

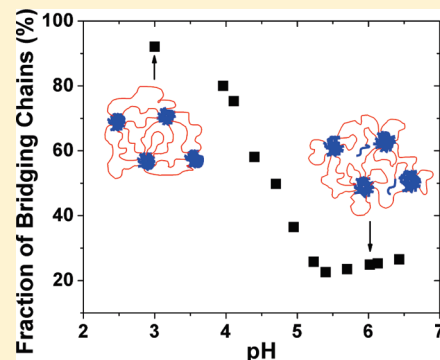
Rheological Properties of Aqueous Micellar Gels of a Thermo- and pH-Sensitive ABA Triblock Copolymer

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Supporting Information

ABSTRACT: This article presents a systematic study of the effect of pH on the rheological properties of aqueous micellar gels formed from 10.0 wt % aqueous solutions of a thermo- and pH-sensitive ABA triblock copolymer, poly(ethoxydi(ethylene glycol) acrylate-*co*-acrylic acid)-*b*-poly(ethylene oxide)-*b*-poly(ethoxydi(ethylene glycol) acrylate-*co*-acrylic acid) (P(DEGEA-*co*-AA)-*b*-PEO-*b*-P(DEGEA-*co*-AA)). The block copolymer was synthesized by atom transfer radical polymerization of DEGEA and *tert*-butyl acrylate with a molar ratio of 100:5 from a difunctional PEO macroinitiator and subsequent removal of *tert*-butyl groups using trifluoroacetic acid. PDEGEA is a thermosensitive water-soluble polymer with a cloud point of 9 °C in water. The thermo-induced sol–gel transition temperature ($T_{\text{sol-gel}}$) of the 10.0 wt % aqueous solution of P(DEGEA-*co*-AA)-*b*-PEO-*b*-P(DEGEA-*co*-AA) can be continuously and reversibly tuned over a wide temperature range by varying the solution pH. The sol–gel transition became broader with the increase of pH, which stemmed from the weaker and broader LCST transition of P(DEGEA-*co*-AA) blocks at higher pH values. The maximum value of dynamic storage modulus, obtained from heating ramp, and the plateau storage moduli (G_N), evaluated from frequency sweeps at three normalized temperatures ($T/T_{\text{sol-gel}} = 1.025, 1.032, \text{ and } 1.039$), decreased with the increase of pH from 3.00 to 5.40 with the sharpest drop observed at pH ~ 4.7 . The decrease in G_N reflects the reduction of the number of bridging polymer chains and simultaneously the increase of the numbers of loops and dangling polymer chains. The ionization of carboxylic acid groups at higher pH values introduced charges onto the thermosensitive blocks and made the polymer chains more hydrophilic, facilitating the formation of loops and dangling chains in the gels. The increase in the number of dangling polymer chains with the increase of pH was supported by fluorescence spectroscopy studies, which showed that the critical micelle concentration of P(DEGEA-*co*-AA)-*b*-PEO-*b*-P(DEGEA-*co*-AA) at a temperature corresponding to $T_{\text{sol-gel}}$ was higher at a higher pH. The results reported in this article showed that both $T_{\text{sol-gel}}$ and gel strength can be tuned by varying the solution pH, providing greater design flexibility for potential applications.



INTRODUCTION

Moderately concentrated aqueous solutions of thermosensitive ABA triblock copolymers are known to undergo reversible sol–gel transitions upon temperature changes.^{1–3} If A blocks are permanently water-soluble and B block is thermosensitive exhibiting a lower critical solution temperature (LCST) in water, the polymer molecules self-assemble into discrete, often spherical, micelles at temperatures above the LCST and the sol-to-gel transition is brought about by the packing of micelles into an ordered structure. Usually, a concentration of ~ 20 wt % is needed for the formation of this type of micellar gels. Representative examples of such polymers are poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) (PEO-*b*-PPO-*b*-PEO) triblock copolymers with various compositions; these polymers have been intensively investigated in the past decades.^{1–4} On the other hand, if A blocks are thermosensitive and B block is permanently water-soluble, a three-dimensional network is produced at elevated temperatures with the dehydrated A blocks associated into micellar cores and the central B blocks forming bridges. Compared with the first type of micellar

gels, 3-D network gels can be more advantageous for some applications because the critical gelation concentration (CGC) is significantly lower.^{5–7} For example, Kirkland et al. reported that a 7.5 wt % aqueous solution of poly(*N*-isopropylacrylamide)-*b*-poly(*N,N*-dimethylacrylamide)-*b*-poly(*N*-isopropylacrylamide) formed a free-standing gel upon heating. Note that poly(*N*-isopropylacrylamide) exhibits an LCST at 32 °C in water⁸ and poly(*N,N*-dimethylacrylamide) is water-soluble. These thermosensitive micellar gels have been investigated for applications in controlled release of substances and tissue engineering because of their unique thermo-induced in situ sol–gel transition and the nature of physical cross-linking.^{9–11}

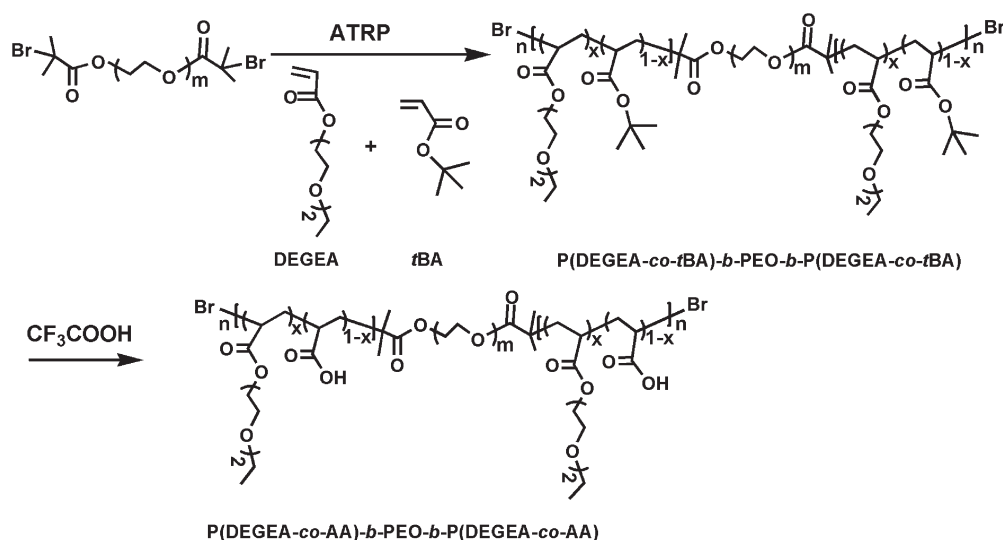
We have been particularly interested in aqueous micellar gels of block copolymers that can respond to two or more physical or chemical stimuli.^{12–28} Such gels would offer greater design flexibility that is needed in many applications. There have been

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Scheme 1. Synthesis of Thermo- and pH-Sensitive ABA Triblock Copolymer P(DEGEA-co-AA)-*b*-PEO-*b*-P(DEGEA-co-AA) by ATRP of DEGEA and *t*BA from a Difunctional PEO Macroinitiator and Subsequent Treatment with Trifluoroacetic Acid



a number of reports on multiresponsive block copolymer aqueous micellar gels;^{9,10,12–28} one common feature of these gels is that they are thermosensitive. For example, thermo- and redox-sensitive hydrophilic block copolymers have been reported by several research groups.^{14–16} Such polymers can be prepared from a difunctional initiator that contains a redox-sensitive disulfide bond; the thermally and biochemically induced sol–gel transitions of their aqueous solutions have been demonstrated.¹⁵ Temperature- and pH-sensitive block copolymer aqueous gels are probably the most studied multiresponsive gels.^{17–27} The block copolymers were usually prepared by either growing pH-sensitive blocks from or introducing pH-responsive groups to the chain ends of an ABA triblock copolymer that can form thermoreversible gels in water (e.g., PEO-*b*-PPO-*b*-PEO).^{17–24} Suh et al. used pyromellitic dianhydride to couple PEO-*b*-PPO-*b*-PEO to make multiblock copolymers with carboxylic acid groups incorporated at the junction points.²⁵ Lee et al. reported pH- and thermosensitive gels of multiblock copolymers composed of PEO and poly(aminourethane).^{26,27}

