δ 3.2), GMA (δ 2.8 and 2.6), and APBA (δ 7.4 ~ 6.8). ¹H-NMR was recorded with 400 MHz NMR spectroscopy from JEOL Co. Ltd., Tokyo, Japan. The ¹H-NMR charts of each step of preparation were orderly illustrated as follow, showing results of PMPC, PM*b*G, and PM*b*B respectively.

PM*b*G
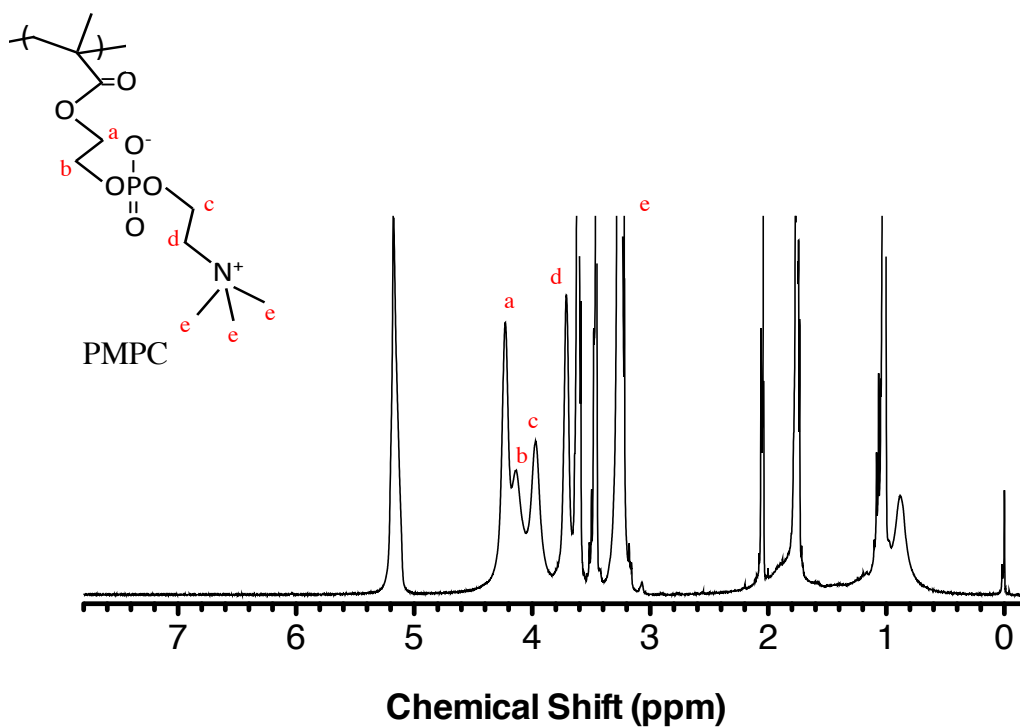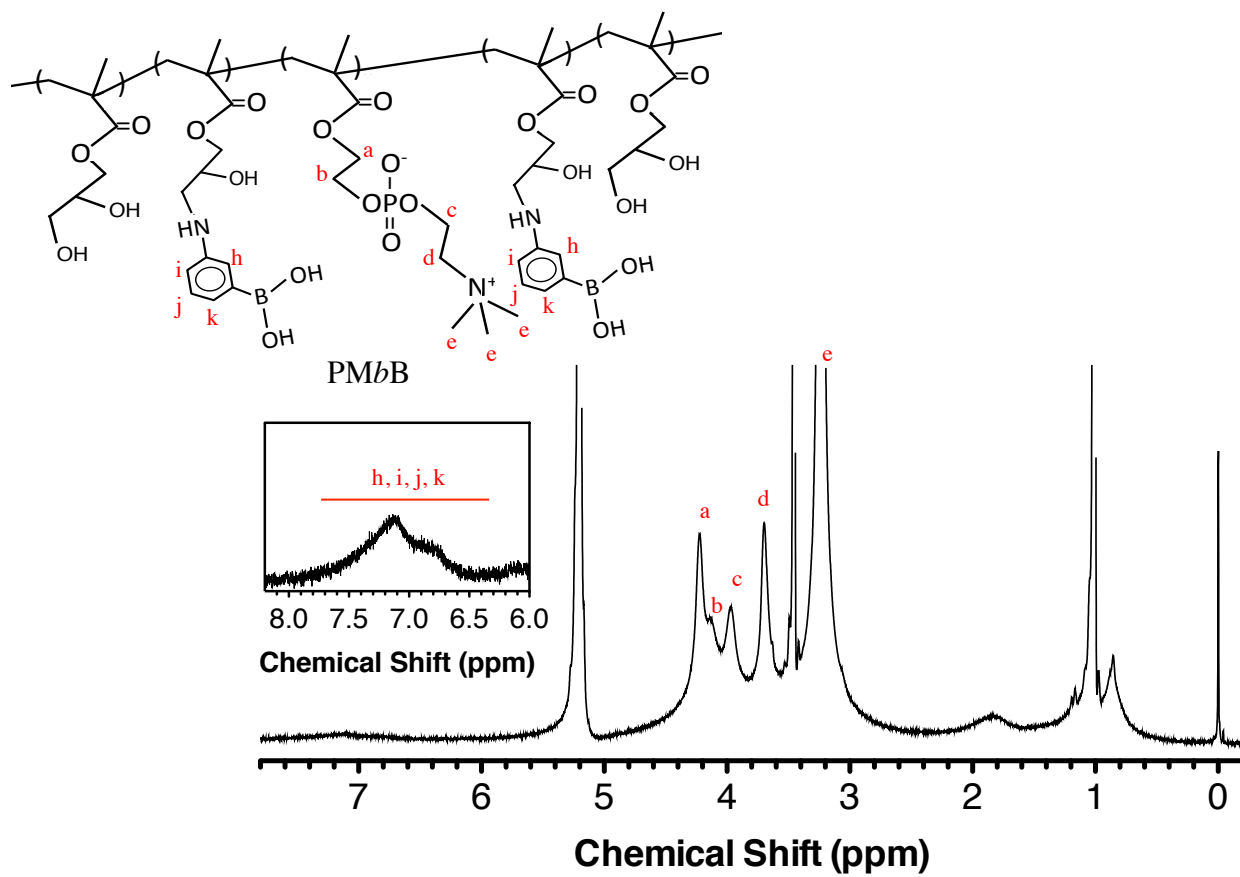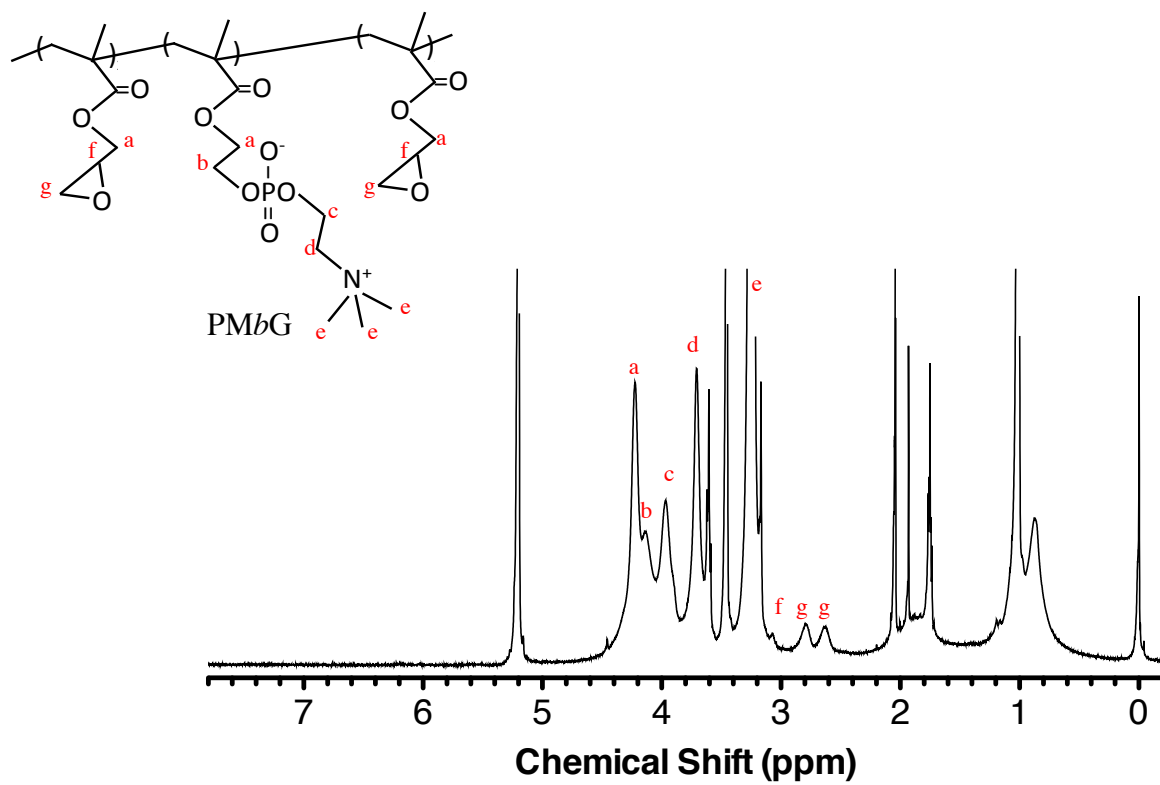
PM*b*B

Supporting Information S3

Formation and Dissociation of PMbB/PVA Hydrogel

Confirmation of PM*b*B/PVA hydrogel formation by test-tube inverting method was conducted.

