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ARTICLE

Stimuli-Induced Multiple Sol−Gel−Sol Transitions of Aqueous Solution of a Thermo- and Light-Sensitive Hydrophilic Block Copolymer

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ABSTRACT: We report in this article that a 20.0 wt % aqueous solution of a thermo- and light-sensitive hydrophilic block copolymer, poly(ethylene oxide)-*b*-poly(ethoxytri(ethylene glycol) acrylate-*co*-*o*-nitrobenzyl acrylate) (PEO-*b*-P(TEGEA-*co*-NBA)), can undergo multiple sol−gel−sol transitions in response to temperature changes and UV irradiation. The 20.0 wt % block copolymer solution was a free-flowing liquid at low temperatures. Upon heating above the lower critical solution temperature (LCST) of the thermo- and light-sensitive P(TEGEA-*co*-NBA) block, micellization occurred with the P(TEGEA-*co*-NBA) block associating into the core and the PEO block forming the corona. The solution turned into an immobile, optically isotropic gel at 33 °C. The gel exhibited a finite yield stress, and its dynamic storage modulus was essentially independent of frequency, suggesting that the gel was composed of cubic-packed micelles. With further increasing temperature to 50 °C, the gel flowed under its weight. This is because the PEO corona shrank at elevated temperatures, and thus the structural constraint among micelles was released. At 33 °C, we irradiated the micellar gel with 365 nm UV light. The *o*-nitrobenzyl group of NBA was cleaved, resulting in an increase in the LCST of the thermosensitive block and the dissociation of micelles. Consequently, the gel was transformed into a free-flowing liquid, which upon heating underwent sol−gel−sol transitions, similar to the solution before UV irradiation.

Introduction

Block copolymers can self-assemble into, often spherical, micelles in a selective solvent with the solvophobic block associating into the core and the solvophilic block forming the corona.[1,2] When the effective volume fraction of micelles exceeds a critical value, micelles are packed into an ordered, usually cubic, structure, and the free-flowing solution is transformed into a free-standing micellar gel.[1−25] The sol-to-gel/gel-to-sol transitions of block copolymer solutions, especially aqueous solutions of thermosensitive hydrophilic block copolymers,[12−34] have been intensively studied in the past decades because of the intriguing changes in structures and rheological properties and the potential uses in technological applications.[35−39]

Considerable effort has been invested in poly(ethylene oxide) (PEO)-based block copolymers, particularly block copolymers of PEO and poly(propylene oxide) (PPO) or poly(butylene oxide) (PBO).[1−3,12−25] At a sufficiently high concentration, aqueous solutions of these block copolymers can undergo sol−gel−sol transitions upon heating. The hard gel boundary at low/moderate concentrations in a phase diagram is usually a C-shaped curve. The lower temperature sol−gel boundary is driven by the enhancement of micellization and the ordering of micelles with increasing temperature, while the upper gel−sol boundary results from the shrinking of PEO corona at elevated temperatures.[1−3] Besides the PEO-containing copolymers, other thermosensitive water-soluble block copolymers that can form micellar gels in water have also been reported.[28−34] For example, Aoshima et al. synthesized a series of block copolymers composed of two or more thermosensitive blocks with different lower critical solution temperatures (LCSTs) by a living cationic polymerization technique.[30−33] They observed that 20 wt % aqueous solutions of these block copolymers underwent multistage transitions from clear liquids to transparent gels, to hot clear liquids, to phase-separated opaque mixtures with the increase of temperature. The sol-to-gel and gel-to-sol transition temperatures corresponded to the LCSTs of the thermosensitive blocks.

Of great interest are aqueous block copolymer micellar gels that can respond to more than one external stimulus.[39−47] Up to date, there are only a few reports on such micellar gels and they are thermo- and pH-responsive. These block copolymers were prepared by either growing pH-responsive blocks from or introducing carboxylic acid groups to the chain ends of an ABA triblock copolymer that can form thermoreversible gels in water (e.g., PEO-*b*-PPO-*b*-PEO)[39−45] or using pyromellitic dianhydride to couple PEO-*b*-PPO-*b*-PEO to make multiblock copolymers with carboxylic acid groups being incorporated at the junction points.[46]