We previously reported a new type of thermo- and pH-sensitive block copolymer aqueous micellar gels.²⁸ A small amount of weak acid groups was incorporated into the thermosensitive outer blocks of an ABA triblock copolymer, poly(methoxydi(ethylene glycol) methacrylate-*co*-methacrylic acid)-*b*-PEO-*b*-poly(methoxydi(ethylene glycol) methacrylate-*co*-methacrylic acid) (P(DEGMMA-*co*-MAA)-*b*-PEO-*b*-P(DEGMMA-*co*-MAA)). PDEGMMA is a biocompatible thermosensitive water-soluble polymer with a LCST of 25 °C in water, which belongs to a new class of thermosensitive polymers with a short oligo(ethylene glycol) pendant from each repeating unit.^{28–49} A characteristic feature of such doubly responsive hydrophilic block copolymers is that the LCST of thermosensitive blocks can be modified by an external stimuli.^{12,13,28} It is known that the cloud point of a thermosensitive polymer that contains a small amount of weak acid or base groups in water depends on the solution pH.^{50–59} We showed that the sol–gel transition temperature ($T_{\text{sol-gel}}$) of a 12.0 wt % aqueous solution of P(DEGMMA-*co*-MAA)-*b*-PEO-*b*-P(DEGMMA-*co*-MAA)

can be precisely, reversibly, and continuously tuned in a wide temperature range by varying the solution pH. Moreover, multiple sol-to-gel/gel-to-sol transitions were realized by controlling both temperature and pH, demonstrating the possibility of achieving on-demand sol–gel transition by combining two external stimuli.²⁸

In the present work, we carried out a detailed study on rheological properties of 10.0 wt % aqueous solutions of a thermo- and pH-sensitive ABA triblock copolymer, poly(ethoxydi(ethylene glycol) acrylate)-*co*-acrylic acid)-*b*-PEO-*b*-poly(ethoxydi(ethylene glycol) acrylate-*co*-acrylic acid)) (P(DEGEA-*co*-AA)-*b*-PEO-*b*-P(DEGEA-*co*-AA)). The triblock copolymer was prepared from a difunctional PEO macroinitiator with a molecular weight of 20 000 g/mol by atom transfer radical polymerization of DEGEA and *tert*-butyl acrylate (*t*BA) with a molar ratio of 100:5 and subsequent removal of *tert*-butyl groups of *t*BA units using trifluoroacetic acid (Scheme 1). We chose PDEGEA rather than PDEGMMA in this work because the LCST of PDEGEA in water is 9 °C and thus the sol-to-gel transition occurs in a more convenient temperature range for rheological measurements. Consistent with the previous report, the $T_{\text{sol-gel}}$ of the 10.0 wt % aqueous solution of P(DEGEA-*co*-AA)-*b*-PEO-*b*-P(DEGEA-*co*-AA) was dependent on pH. The sol-to-gel transition became broader with the increase of pH. Moreover, we found that the plateau dynamic storage moduli, obtained from frequency sweeps, decreased with the increase of pH with the sharpest drop observed at pH of ~4.7. The results showed that both $T_{\text{sol-gel}}$ and gel strength can be tuned by varying the solution pH.

EXPERIMENTAL SECTION

Materials. Ethoxydi(ethylene glycol) acrylate (or di(ethylene glycol) ethyl ether acrylate, DEGEA, 90%, Aldrich) and *tert*-butyl acrylate (*t*BA, 99%, Fisher Scientific) were dried with calcium hydride overnight, distilled under reduced pressure, and stored in a refrigerator prior to use. CuBr (98%, Aldrich) was stirred in glacial acetic acid, filtered, and washed with absolute ethanol and

diethyl ether. The purified CuBr was then dried in vacuum and stored in a desiccator. *N,N,N',N',N''*-Pentamethyldiethylenetriamine (99%, Aldrich), dichloromethane, and anisole (99%, Acros) were dried with calcium hydride, vacuum distilled, and stored in storage flasks. Potassium hydrogen phthalate (KHP, primary standard, p.a.), trifluoroacetic acid (99%), acetone (HPLC grade), and Nile Red (99%) were obtained from Acros and used as received. Poly(ethylene oxide) (HO-PEO-OH, MW = 20 000 g/mol, Aldrich) was end-functionalized by reacting with 2-bromoisobutyl bromide to give a difunctional PEO macroinitiator, Br-PEO-Br, as described in a previous publication.²⁸ Hexanes, diethyl ether, 1.0 M KOH solution (volumetric standard solution), and 1.0 M HCl solution (volumetric standard solution) were obtained from Fisher Scientific. All other chemicals were purchased from either Aldrich or Fisher/Acros and used without further purification.

General Characterization. Size exclusion chromatography (SEC) was carried out at ambient temperature using PL-GPC 20 (an integrated GPC system from Polymer Laboratories, Inc.) with a differential refractive index detector, one PLgel 5 μ m guard column (50 \times 7.5 mm), and two PLgel 5 μ m mixed-C columns (each 300 \times 7.5 mm, linear range of molecular weight from 200 to 2 000 000 according to Polymer Laboratories). THF was used as the carrier solvent at a flow rate of 1.0 mL/min. Polystyrene standards (Polymer Laboratories) were employed for calibration. The data were processed using Cirrus GPC/SEC software (Polymer Laboratories). The ¹H (300 MHz) NMR spectra were recorded on a Varian Mercury 300 NMR spectrometer.

Synthesis of P(DEGEA-co-tBA)-b-PEO-b-P(DEGEA-co-tBA). Copper(I) bromide (9.9 mg, 6.9×10^{-5} mol) and difunctional macroinitiator Br-PEO-Br (0.651 g, 3.26×10^{-5} mol) were weighed into a two-necked flask, followed by the addition of DEGEA (4.237 g, 22.5 mmol), tBA (0.152 g, 1.19 mmol), and anisole (2.147 g). The mixture was stirred under nitrogen atmosphere. *N,N,N',N',N''*-Pentamethyldiethylenetriamine (10.5 mg, 6.04×10^{-5} mol) was then injected into the flask via a microsyringe. After the reaction mixture was degassed by three freeze-pump-thaw cycles, the flask was placed into an oil bath with a preset temperature of 90 °C. The polymerization was monitored by SEC. After 180 min, the flask was removed from the oil bath and opened to air. The polymerization mixture was diluted with THF, and the copper catalyst was removed by passing the solution through a short basic aluminum oxide/silica gel column. The polymer was purified by precipitation in hexanes four times and then dried under high vacuum at 50 °C for 3 h. SEC analysis results (polystyrene standards): $M_{n,SEC} = 47\,900$ g/mol, polydispersity index (PDI) = 1.09.

Synthesis of P(DEGEA-co-AA)-b-PEO-b-P(DEGEA-co-AA). P(DEGEA-co-tBA)-b-PEO-b-P(DEGEA-co-tBA) (1.277 g) was dried in a preweighed round-bottom flask for 2 h. Dry dichloromethane (6 mL) was added into the flask to dissolve the polymer, followed by the addition of trifluoroacetic acid (3.321 g). After the reaction mixture was stirred at ambient temperature for 67 h, the volatiles were removed by a rotary evaporator. The polymer was precipitated four times in a mixture of hexanes and diethyl ether (10/4, v/v) and then dried under high vacuum at 50 °C. ¹H NMR spectroscopy analysis showed that the *tert*-butyl groups in the polymer were removed.

Preparation of 10.0 wt % Aqueous Solution of P(DEGEA-co-AA)-b-PEO-b-P(DEGEA-co-AA). P(DEGEA-co-AA)-b-PEO-b-P(DEGEA-co-AA) was added into a preweighed round-bottom

flask and dried under high vacuum at 50 °C for >3 h. The mass of the dried polymer was 0.958 g. Milli-Q water (8.641 g) was added into the flask and the mixture was sonicated in an ice/water ultrasonic bath (Fisher Scientific Model B200 Ultrasonic Cleaner) to dissolve the ABA triblock copolymer. The flask was then stored in a refrigerator (~4 °C) overnight and a homogeneous clear solution was obtained. The pH value of the polymer solution was 3.00, measured by a pH meter (Accumet AB15 pH meter from Fisher Scientific, calibrated with pH = 4.01, 7.00, and 10.01 standard buffer solutions) at 0 °C (the solution was placed in an ice/water bath).

Dynamic Light Scattering Study of Thermo-Induced Micellization of 0.02 wt % Aqueous Solutions of P(DEGEA-co-AA)-b-PEO-b-P(DEGEA-co-AA) in 10 mM KHP Buffers with Various pH Values. The thermo-induced micellization of P-(DEGEA-co-AA)-b-PEO-b-P(DEGEA-co-AA) at a concentration of 0.02 wt % in 10 mM KHP buffers with various pH values was studied by dynamic light scattering (DLS). The pH values of 10 mM aqueous KHP buffers were adjusted by the addition of a 1.0 M KOH aqueous solution or a 1.0 M HCl aqueous solution. Four 0.02 wt % aqueous solutions of P-(DEGEA-co-AA)-b-PEO-b-P(DEGEA-co-AA) with pH values of 3.00, 4.11, 5.07, and 6.00 were prepared by diluting a certain amount of the aforementioned 10.0 wt % aqueous polymer solution with corresponding KHP buffers. All 0.02 wt % polymer solutions were sonicated in an ice/water ultrasonic bath for 2 min to ensure that the solutions were homogeneous. The pH values of the solutions were remeasured by a pH meter (essentially the same as the pH values of KHP buffers).