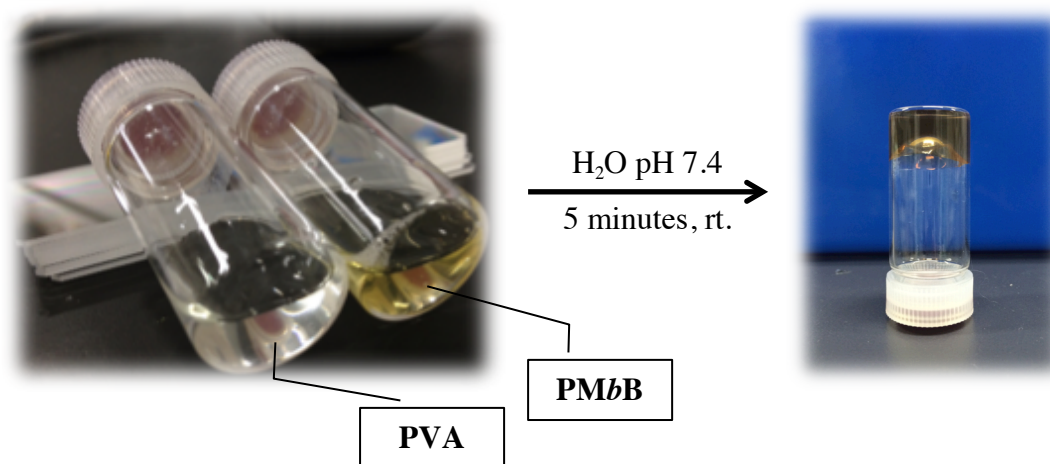Gelation by mixing of 10 % wt. of PM*b*B50 and 10 % wt. PVA was observed.

H_2O pH 7.4

5 minutes, rt.

PMbB

PVA

Figure S3-1 Formation of PM*b*B/PVA hydrogel by mixing PM*b*B solution
and PVA solution at physiological conditions.

Dissociation of PM*b*B/PVA hydrogel by sugar molecule (*i.e.* sorbitol) was tested. By putting

PM*b*B/PVA hydrogel in 0.1 M of sorbitol in water, the dissociation of hydrogel was observed and
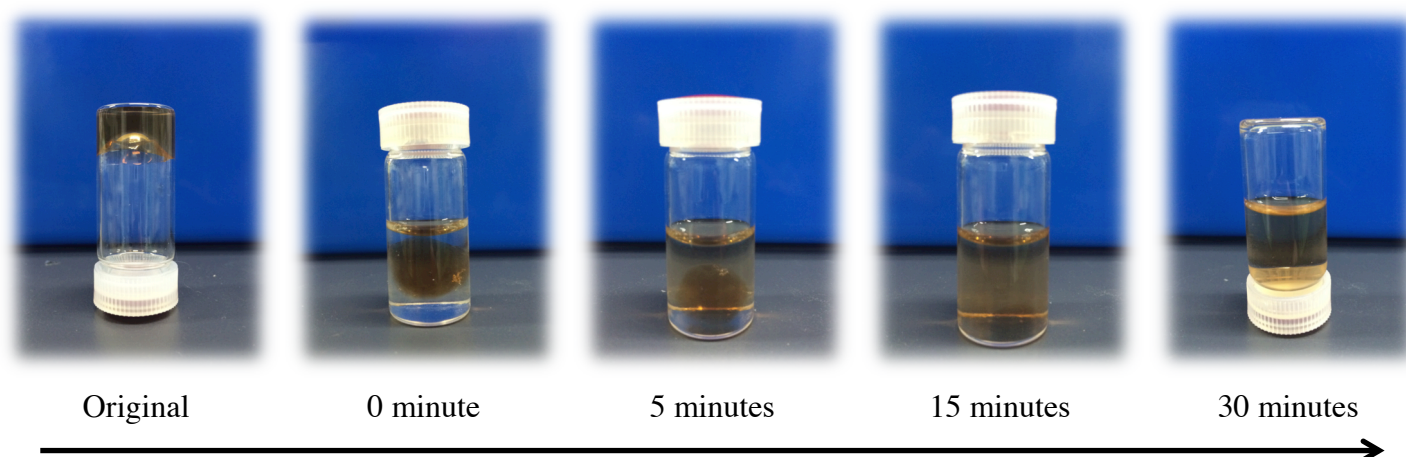
illustrated below.

| Original | 0 minute | 5 minutes | 15 minutes | 30 minutes |

Figure S3-2 Dissociation of PM*b*B/PVA hydrogel in sorbitol solution (0.1 M).
The hydrogel can be simultaneously dissociated within 30 minutes.