In this article, we report that a 20.0 wt % aqueous solution of a thermo- and light-sensitive block copolymer, poly(ethylene oxide)-*b*-poly(ethoxytri(ethylene glycol) acrylate-*co*-*o*-nitrobenzyl acrylate) (PEO-*b*-P(TEGEA-*co*-NBA)), can undergo multiple sol−gel−sol transitions in response to temperature changes and UV irradiation. PTEGEA is a thermosensitive water-soluble polymer with a LCST of 36 °C in water;[48] it belongs to a new family of thermoresponsive hydrophilic polymers.[48−60] The *o*-nitrobenzyl group is known to undergo a photocleavage reaction when exposed to long wavelength UV light.[48,61,62] The key feature of this type of doubly responsive hydrophilic block copolymers is that the LCST of the thermosensitive block can be modulated by a second external stimulus. We previously reported that PEO-*b*-P(TEGEA-*co*-NBA) dissolved molecularly

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in a 0.2 wt % aqueous solution at temperatures below 25 °C and self-assembled into micelles at elevated temperatures.[48] Upon UV irradiation, the *o*-nitrobenzyl group was cleaved and the LCST of the thermosensitive block was increased, causing the micelles to dissociate into unimers. Further increasing the temperature induced the formation of micelles again. In the present work, we examined the solution behavior of a 20.0 wt % aqueous solution of PEO-*b*-P(TEGEA-*co*-NBA) under various conditions by visual inspection (the vial inversion test), rheological measurements, polarized light microscopy, and dynamic light scattering. The sol−gel phase diagrams of the block copolymer in water before and after UV irradiation were mapped out by the vial inversion method.

Experimental Section

Materials. The thermo- and light-sensitive block copolymer used in the present work, PEO-*b*-P(TEGEA-*co*-NBA), was synthesized by atom transfer radical polymerization of a mixture of TEGEA and NBA with a molar ratio of 100: 10 from a PEO macroinitiator with a molecular weight of 5000 Da. The details of synthesis were reported in a previous publication.[48] Size exclusion chromatography analysis using polystyrene standards showed that the number-average molecular weight ($M_{n,SEC}$) was 21 600 Da and the polydispersity index was 1.12. The numbers of TEGEA and NBA units in the thermosensitive block were 88 and 11, respectively, which were determined by the analysis of the ^{1}H NMR spectrum based on the fact that the molecular weight of the PEO block was 5000 Da (i.e., the degree of polymerization of the PEO block was 113).

General Characterization. Gel permeation chromatography (GPC) was carried out at room temperature using PL-GPC 20 (an integrated GPC system from Polymer Laboratories, Inc.) with a refractive index detector, one PLgel 5 μm guard column (50 × 7.5 mm), and two PLgel 5 μm mixed-C columns (each 300 × 7.5 mm, linear range of molecular weight from 200 to 2 000 000 Da according to Polymer Laboratories). The data were processed using Cirrus GPC/SEC software (Polymer Laboratories). Tetrahydrofuran was used as a carrier solvent at a flow rate of 1.0 mL/min. Standard monodisperse polystyrenes (Polymer Laboratories, Inc.) were used for calibration. The ^{1}H (300 MHz) spectra were recorded on a Varian Mercury 300 NMR spectrometer, and the residual solvent proton signal was used as the internal standard.

Preparation of 20.0 wt % Aqueous Solution of PEO-*b*-P(TEGEA-*co*-NBA). The block copolymer was added into a preweighed 3.7 mL vial with an inner diameter of 12 mm. The vial was then placed in a large flask and dried in high vacuum at 55 °C for at least 3 h. The mass of the dried polymer inside the vial was 0.478 g. Milli-Q water (1.917 g) was added into the vial. The mixture was then sonicated in an ice/water ultrasonic bath (Fisher Scientific Model B200 Ultrasonic Cleaner) until the block copolymer was dissolved. The vial was then stored in a refrigerator (~4 °C) overnight to ensure that a homogeneous solution was obtained.

Rheological Measurements. Rheological experiments were conducted using a stress-controlled rheometer (TA Instruments Model TA AR2000). A cone−plate geometry with a cone diameter of 20 mm and an angle of 2° (truncation 57 μm) was employed; the temperature was controlled by the bottom Peltier plate. In each measurement, 90 μL 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 a polymer solution 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. A strain amplitude of $\gamma = 0.2\%$ was used in all dynamic tests to ensure that the deformation was within the linear viscoelastic regime. At each temperature, the solution was equilibrated for at least 2 min prior to data recording. The flow properties (shear stress−shear rate curves) of a polymer solution at selected temperatures were measured by a shear rate ramp from 12 to 300 s^{-1} for duration of 3 min. The apparent viscosities of a polymer solution at different temperatures were measured by a temperature ramp experiment performed at a heating rate of 3 °C/min and a shear rate of 10 s^{-1}.