DLS measurements were conducted with a Brookhaven Instruments BI-200SM goniometer equipped with a PCI BI-9000AT digital correlator, a temperature controller, and a solid-state laser (model 25-LHP-928-249, $\lambda = 633$ nm) at scattering angle of 90°. The polymer solutions were filtered into borosilicate glass tubes with an inner diameter of 7.5 mm by the use of 0.2 μ m filters. The glass tubes were then sealed with PE stoppers. The solutions were gradually heated. At each temperature, the solutions were equilibrated for 30 min prior to data recording. The time correlation functions were analyzed with a Laplace inversion program (CONTIN).

Rheological Measurements. Rheological experiments were conducted on a stress-controlled rheometer (TA Instruments Model TA AR2000ex). A cone-plate geometry with a cone diameter of 20 mm and an angle of 2° (truncation 52 μ m) was employed; the temperature was controlled by the bottom Peltier plate. In each measurement, 85 μ L of a polymer solution was loaded onto the plate by a micropipet. The solvent trap was filled with water and a solvent trap cover was used to minimize water evaporation. Dynamic viscoelastic properties (dynamic storage modulus G' and loss modulus G'') of polymer solutions were measured by oscillatory shear experiments performed at a fixed frequency of 1 Hz in a heating ramp at a heating rate of 3 °C/min. The frequency dependences of G' and G'' of a polymer solution at selected temperatures were obtained by frequency sweep tests from 0.1 to 100 Hz (or 0.001 to 100 Hz at some selected temperatures). At each temperature, the solution was equilibrated for at least 2 min prior to data recording. A strain amplitude of $\gamma = 0.2\%$ was used in all dynamic tests to ensure that the deformation was within the linear viscoelastic regime.

Determination of Critical Micelle Concentration of P(DEGEA-co-AA)-b-PEO-b-P(DEGEA-co-AA) in Aqueous Buffers by Fluorescence Spectroscopy. The critical micelle

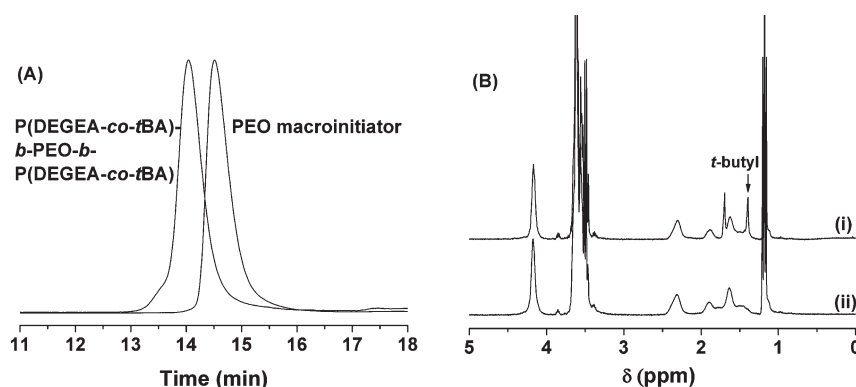


Figure 1. (A) Size exclusion chromatography traces of PEO macroinitiator and ABA triblock copolymer poly(ethoxydi(ethylene glycol) acrylate-*co-tert*-butyl acrylate)-*b*-poly(ethylene oxide)-*b*-poly(ethoxydi(ethylene glycol) acrylate-*co-tert*-butyl acrylate) (P(DEGEA-*co-tBA*)-*b*-PEO-*b*-P(DEGEA-*co-tBA*)) and (B) ¹H NMR spectra of P(DEGEA-*co-tBA*)-*b*-PEO-*b*-P(DEGEA-*co-tBA*) (i) before and (ii) after the removal of *tert*-butyl groups using trifluoroacetic acid.

concentration (cmc) of P(DEGEA-*co-AA*)-*b*-PEO-*b*-P(DEGEA-*co-AA*) in water at a specific pH and a temperature that corresponded to the sol-to-gel transition temperature of the 10.0 wt % aqueous polymer solution at that pH was determined by fluorescence spectroscopy using Nile Red as fluorescence probe. For each pH, a series of triblock copolymer solutions with different concentrations in a 10 mM KHP buffer were prepared by the following procedure. Ten microliters of a stock solution of Nile Red in acetone (concentration: 0.63 mg/g, 6.3 mg of Nile Red in 10.007 g of HPLC grade acetone) was added into empty vials using a micropipet. The vials were weighed immediately and then placed in vacuum for >3 h to remove the solvent. A calculated amount of a stock polymer solution (concentration 1.46 wt %) was injected into each vial via a microsyringe and weighed. A certain amount of the 10.0 mM KHP buffer was then added into each vial to bring the total weight of the solution to 2.000 g. The nominal concentration of Nile Red was 7.8×10^{-6} M. After the sonication in an ice/water ultrasonic bath for 30 min, the solutions were equilibrated overnight in an oil bath at a temperature that corresponded to the $T_{\text{sol-gel}}$ of 10.0 wt % polymer solution at the same pH. Fluorescence emission spectra of Nile Red in these solutions at a specific temperature were recorded from PerkinElmer LS 55 fluorescence spectrometer equipped with a 20 kW xenon discharge lamp. The excitation wavelength was 550 nm and the fluorescence emission spectra were recorded from 560 to 720 nm. The slit width was 10 nm. The sample cell was thermostated with an external water bath of a Fisher Scientific Isotemp refrigerated circulator for at least 20 min before data recording. The maximum fluorescence intensity was then plotted against the logarithm of polymer concentration for the determination of cmc.

Salt Effect on Sol-to-Gel Transition Temperature and Gel Properties of Aqueous Solution of P(DEGEA-*co-AA*)-*b*-PEO-*b*-P(DEGEA-*co-AA*) with pH of 4.64 and a Nominal Polymer Concentration of 10.0 wt %. The amount of COOH/COOK in a 10 wt % aqueous solution of the ABA triblock copolymer was calculated on the basis of the polymer composition and the polymer concentration. 1.0 M KCl aqueous solution was prepared by dissolving KCl (7.456 g, > 99.0%, Fisher Scientific) in Milli-Q water in a 100 mL volumetric flask. The polymer solution used here was obtained by changing the pH value of the original 10.0 wt % aqueous solution of P(DEGEA-*co-AA*)-*b*-PEO-*b*-P(DEGEA-*co-AA*) to 6.43 by the addition of 1.0 M KOH

solution and then to 3.10 by the addition of 1.0 M HCl solution, followed by the injection of 1.0 M KOH to increase the pH to 4.64. Calculated amounts of 1.0 M KCl aqueous solution were injected via a microsyringe into this polymer solution in a stepwise fashion until the total amount of the added KCl was twice that of COOH/COOK in the solution (excluding the amount of KCl produced in the processes of adding KOH and HCl). After each injection, the polymer solution was sonicated for 2 min in an ice/water bath to ensure that the solution was homogeneous. The sample was then subjected to rheological measurements.

Differential Scanning Calorimetry (DSC) Study of Thermo-induced Phase Transitions of 10.0 wt % Aqueous Solutions of P(DEGEA-*co-AA*)-*b*-PEO-*b*-P(DEGEA-*co-AA*). Differential scanning calorimetry analysis of polymer solutions was conducted on a TA Q-1000 DSC instrument that was calibrated with sapphire disks. Polymer solutions (20 μ L, ~20 mg) were loaded into preweighed aluminum hermetic pans and sealed carefully. A heating rate of 1 $^{\circ}$ C/min was used to obtain DSC thermograms with an empty pan as reference.

RESULTS AND DISCUSSION

Synthesis of Thermo- and pH-Sensitive ABA Triblock Copolymer P(DEGEA-*co-AA*)-*b*-PEO-*b*-P(DEGEA-*co-AA*). The doubly responsive ABA triblock copolymer P(DEGEA-*co-AA*)-*b*-PEO-*b*-P(DEGEA-*co-AA*) was prepared by a two-step procedure (Scheme 1). The precursor polymer P(DEGEA-*co-tBA*)-*b*-PEO-*b*-P(DEGEA-*co-tBA*) was synthesized from a difunctional PEO macroinitiator by ATRP of DEGEA and *tBA* with a molar ratio of 100: 5 at 90 $^{\circ}$ C using CuBr/*N,N,N',N',N''*-pentamethyldiethylenetriamine as catalyst. Figure 1A shows the SEC traces of PEO macroinitiator and P(DEGEA-*co-tBA*)-*b*-PEO-*b*-P(DEGEA-*co-tBA*). The peak shifted to the high molecular weight side and remained narrow, indicating that the polymerization was well controlled. The number-average molecular weight and polydispersity index of the triblock copolymer were 47.9 kDa and 1.09, respectively (relative to polystyrene standards). The *tert*-butyl groups in the copolymer were then removed using trifluoroacetic acid (TFA). We previously confirmed that other ester bonds were not affected by TFA.²⁹ Figure 1B shows the ¹H NMR spectra of the triblock copolymer before and after the treatment with TFA. The successful removal of *tert*-butyl groups