Supporting Information S4

Plot of Storage Modulus (G') versus Loss Modulus (G'') of PMbB/PVA Hydrogels
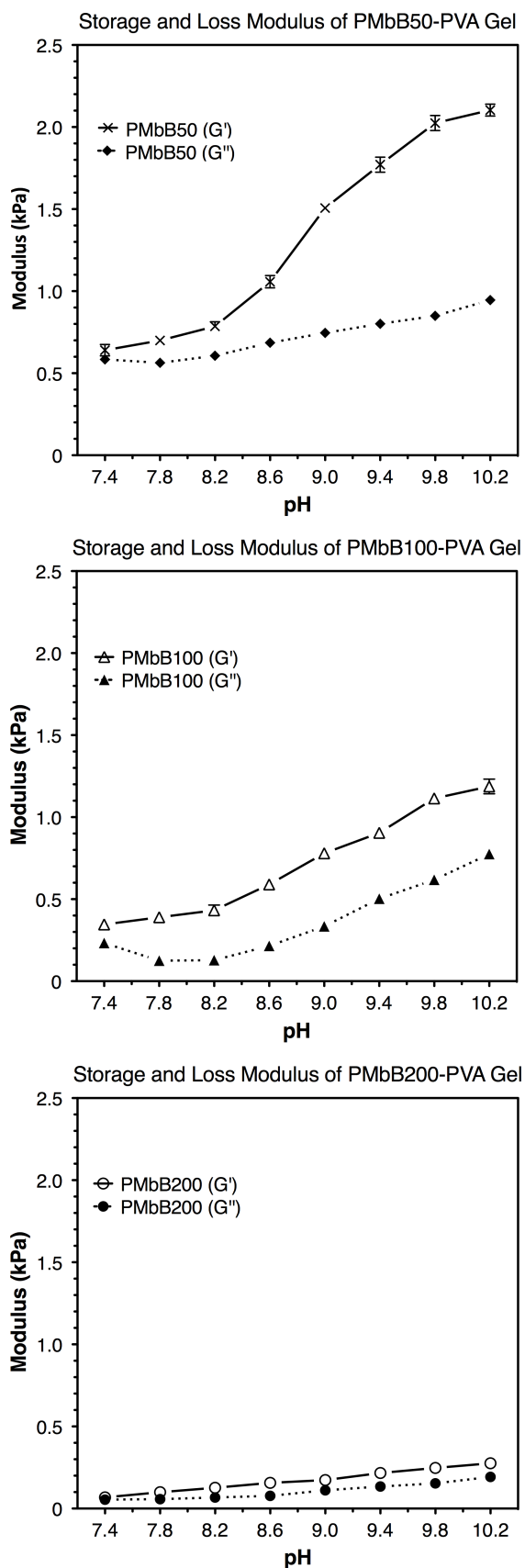

Figure S4 Storage modulus (G') and loss modulus (G'') of PM*b*B/PVA hydrogels versus pH.

Figure S4 illustrates the comparison and changing of storage and loss modulus (G' and G'') of each PMbB/PVA hydrogels. As explained in main article, hydrogel from PMbB50 contained highest fraction of crosslink (implicitly includes largest amount of elastically active chain) in hydrogel mass and give hydrogel with high strength compared to PMbB100 and PMbB200. In case of PMbB50, difference of G' and G'' was large, indicates the hydrogel of PMbB50/PVA shows stronger elastic characteristics than viscosity. For hydrogel which high fraction of phenylboronic acid (*i.e*. PMbB50) Storage modulus of hydrogel tends to be influenced strongly by pH condition as the storage modulus increased significantly during pH 8.2 – 9.8, while loss modulus slightly increased. For hydrogel with low crosslink density such as PMbB200/PVA hydrogel, at pH 7.4, the mixture remained in solution state as G'' > G'. As pH increased, the mixture gradually became more viscous solution. Free-standing hydrogel from PMbB200 became observable by test-tube inverting technique when pH condition of the hydrogel is beyond pH 8.6.

Supporting Information S4

ANS Fluorescence Spectra of PMbB in different pH

Phenylboronic acid has two main formations, which are native neutral trigonal formation and anionic tetrahedral formation. These two structures of phenylboronic acid are reversible as effect from surrounding *e.g.* pH and free hydroxyl group. To create crosslinking point by *cis-diol* interaction between phenylboronic acid and diol in PVA, the active anionic tetrahedral structure was preferable. To study effect of pH on microstructure of phenylboronic acid in PM*b*B, hydrophobic dye (ANS) was employed for the task. The rationale and detailed method was described in our main article.

Figure S4 shows the raw data of fluorescence spectra derived from PM*b*B solutions in different pH condition with diluted ANS.