Photocleavage of *o*-Nitrobenzyl Group of NBA in PEO-*b*-P(TEGEA-*co*-NBA). The long wavelength (365 nm) UV light from a Spectroline ENF-240C hand-held UV lamp equipped with one 4 W long wavelength tube filtered at 365 nm and one short wavelength tube filtered at 254 nm was used for the photocleavage of *o*-nitrobenzyl group of NBA in PEO-*b*-P(TEGEA-*co*-NBA). A 3.7 mL vial that contained a 20.0 wt % aqueous solution of PEO-*b*-P(TEGEA-*co*-NBA) (1.650 g) was placed in a water bath with a preset temperature of 33 °C. After the solution turned into a transparent gel, the gel was irradiated with 365 nm UV light at a distance of ~1 cm for 6 days. The irradiated polymer solution was then analyzed with rheological and dynamic light scattering experiments.

Polarized Light Microscopy Experiments. Polarized light microscopy experiments were conducted on a Leica (DM LB2) polarized light microscope coupled with a Mettler hot stage (FP-90). A 20.0 wt % aqueous solution of PEO-*b*-P(TEGEA-*co*-NBA) and the irradiated solution (a 18.9 wt % aqueous solution of PEO-*b*-P(TEGEA-*co*-acrylic acid) (PEO-*b*-P(TEGEA-*co*-AA))) were added into a thin (0.5 mm) quartz demountable cell. The temperature of the cell was controlled by a Mettler hot stage (FP-90).

Dynamic Light Scattering Studies of Aqueous Solutions of PEO-*b*-P(TEGEA-*co*-NBA) and PEO-*b*-P(TEGEA-*co*-AA). Dynamic light scattering (DLS) studies of aqueous solutions of PEO-*b*-P(TEGEA-*co*-NBA) and PEO-*b*-P(TEGEA-*co*-AA) 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 a scattering angle of 90°. For studies of dilute aqueous solutions, a 20.0 wt % solution of PEO-*b*-P(TEGEA-*co*-NBA) and the UV-irradiated solution (i.e., a 18.9 wt % aqueous solution of PEO-*b*-P(TEGEA-*co*-AA)) were diluted with Milli-Q water to a concentration of 0.20 wt %. The diluted solutions were filtered into borosilicate glass tubes with an inner diameter of 7.5 mm using Millipore hydrophilic PTFE filters (0.2 μm pore size), and the glass tubes were sealed with PE stoppers. The DLS tube was placed in the cell holder of the light scattering instrument and gradually heated. At each temperature, the solution was equilibrated for 15 min prior to data recording. The time intensity−intensity correlation functions were analyzed with a Laplace inversion program (CONTIN).

For studies of concentrated solutions, a 20.0 wt % aqueous solution of PEO-*b*-P(TEGEA-*co*-NBA) and the irradiated solution were filtered into DLS tubes with Millipore hydrophilic PTFE filters (0.2 μm pore size) and sealed with PE stoppers. The tube was placed in the cell holder of the DLS instrument and gradually heated. At each temperature, the solution was equilibrated for 15 min before the scattered light intensity was recorded over duration of 5 min. For each measurement, the sampling position of the DLS tube was changed randomly every 15 s.[29]

Determination of Phase Diagrams of PEO-*b*-P(TEGEA-*co*-NBA) and PEO-*b*-P(TEGEA-*co*-AA) in Water by the Vial Inversion Test. A 3.7 mL vial that contained an aqueous solution of PEO-*b*-P(TEGEA-*co*-NBA) or PEO-*b*-P(TEGEA-*co*-AA) with a known concentration was placed in the water bath of a Fisher Scientific Isotemp refrigerated circulator. The temperature was increased at a step of 1 °C. At each temperature, the solution was equilibrated for 10 min before the vial was tilted or inverted to visually examine if the solution was a mobile liquid