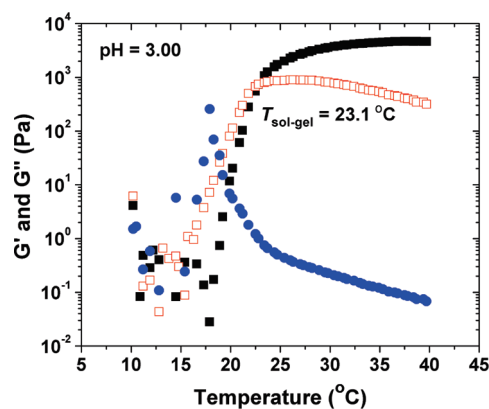


Figure 2. Plot of dynamic storage modulus G' (■), dynamic loss modulus G'' (□), and $\tan \delta$ (●) versus temperature for a 10.0 wt % aqueous solution of P(DEGEA-co-AA)-*b*-PEO-*b*-P(DEGEA-co-AA) with pH of 3.00. The data were collected from a temperature ramp experiment performed by using a fixed frequency of 1 Hz, a strain amplitude of 0.2%, and a heating rate of 3 °C/min.

was evidenced by the disappearance of the *tert*-butyl peak in the ^1H NMR spectrum. By using the integrals of the peak located at 1.2 ppm, which was from the methyl group of DEGEA unit, and the peak at 3.2–4.0 ppm, which was from the PEO block and $-\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$ of DEGEA units, along with the difference between the integrals of the peaks at 1.3–1.5 ppm before and after the removal of *tert*-butyl groups of *t*BA units, the numbers of DEGEA and *t*BA (or AA) units in the ABA triblock copolymer were calculated and they were 140 and 7, respectively. The molar ratio of *t*BA to DEGEA units in the copolymer was essentially the same as in the feed.

Thermo-induced Sol–Gel Transition of 10.0 wt % Solution of P(DEGEA-co-AA)-*b*-PEO-*b*-P(DEGEA-co-AA) in Milli-Q water. A 10.0 wt % aqueous solution of P(DEGEA-co-AA)-*b*-PEO-*b*-P(DEGEA-co-AA) was made using Milli-Q water. The pH value of the solution was 3.00, measured with a pH meter (Accumet AB15 from Fisher Scientific) in an ice/water bath. The sample was a free-flowing liquid at ~ 0 °C; upon warming to room temperature, it turned into a clear gel that remained immobile even when the vial was inverted. This thermo-induced sol–gel transition was reversible; lowering the temperature converted the gel into a free-flowing liquid. To study its rheological properties, we carried out an oscillatory shear experiment at a fixed frequency of 1 Hz in a heating ramp at a heating rate of 3 °C/min. A strain amplitude of $\gamma = 0.2\%$ was used to ensure that the measurement was taken in the linear viscoelastic regime. As shown in Figure 2, when the temperature was below 15 °C, the values of dynamic storage modulus G' and loss modulus G'' were small and the data points were scattered. In the range of 15–23 °C, both G' and G'' increased with the increase of temperature; the value of G'' was larger than G' , indicating that the sample was a viscous liquid. Above 23 °C, G' became greater than G'' , suggesting that the solution turned into a gel. The crossover, $G' = G''$, is commonly used as an indicator of the sol–gel transition. Therefore, using this simple and convenient method, the sol-to-gel transition temperature ($T_{\text{sol-gel}}$) of this 10.0 wt % aqueous solution is 23.1 °C.⁶⁰

This temperature-induced sol–gel transition stems from the LCST behavior of thermosensitive outer blocks of the ABA triblock copolymer. When the temperature is raised above the LCST of P(DEGEA-co-AA) blocks, they undergo a hydration-to-dehydration

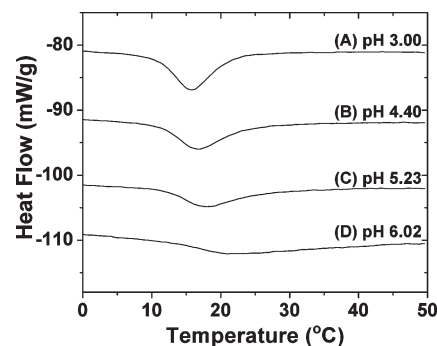


Figure 3. Differential scanning calorimetry thermograms of the 10.0 wt % aqueous solution of P(DEGEA-co-AA)-*b*-PEO-*b*-P(DEGEA-co-AA) at pH of (A) 3.00, (B) 4.40, (C) 5.23, and (D) 6.02. The heating rate was 1 °C/min. For the sake of clarity, the thermograms were shifted vertically.

transition and self-assemble into hydrophobic domains (micellar cores). At a sufficiently high concentration (i.e., >CGC), a 3-dimensional network is formed with the central PEO blocks forming bridges among micellar cores. Decreasing temperature dissolves the P(DEGEA-co-AA) blocks and dissociates the network, resulting in a gel-to-sol transition. The origin of the thermo-induced gelation can be seen from the differential scanning calorimetry (DSC) analysis of the sample (Figure 3A). An endothermic peak was observed in the DSC thermogram with the onset temperature at ~ 8 °C and the peak position located at ~ 16 °C, indicating that the transition was an entropically driven process. To further confirm the thermo-induced micellization, we conducted a dynamic light scattering (DLS) study of a 0.02 wt % solution of P(DEGEA-co-AA)-*b*-PEO-*b*-P(DEGEA-co-AA) in an aqueous potassium hydrogen phthalate (KHP) buffer at pH = 3.00 (Figure 4). Below 15 °C, the scattering intensity was low and the apparent hydrodynamic size (D_h), obtained from CONTIN analysis, was <10 nm, confirming that the triblock copolymer was dissolved molecularly in water. With the increase of temperature above 15 °C, the scattering intensity began to increase. The critical micellization temperature (cmt) determined from the plot of scattering intensity versus temperature was 15 °C, slightly higher than the onset temperature in the DSC thermogram (~ 8 °C), which can be attributed to the concentration effect. The apparent D_h of micelles at 25 °C was 64 nm. Note that the transition temperatures from both DSC and DLS studies were lower than the $T_{\text{sol-gel}}$ (23.1 °C) of the 10.0 wt % solution. This is understandable because the sol–gel transition is closely related to the mechanical property of the 3-D network gel and a slightly higher temperature is usually needed for the sample to exhibit a sufficient elastic property.

A consequence of the formation of bridges by the midblock of an ABA triblock copolymer among micellar cores is that the gel exhibits stronger strain robustness compared with diblock copolymer micellar gels.⁶¹ Figure 5 shows dynamic strain amplitude sweeps of the 10.0 wt % aqueous solution of P(DEGEA-co-AA)-*b*-PEO-*b*-P(DEGEA-co-AA) at pH of 3.00 and 30.5 °C at frequencies of 0.5, 1.0, 2.5, and 5.0 Hz. For all four frequencies, the gel exhibited a linear response up to at least 15% strain, which was almost the same as supramolecular ABA triblock copolymer ion gels reported by Lodge et al.⁶¹ In contrast, diblock copolymer ion gels showed nonlinear viscoelasticity above 4–5% strain.⁶¹ Thus, the dynamic strain sweep study also suggested the formation of a 3-dimensional network with the central PEO blocks forming bridges among micellar cores at temperatures above the $T_{\text{sol-gel}}$.

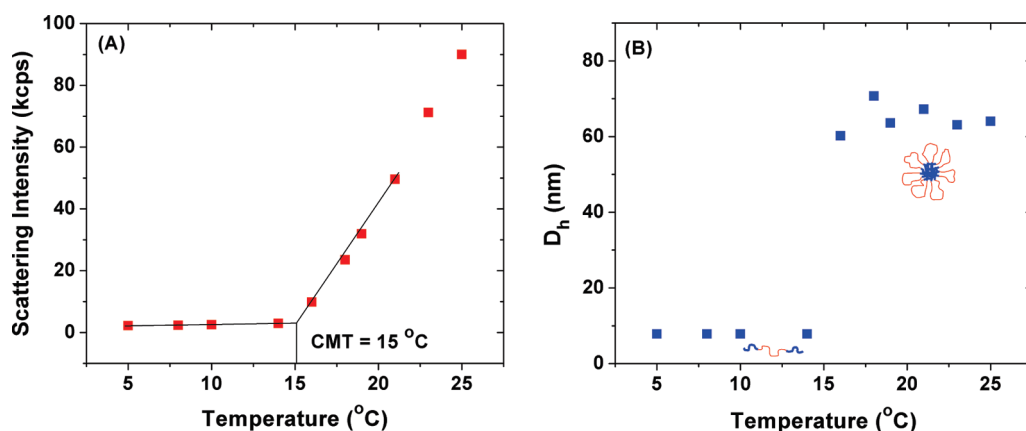


Figure 4. Scattering intensity at scattering angle of 90° and apparent hydrodynamic size D_h , obtained from CONTIN analysis, as a function of temperature in a dynamic light scattering study of a 0.02 wt % solution of P(DEGEA-*co*-AA)-*b*-PEO-*b*-P(DEGEA-*co*-AA) in an aqueous KHP buffer with pH = 3.00.

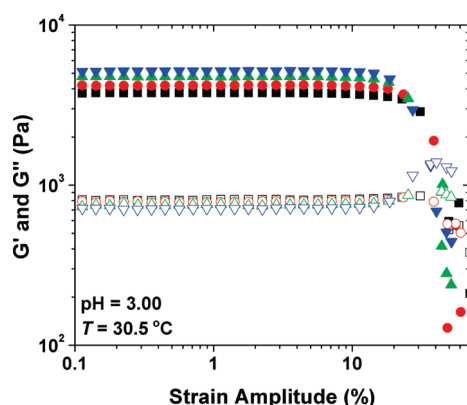


Figure 5. Dynamic strain amplitude sweeps for the 10.0 wt % aqueous solution of P(DEGEA-*co*-AA)-*b*-PEO-*b*-P(DEGEA-*co*-AA) with pH of 3.00 at 30.5 °C at frequencies of 0.50 Hz (dynamic storage modulus G' , ■, and dynamic loss modulus G'' , □), 1.00 Hz (G' , ●, and G'' , ○), 2.50 Hz (G' , ▲, and G'' , △), and 5.00 Hz (G' , ▼, and G'' , ▽).

To further look into the sol–gel transition and gel characteristics, we conducted frequency sweeps at various temperatures using a strain amplitude of 0.2% for the 10.0 wt % aqueous solution of the triblock copolymer. At 18 °C, G' and G'' exhibited different power law dependences on frequency f in the low-frequency region of 0.1–3 Hz: $G' \sim f^2$ and $G'' \sim f$ (Figure 6A). This is the typical rheological behavior of a viscous liquid.⁶² At 24.5 °C, just above the $T_{\text{sol-gel}}$ (23.1 °C), a frequency sweep in a wider range (0.001–100 Hz, spanning 5 orders in magnitude) was collected and both the terminal flow and gel behavior were observed (Figure 6B). In the extremely low frequency region, G' and G'' exhibited power law dependences on f , the characteristic of terminal flow behavior. At higher frequencies, G' became larger than G'' and both G' and G'' showed much weaker frequency dependences; these are the gel characteristics. Clearly, the gel was a transient network possessing physical cross-links of a finite dissociation time. The crossover of G' and G'' versus frequency curves occurred at $f = 0.02$ Hz, from which we can estimate the terminal relaxation time τ of polymer chains or the average lifetime of a thermosensitive P(DEGEA-*co*-AA) block in a micellar core at this temperature through

$$\tau = 1/(2\pi f)$$

where f is the frequency at the crossover point.⁶¹ The estimated τ at this temperature was 8.0 s. With further increasing temperature, the relaxation time would become longer and the crossover point would shift to an even lower frequency.

At 30.5, 32.6, and 34.6 °C, the sample was a transparent gel. G' was significantly higher than G'' and was nearly independent of f in the frequency range of 0.1–100 Hz (Figure 6, C, D, and E), which are the characteristics of elastic solidlike behavior. The plateau modulus G_N of the gel can be obtained from the frequency sweep and it is known that the G_N of a transient gel is a measure of the number density of elastically active polymer chains (or effective gel network strands):

$$G_N = \nu k_B T$$

where ν is the number density of elastically active polymer chains (number of elastically active bridging chains per unit volume), k_B is Boltzmann constant, and T is the absolute temperature. The G_N is usually evaluated as the G' value at the frequency where G'' exhibits the minimum value, because the increase of G'' at higher frequencies indicates a fast relaxation process separate from the terminal flow process. This method for the determination of G_N is well established for the entangled homopolymer melts and has also been recently used in the study of thermoreversible transient gels.⁶³ The frequencies at which G'' exhibited minimum values at 30.5, 32.6, and 34.6 °C were 12.59, 10, and 12.59 Hz, respectively; therefore, the values of G_N were 4.9×10^3 , 5.0×10^3 , and 5.3×10^3 Pa, respectively, which were close to the modulus in the plateau zone in the heating ramp (4.6×10^3 Pa, Figure 2). If the central block of every polymer chain is elastically active in the gel, calculations show that the value of G_N is 5.4×10^3 Pa at 30.5 °C, 5.4×10^3 Pa at 32.6 °C, and 5.5×10^3 Pa at 34.6 °C.^{61,64} This means that 91, 93, and 96% of polymer chains formed effective network strands in the gel at 30.5, 32.6, and 34.6 °C, respectively. The observed high percentages of polymer chains that were elastically active in the gels might result from the well-defined architecture of the ABA triblock copolymer and the relatively hydrophobic outer blocks (the LCST of PDEGEA is 9 °C).

pH Effect on Sol–Gel Transition of 10.0 wt % Aqueous Solution of P(DEGEA-*co*-AA)-*b*-PEO-*b*-P(DEGEA-*co*-AA). To investigate the pH effects on sol-to-gel transition temperature ($T_{\text{sol-gel}}$) and gel properties, we gradually increased the pH value of the 10.0 wt % aqueous solution of P(DEGEA-*co*-AA)-*b*-PEO-*b*-P(DEGEA-*co*-AA) by injecting a small amount of 1.0 M KOH

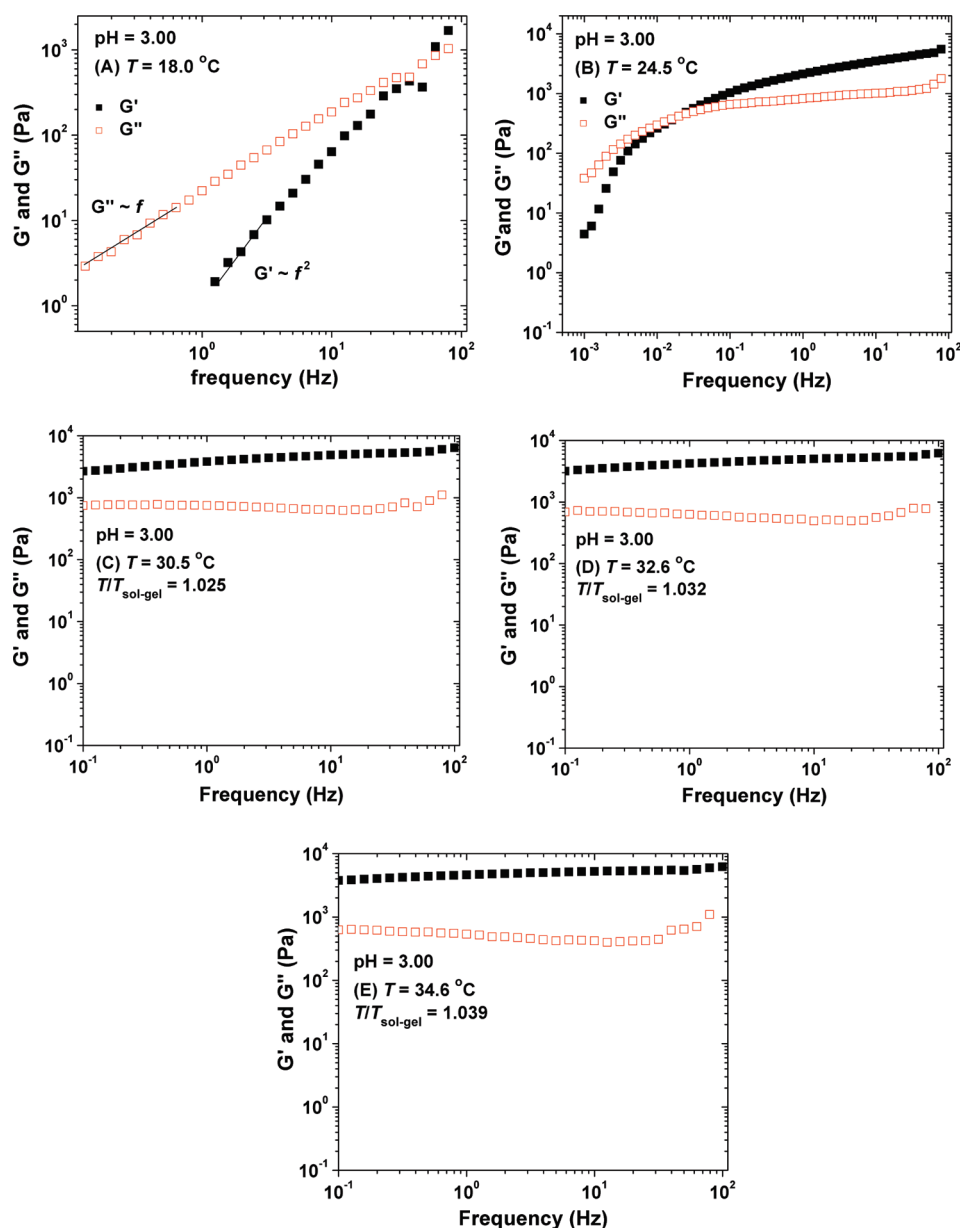


Figure 6. Frequency dependences of dynamic storage modulus G' (■) and loss modulus G'' (□) of the 10.0 wt % aqueous solution of P(DEGEA-*co*-AA)-*b*-PEO-*b*-P(DEGEA-*co*-AA) with a pH of 3.00 at (A) 18, (B) 24.5, (C) 30.5, (D) 32.6, and (E) 34.6 °C. A strain amplitude of 0.2% was used in the frequency sweep experiments.