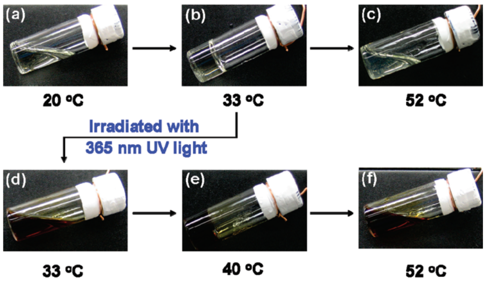


Figure 1. Digital optical pictures of a 20.0 wt % aqueous solution of poly(ethylene oxide)-*b*-poly(ethoxytri(ethylene oxide) acrylate-*co*-*o*-nitrobenzyl acrylate) (PEO-*b*-P(TEGEA-*co*-NBA)) at (a) 25 °C, (b) 33 °C, and (c) 52 °C before UV irradiation and at (d) 33 °C, (e) 40 °C, and (f) 52 °C after UV irradiation. At 33 °C, the 20.0 wt % aqueous solution of PEO-*b*-P(TEGEA-*co*-NBA) was irradiated for 6 days with 365 nm UV light from a Spectroline ENF-240C hand-held UV lamp.

or an immobile gel under its own weight. The temperature at which the solution changed from a mobile to an immobile state (or vice versus) was taken as the sol-to-gel (or gel-to-sol) transition temperature. Polymer solutions with different concentrations were obtained by adding a predetermined amount of water into the vial or evaporating water from the solution; their sol-to-gel/gel-to-sol transition temperatures were determined by the vial inversion method described above.

Results and Discussion

Multiple Sol−Gel−Sol Transitions of a 20.0 wt % Aqueous Solution of PEO-*b*-P(TEGEA-*co*-NBA) in Response to Temperature Changes and UV Irradiation. For study of sol−gel−sol transitions, a 20.0 wt % aqueous solution was made by dissolving PEO-*b*-P(TEGEA-*co*-NBA) in Milli-Q water in a vial with an inner diameter of 12 mm and heated at a step of 1 °C in a water bath. At each temperature, the solution was equilibrated for 10 min, and the vial was tilted or inverted to visually examine if the solution was a flowing liquid or an immobile gel. Figure 1 shows the digital pictures of the block copolymer solution under different conditions. Evidently, the polymer solution was a free-flowing liquid at 20 °C (Figure 1a). Upon gradually heating to 33 °C, the solution turned into a free-standing gel (Figure 1b), which remained immobile even if the vial was inverted. With further increasing the temperature to 50 °C, the gel again flowed. Figure 1c shows the picture of the vial at 52 °C; the solution was a free-flowing liquid again. Note that throughout the studied temperature range from ~0 to ~ 60 °C the polymer solution remained clear.

The DLS study showed that in a 0.20 wt % aqueous solution the critical micellization temperature (CMT) of PEO-*b*-P(TEGEA-*co*-NBA) was 25 °C, and micelles with an apparent hydrodynamic diameter of ~30 nm were observed at temperatures ≥29 °C. From our previous work, the CMT of a 0.20 wt % aqueous solution of a block copolymer with essentially the same chemical composition in the thermosensitive block as the present one increased from 25 to 36 °C after the *o*-nitrobenzyl groups of NBA units were photocleaved.[48] Thus, in principle, the gel at 33 °C shown in Figure 1b can be converted to a free-flowing solution if the CMT of the present sample increases by the same or a similar magnitude after UV irradiation. In light of this consideration, we irradiated the gel at 33 °C with 365 nm UV light. After several hours, a brown-red color appeared, indicating that the photochemical reaction occurred. The solution became a free-flowing liquid after 2 days. To achieve a maximum degree of photocleavage of *o*-nitrobenzyl groups in the block copolymer, we kept irradiating the solution for an additional 4 days. The final solution was a deep-red but clear, free-flowing liquid with a very low viscosity at 33 °C (Figure 1d).[63] ^{1}H NMR spectroscopy analysis showed that the peak at 5.45 ppm, a characteristic peak of NBA ($-OCH_2$-$(CH)_2$), almost disappeared after UV irradiation (Figure 2). A quantitative analysis indicated that ~95% of *o*-nitrobenzyl groups were cleaved. The CMT of PEO-*b*-P(TEGEA-*co*-acrylic acid) (PEO-*b*-P(TEGEA-*co*-AA), formed from PEO-*b*-P(TEGEA-*co*-NBA) after the UV irradiation) in a 0.20 wt % aqueous solution was 35 °C, close to the predicted CMT (36 °C). The irradiated solution turned into an immobile gel when the temperature was increased to 40 °C (Figure 1e). Upon further heating, the gel started to flow at 48 °C, which was slightly lower than the gel-to-sol transition temperature (50 °C) of the nonirradiated solution. Figure 1f shows that the solution was a free-flowing liquid at 52 °C. Thus, the 20.0 wt % aqueous solution of PEO-*b*-P(TEGEA-*co*-NBA) can undergo multiple sol−gel−sol transitions under different conditions in response to temperature changes and UV irradiation.