solution via a microsyringe in a stepwise fashion. Each time, the sample was sonicated in an ice/water ultrasonic bath for a few minutes to ensure that the solution was homogeneous before the pH value was measured. The sample was then subjected to dynamic viscoelastic measurements using the same conditions as for the original polymer solution. Figure 7 shows the sol–gel transition temperature as a function of pH (the original rheological data for some selected pH values are included in the Supporting Information). Similar to our previous observation for the 12.0 wt % aqueous solution of thermo- and pH-sensitive P(DEGMMA-*co*-MAA)-*b*-PEO-*b*-P(DEGMMA-*co*-MAA),²⁸ the $T_{\text{sol-gel}}$ initially increased slowly with the increase of pH, from 23.1 °C at pH = 3.00, to 26.4 °C at pH = 4.11, and 30.1 °C at pH = 4.70. Above pH = 4.95, the increase of the sol–gel transition temperature with pH became slightly faster. In 1.5

pH units, the sol–gel transition temperature jumped by nearly 20 °C, from 31.5 °C at pH = 4.95 to 50.5 °C at pH 6.43. The pH of the polymer solution was then gradually brought back to 3.10 by injection of a 1.0 M HCl solution in a similar stepwise fashion. As shown in Figure 7, the sol–gel transition temperatures from the process of decreasing pH were essentially right on the curve of $T_{\text{sol-gel}}$ versus pH from the process of increasing pH, indicating that the $T_{\text{sol-gel}}$ can be precisely controlled by the solution pH and can be continuously and reversibly tuned in a large temperature range.

To confirm that the tunability of $T_{\text{sol-gel}}$ of the 10.0 wt % aqueous solution of P(DEGEA-*co*-AA)-*b*-PEO-*b*-P(DEGEA-*co*-AA) originated from the pH dependence of the LCST of thermosensitive P(DEGEA-*co*-AA) blocks, we conducted DLS studies of the triblock copolymer in aqueous buffers with a

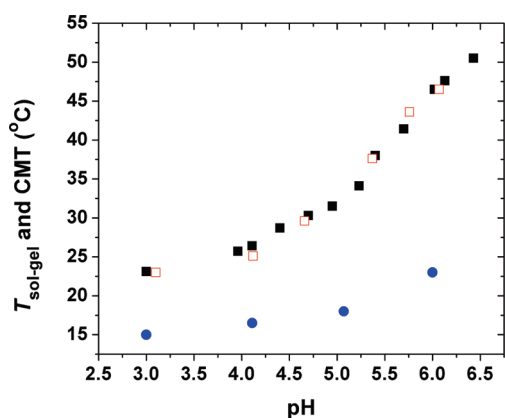


Figure 7. Sol–gel transition temperature ($T_{\text{sol-gel}}$) of 10.0 wt % aqueous solution of P(DEGEA-co-AA)-b-PEO-b-P(DEGEA-co-AA) as a function of pH in the processes of increasing (■) and decreasing pH (□), and the plot of critical micellization temperature (cmt, ●) of the triblock copolymer in the aqueous buffer at a concentration of 0.02 wt % versus pH. The sol-to-gel transition temperatures were determined by dynamic viscoelastic measurements using a heating rate of 3 °C/min, a strain amplitude of 0.2%, and a fixed frequency of 1 Hz. The cmts were determined by dynamic light scattering.

concentration of 0.02 wt % at three more pH values. The cmt of P(DEGEA-co-AA)-b-PEO-b-P(DEGEA-co-AA) gradually increased with the increase of pH, from 15 °C at pH = 3.00, to 16.5 °C at pH = 4.11, to 18 °C at pH = 5.07, and to 23 °C at pH = 6.00.⁶⁵ The cmt curve of the triblock copolymer in 0.02 wt % aqueous solutions exhibited a trend similar to the $T_{\text{sol-gel}}$ curve but there was a shift. It is understandable that at a particular pH the $T_{\text{sol-gel}}$ is higher than the cmt because the gelation requires the formation of a 3-dimensional network with a sufficient mechanical strength, while the cmt is the temperature at which the thermosensitive P(DEGEA-co-AA) blocks begins to self-assemble to form micelles in a dilute aqueous solution. The wider gap between cmt and $T_{\text{sol-gel}}$ curves at high pH values can be attributed to the different effects of charges, formed from the ionization of carboxylic acid groups, on cmt and $T_{\text{sol-gel}}$. Although these results were similar to our previous report, the increase of cmt with pH (from 15 °C at pH = 3.00 to 23 °C at pH = 6.00) was slower compared with a similar thermo- and pH-sensitive ABA triblock copolymer, P(DEGMMA-co-MAA)-b-PEO-b-P(DEGMMA-co-MAA),²⁸ where the cmt jumped by 14 °C from pH = 3.2 to 6.0. We speculate that this is because PDEGEA (cloud point 9 °C) is more hydrophobic than PDEGMMA (cloud point 25 °C); the ionization of a small amount of carboxylic acid groups (3.5 carboxylic acid groups per thermosensitive block) did not increase the hydrophilicity of thermosensitive blocks as much as for P(DEGMMA-co-MAA).

In the examination of heating ramps for different pH values, we noticed that the sol-to-gel transition became broader with the increase of pH. This can be better seen from the curves of G' normalized by the maximum value of G' versus absolute temperature normalized by $T_{\text{sol-gel}}$ and the curves of $\tan\delta$ ($=G''/G'$) versus normalized temperature ($T/T_{\text{sol-gel}}$) for four selected pH values (3.00, 4.11, 5.23, and 6.13) in Figure 8. The graphs illustrate how sharply the solution is transformed into a gel and how closely it approaches the elastic limit. From both plots in Figure 8, the sample at the original pH (3.00) exhibited the sharpest liquid-to-solid transition and the sol-to-gel transition at pH = 6.13 was significantly broader. This phenomenon stems

from the weaker and broader LCST transition of thermosensitive P(DEGEA-co-AA) blocks at a higher pH, which can be seen from DSC thermograms in Figure 3. With the increase of pH, the maximum peak position shifted to a higher temperature and the peak became significantly broader, similar to the observation reported in the literature.⁶⁶ As discussed by Urry,⁶⁶ the introduction of charges onto a thermosensitive polymer disrupts the structured water, weakening the LCST transition. In addition, the random distribution of a small amount of charges along the polymer chain also contributes to the broader LCST transition (on average there were only 3.5 carboxylic acid groups per P(DEGEA-co-AA) block).

pH Effect on Gel Property of 10.0 wt % Aqueous Solution of P(DEGEA-co-AA)-b-PEO-b-P(DEGEA-co-AA). Three normalized temperatures, $T/T_{\text{sol-gel}} = 1.025$, 1.032, and 1.039, where T and $T_{\text{sol-gel}}$ were absolute temperatures, were chosen to conduct frequency sweeps to compare the gel properties at a series of pH values in the processes of both increasing and decreasing pH.⁶⁵ Because the sol–gel transition became broader with the increase of pH, we found that above pH 5.40 the minimum value of G'' was not observed in the studied frequency range for all three normalized temperatures and thus the plateau value of G' could not be determined by the aforementioned method for the original pH. In the examination of frequency sweeps from pH 3.00 to 5.23, we noticed that most of plateau values of G' appeared at ~ 10 Hz. To make the comparison easier, we used the value of G' at $f = 10$ Hz as G_N for all pH values and made a plot of G_N versus pH for each normalized temperature (Figure 9). In addition, a plot of the maximum G' obtained from the heating ramp versus pH was included.

As can be seen from Figure 9, the highest moduli appeared at pH = 3.00, which were $\sim 5 \times 10^3$ Pa. At a particular pH, the G_N value either remained about the same or increased slightly with the increase of normalized temperature $T/T_{\text{sol-gel}}$ from 1.025 to 1.039. For example, the G_N at pH = 4.40 was 3.0×10^3 Pa at $T/T_{\text{sol-gel}} = 1.025$, 3.2×10^3 Pa at $T/T_{\text{sol-gel}} = 1.032$, and 3.2×10^3 Pa at $T/T_{\text{sol-gel}} = 1.039$. These G_N values were close to the maximum G' from the heating ramp (2.9×10^3 Pa) at this pH. With the increase of pH from 3.00 to ~ 5.40 , the values of G_N at three normalized temperatures evaluated from frequency sweeps and the maximum G' obtained from the heating ramp all decreased and the sharpest drop occurred at pH of ~ 4.7 . For example, the G_N at $T/T_{\text{sol-gel}} = 1.025$ was only 1.1×10^3 Pa at pH = 5.40, significantly lower than that at pH = 3.00 (4.9×10^3 Pa). Clearly, at all three normalized temperatures, the gel became weaker with the increase of pH. When the pH was above 5.5, the dynamic moduli appeared to level off. This is somewhat different from the pH effect on $T_{\text{sol-gel}}$, which continued to increase (Figure 7). For the process of decreasing pH by the addition of HCl, the moduli exhibited a pH dependence similar to that in the process of increasing pH, but appeared to be slightly lower, especially in the low pH region (e.g., at pH = 4.12 and 3.10).

As mentioned earlier, the G_N of a 3-dimensional physical network gel is a measure of the number density of elastically active polymer chains ($G_N = \nu k_B T$). The decrease in G_N means the reduction of the number of bridging polymer chains in the gel. To better view how pH affected the gel property, we calculated the percentages of PEO blocks that were elastically active at three normalized temperatures (Figure 10). The percentage of effective network strands decreased with the increase of pH for all three normalized temperatures in the pH range of 3.00–5.40. Below pH = 4.0, the change was moderate.

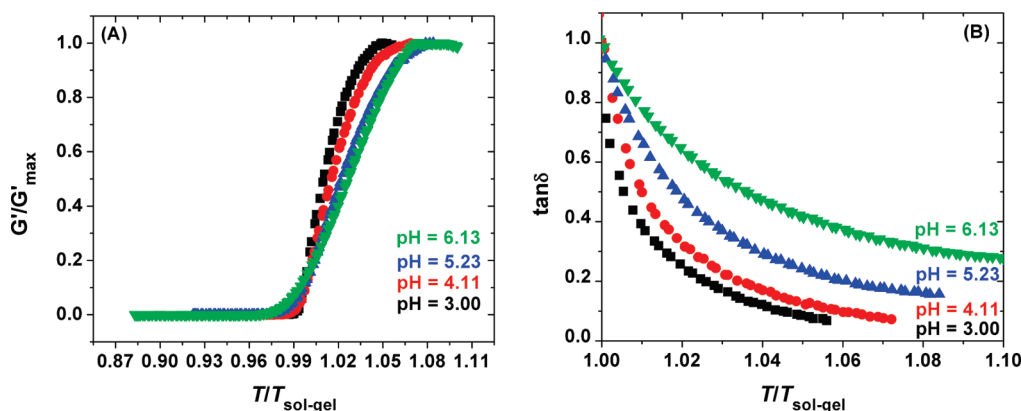


Figure 8. Plot of (A) normalized dynamic storage modulus G'/G'_{\max} , where G'_{\max} is the maximum value of G' observed in the heating ramp experiment, and (B) $\tan \delta$ ($=G''/G'$) versus normalized temperature $T/T_{\text{sol-gel}}$, where T and $T_{\text{sol-gel}}$ are absolute temperatures, for the 10.0 wt % aqueous solution of P(DEGEA-co-AA)-*b*-PEO-*b*-P(DEGEA-co-AA) with pH values of 3.00 (■), 4.11 (●), 5.23 (▲), and 6.13 (▼).

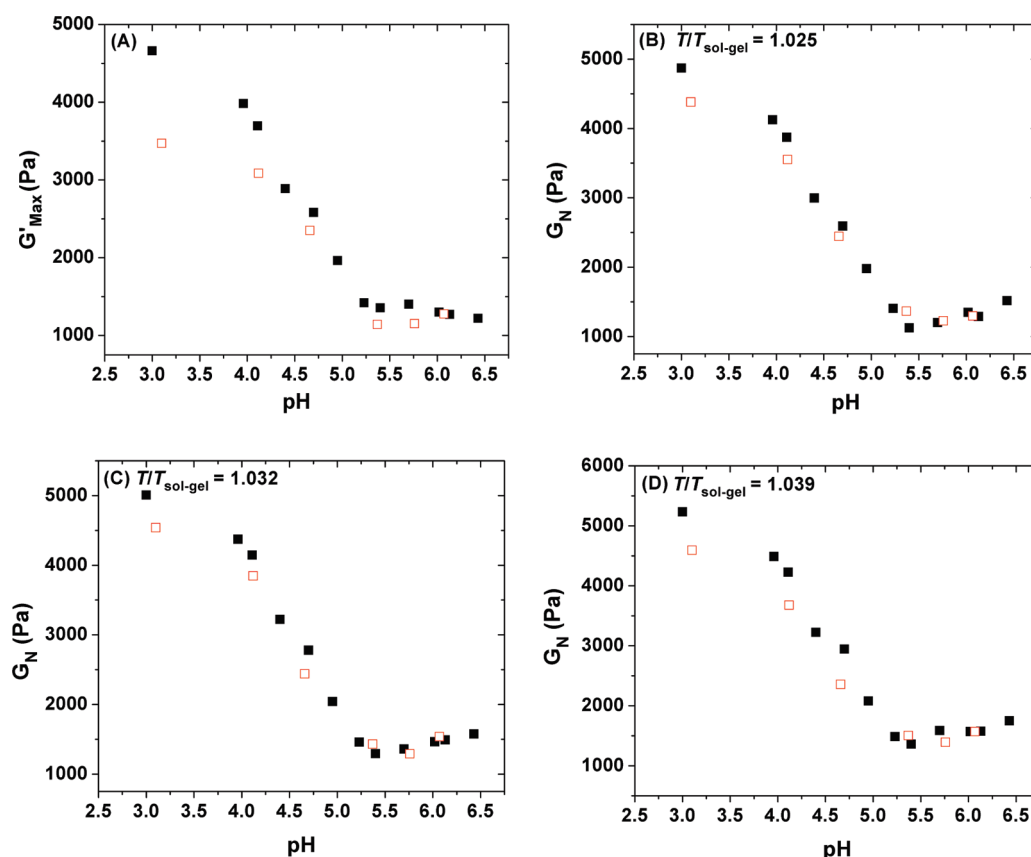


Figure 9. Maximum G' from heating ramp (A) and plateau moduli G_N at three normalized temperatures, $T/T_{\text{sol-gel}} = 1.025$ (B), 1.032 (C), and 1.039 (D), obtained from frequency sweeps as a function of pH obtained from the processes of gradually increasing pH (up to 6.43, ■) by the addition of 1.0 M KOH solution and then gradually decreasing pH (□) by the addition of 1.0 M HCl. T and $T_{\text{sol-gel}}$ are absolute temperatures.

For example, for $T/T_{\text{sol-gel}} = 1.025$, the fraction decreased from 90% at pH 3.00 to 71% at pH 4.11. With the increase of pH from 4.11 to 5.40, a dramatic drop in the fraction of bridging chains was observed, e.g., from 71% at pH 4.11 to 21% at pH 5.70 at the normalized temperature of $T/T_{\text{sol-gel}} = 1.025$. Above pH 5.4, the apparent number of bridging polymer chains changed little with pH.

Decreasing the solution pH from 6.43 to 3.10 gave essentially the same pH dependence as in the process of increasing pH.

However, just like the G_N , the fraction of elastically active polymer chains at a particular pH (below 5.0) in the process of decreasing pH appeared to be slightly lower than that at the same pH in the process of increasing pH. We speculate that two factors could be responsible for this observation. (1) The addition of 1.0 M KOH and later 1.0 M HCl aqueous solution to change the pH diluted the polymer solution. Calculations show that the polymer concentration decreased from 10.0% to 9.7% if the carboxylic acid groups were fully ionized by KOH and then fully protonated

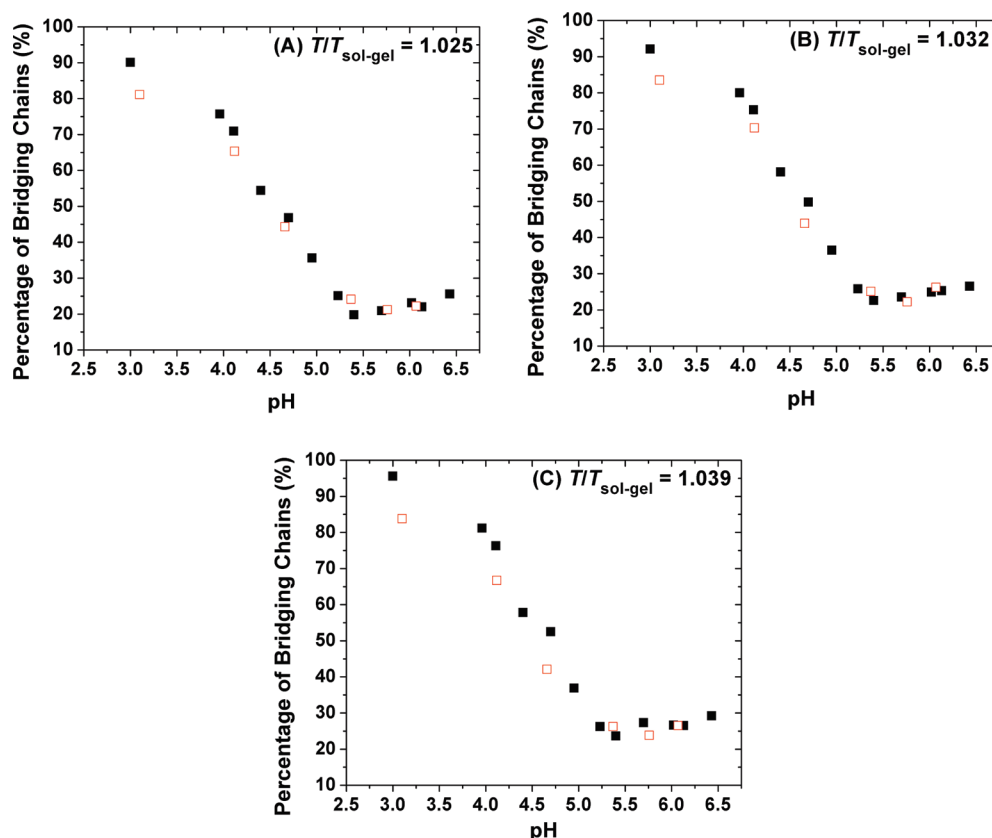


Figure 10. Percentage of PEO blocks that were elastically active in the gels at normalized temperature $T/T_{\text{sol-gel}} = 1.025$ (A), 1.032 (B), and 1.039 (C), respectively, in the processes of increasing (■) and decreasing pH (□).