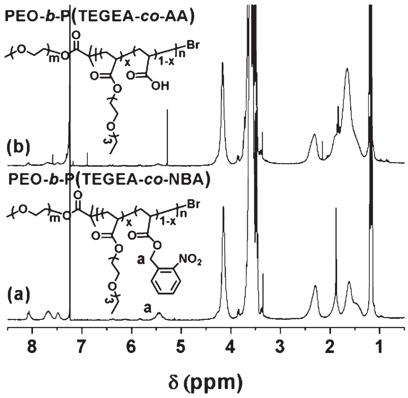
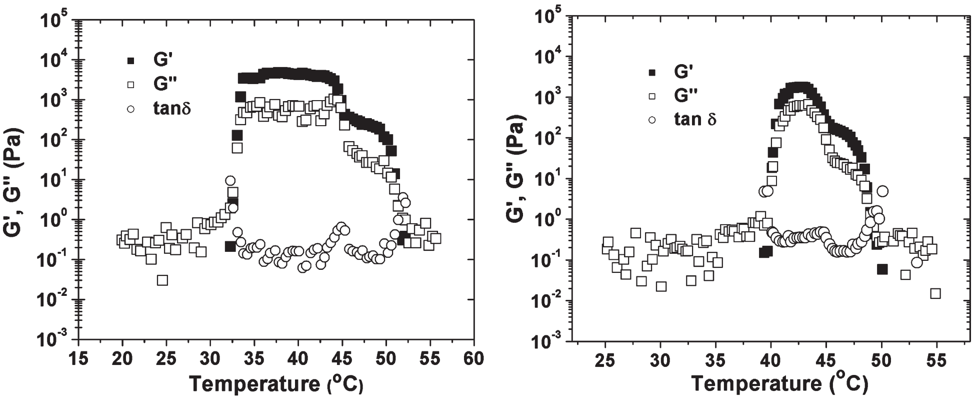


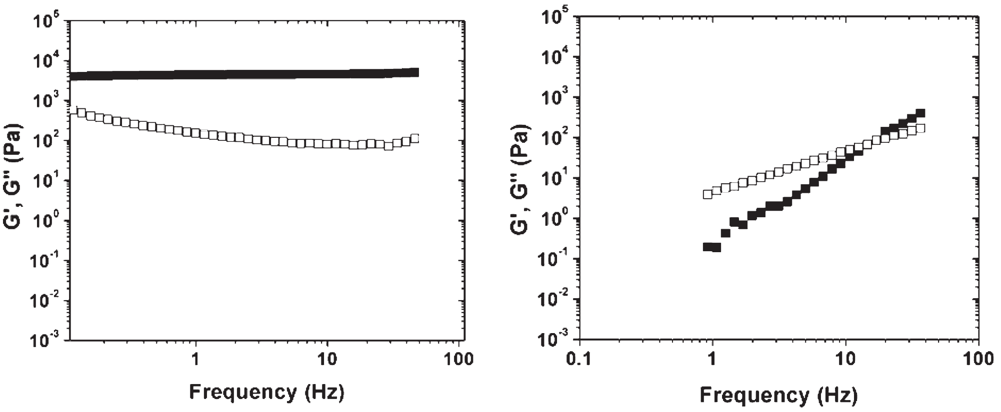
Figure 2. ^{1}H NMR spectra of (a) PEO-*b*-P(TEGEA-*co*-NBA) and (b) PEO-*b*-P(TEGEA-*co*-AA), which was formed from PEO-*b*-P-(TEGEA-*co*-NBA) after UV irradiation at 33 °C for 6 days. $CDCl_3$ was used as the solvent.