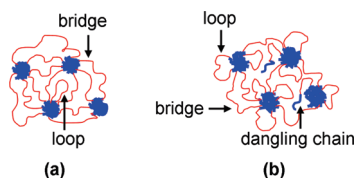
by HCl. Everything being equal, the value of G_N would decrease by 3%. This means that at pH = 3.00, the G_N would be $4869 \text{ Pa} \times 97\% = 4722 \text{ Pa}$. (2) KCl, an inorganic salt, was produced when 1.0 M HCl was added to decrease the solution pH to 3.10. The presence of a salt could affect sol-to-gel transition and gel characteristics. To look into the possible salt effect, we conducted a study by gradually adding 1.0 M KCl solution into a polymer solution with pH = 4.64. This polymer solution was obtained by changing the pH value of the original 10.0 wt % aqueous solution of P(DEGEA-co-AA)-*b*-PEO-*b*-P(DEGEA-co-AA) to 6.43 by the addition of 1.0 M KOH solution and then to 3.10 by the addition of 1.0 M HCl solution, followed by the injection of 1.0 M KOH until the solution pH reached 4.64.

We found that there was very little change in the $T_{\text{sol-gel}}$ even after the addition of KCl twice the amount of COOH/COOK in the solution (the $T_{\text{sol-gel}}$ decrease $\leq 0.6^\circ\text{C}$).⁶⁵ Similarly, the values of G_N only decreased slightly with the addition of KCl at three normalized temperatures except for $[\text{KCl}]/[\text{AA}] = 200\%$, where noticeable decreases were observed.⁶⁵ Nevertheless, there seemed to be a trend that the G_N decreased with the increase of the amount of added KCl, though quite small. Again, the situation was complicated by the dilution; the polymer concentration decreased by 3% after the addition of KCl twice the amount of COOH/COOK. From this control experiment, it appeared that both the dilution and the formation of KCl from the injection of 1.0 M KOH and HCl contributed to the difference in the values of G_N at a particular pH in the processes of increasing and decreasing pH and likely the dilution was the main factor.

The decrease of the fraction of bridging polymer chains with the increase of pH was undoubtedly accompanied by the increase

in the numbers of loops (the two outer blocks of an ABA triblock copolymer located in the same micelle core) and dangling chains (one outer block staying in bulk water rather than in a micellar core) (see Scheme 2 for the schematic illustration of the gel structures of the ABA triblock copolymer at a low pH and a high pH value). Despite the DLS studies showing that there were no significant differences in micelle sizes at pH of 3.00 (apparent $D_h = \sim 64 \text{ nm}$, Figure 4B), 4.11 (apparent $D_h = \sim 64 \text{ nm}$), 5.07 (apparent $D_h = \sim 69 \text{ nm}$), and 6.00 (apparent $D_h = \sim 60 \text{ nm}$) at the concentration of 0.02 wt %, ⁶⁵ we speculated that in the 10.0 wt % polymer solution the size of micellar cores formed by the dehydrated P(DEGEA-co-AA) blocks increased slightly at higher pH values because of the charge–charge interaction inside the micellar core. A larger micellar core would facilitate the formation of loops because the larger core size lowers the entropy penalty for polymer chains to loop back to the same core. On the other hand, the ionization of carboxylic acid groups increases the overall hydrophilicity of polymer chains, which may increase the number of dangling polymer chains in water. To look into this possibility, we measured the critical micellization concentrations (cmc) of P(DEGEA-co-AA)-*b*-PEO-*b*-P(DEGEA-co-AA) at four pH values (pH = 3.00, 4.01, 5.00, and 6.02) and at temperatures corresponding to the sol–gel transition temperatures of the 10.0 wt % polymer solution by fluorescence spectroscopy using Nile Red as fluorescence probe. The cmc of the triblock copolymer was 0.019 mg/mL at pH = 3.00 (23 °C), 0.020 mg/mL at pH = 4.01 (26 °C), 0.023 mg/mL at pH = 5.00 (32 °C), and 0.024 mg/mL at pH 6.02 (47 °C).⁶⁵ Although the increase of the cmc with the increase of pH was small, the trend was discernible, evidencing that the polymer

Scheme 2. Schematic Illustration of the Gel Structures of 10.0 wt % Aqueous Solution of P(DEGEA-co-AA)-*b*-PEO-*b*-P(DEGEA-co-AA) at a Low pH (a) and a High pH (b) Value^a



^aThe increased formation of loops and dangling chains contributes to the decrease in the gel strength at high pH values.

chains became more hydrophilic at higher pH values and likely more thermosensitive end blocks were located in bulk water as dangling chains.

It is believed that both the loop formation and the increased presence of dangling chains contribute to the observed decreases of G_N and the percentage of elastically active polymer chains with the increase of pH from 3.00 to 5.40. Above pH = 5.4, it appeared that the ionization of the remaining carboxylic acid groups on the thermosensitive blocks had a negligible effect on the gel strength.

CONCLUSIONS

We synthesized a well-defined thermo- and pH-sensitive ABA triblock copolymer, P(DEGEA-co-AA)-*b*-PEO-*b*-P(DEGEA-co-AA), and conducted a systematic study on thermo-induced sol–gel transitions and gel properties of 10.0 wt % aqueous solution of this block copolymer at various pH values. The $T_{\text{sol-gel}}$ can be continuously and reversibly tuned in a large temperature range by changing the solution pH. The sol–gel transition became broader with the increase of pH, which was caused by the weaker and broader LCST transition of P(DEGEA-co-AA) blocks at higher pH values. The plateau moduli G_N of the gels at three normalized temperature ($T/T_{\text{sol-gel}} = 1.025, 1.032, \text{ and } 1.039$) decreased with the increase of pH with the sharpest change observed at pH = ~ 4.7 ; accordingly, the percentages of elastically active polymer chains, calculated from G_N through $G_N = \nu k_B T$, dropped from $\sim 90\%$ at pH 3.00 to $\sim 25\%$ at pH of 5.23. Above pH 5.4, the G_N and the fraction of bridging polymer chains leveled off. Decreasing the pH gave a pH dependence of G_N similar to that in the process of increasing pH, but the value of G_N at a particular pH appeared to be slightly lower. This is believed to result from the dilution of the polymer solution and the formation of KCl in the process of changing the solution pH. The reduction of the number density of bridging polymer chains at a higher pH was undoubtedly accompanied by the increase of number of nonbridging chains (loops and dangling polymer chains). With the increase of pH, the carboxylic acid groups on the polymer chains were ionized and the polymer became more hydrophilic. The charge–charge interaction in the micellar core could cause the core to be larger, which could facilitate the loop formation. The increase in the number of dangling polymer chains with the increase of pH was supported by the results from fluorescence spectroscopy studies, which showed that the cmc of P(DEGEA-co-AA)-*b*-PEO-*b*-P(DEGEA-co-AA) at a temperature corresponding to $T_{\text{sol-gel}}$ was higher at a higher pH value. The results reported in this article showed that both the sol–gel transition temperature and gel strength can be tuned by varying the solution pH. Considering that the type and amount of weak acid or base groups on thermosensitive end blocks can be easily

changed, this type of doubly responsive ABA triblock copolymers could offer greater design flexibility for many potential applications.

ASSOCIATED CONTENT

S Supporting Information. Calculation of plateau moduli of an ideal gel at different temperatures; heating ramps and frequency sweeps for the 10.0 wt % aqueous solution of P-(DEGEA-co-AA)-*b*-PEO-*b*-P(DEGEA-co-AA) at selected pH values; DLS data for 0.02 wt % solutions of P(DEGEA-co-AA)-*b*-PEO-*b*-P(DEGEA-co-AA) in 10 mM KHP buffers with pH values of 4.11, 5.07, and 6.00; heating ramps and frequency sweeps for the polymer solution after the addition of various amounts of KCl; effect of added KCl on $T_{\text{sol-gel}}$ and plateau moduli G_N ; fluorescence spectra of Nile Red in aqueous polymer solutions with various polymer concentrations at different pH values. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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