Rheological Properties of the 20.0 wt % Aqueous Solution of PEO-*b*-P(TEGEA-*co*-NBA) and the UV-Irradiated Solution. To quantitatively study the solution property changes in the sol−gel−sol transitions shown in Figure 1, we conducted rheological measurements. Figure 3 shows the dynamic viscoelastic properties of the 20.0 wt % aqueous solution before and after UV irradiation at a constant frequency of 1 Hz in a heating ramp with a heating rate of 3 °C/min. A strain amplitude of $\gamma = 0.2\%$ was used to ensure that the measurements were taken in the linear viscoelastic regime. For the solution before UV irradiation, when the temperature was raised from 32 to 33 °C, both dynamic storage G' and loss modulus G'' increased dramatically and G' became larger than G'', indicating that the solution turned into a gel.[1−3] From 33 to 51 °C, G' remained greater than G'', suggesting that the solution was in the gel state in this temperature range. At $T >$ 51 °C, both G' and G'' decreased sharply and G'' became larger than G', which is a characteristic of a free-flowing liquid. The crossover point, $G' = G''$, is commonly used as an indicator of the sol-to-gel or gel-to-sol transition.[1−3] Using this criterion, the sol−gel and gel−sol transition temperatures determined from rheological measurements were 33 and 51 °C, respectively, essentially the same as those estimated by the vial inversion method (33 and 50 °C). A similar phenomenon was observed for the irradiated polymer solution except that the two transitions occurred at 40 and 49 °C, which were again



(a) (b)

Figure 3. Plot of dynamic storage modulus G' (■), loss modulus G'' (□), and tan δ versus temperature for (a) the 20.0 wt % aqueous solution of PEO-*b*-P(TEGEA-*co*-NBA) and (b) the UV-irradiated solution (a 18.9 wt % aqueous solution of PEO-*b*-P(TEGEA-*co*-AA)). The data were collected from temperature ramp experiments with a heating rate of 3 °C/min. A strain amplitude of 0.2% and an oscillation frequency of 1 Hz were used.



(a) (b)

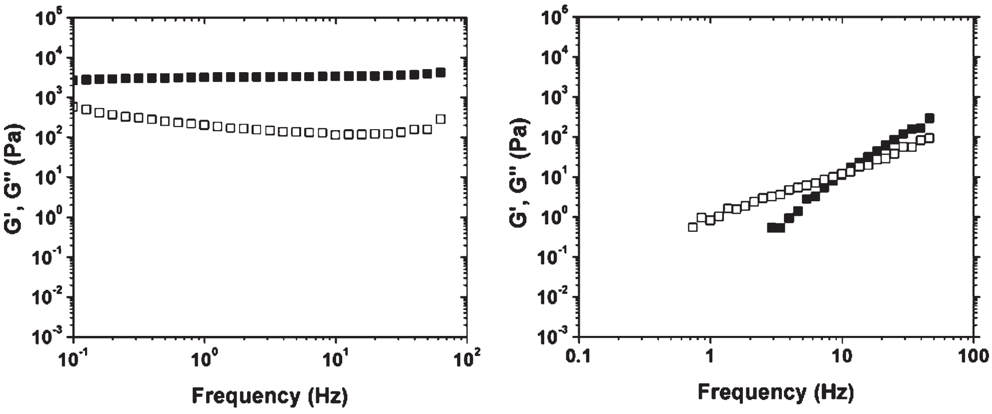
Figure 4. Frequency dependences of dynamic storage modulus G' (■) and dynamic loss modulus G'' (□) of the 20.0 wt % aqueous solution of PEO-*b*-P(TEGEA-*co*-NBA) at (a) 33 and (b) 31 °C. A strain amplitude of 0.2% was used in the frequency sweep experiments.

in good agreement with those determined by the vial inversion test (40 and 48 °C). The gel zone of the irradiated solution, from 40 to 49 °C, was narrower than that of the solution before UV irradiation, from 33 to 51 °C. A closer examination showed that the highest value of G' (4.7 kPa) for the solution before UV irradiation was much higher than that of the irradiated solution (1.7 kPa). A possible reason for this observation is that the concentration of the block copolymer decreased from 20.0 to 18.9 wt % after UV irradiation because of the removal of *o*-nitrobenzyl groups. Thus, the packing of micelles in the gel of the irradiated sample was not as tight as in the gel of the 20.0 wt % solution before UV irradiation.

Interestingly, when the temperature reached 45 °C, G' and G'' of both nonirradiated and irradiated solutions decreased noticeably (Figure 3), but G' was still larger than G'' in the temperature range from 45 to 51 °C for the nonirradiated sample and from 45 to 49 °C for the irradiated sample. A similar phenomenon was observed by Li et al. in a study of the rheological properties of a 27 wt % aqueous solution of PEO-*b*-PBO.[64] Such a gel with lower values of G' and G'' is commonly called a soft gel, which presumably comprised a dynamic network of weakly interacting spherical micelles.[1−3,15,64]

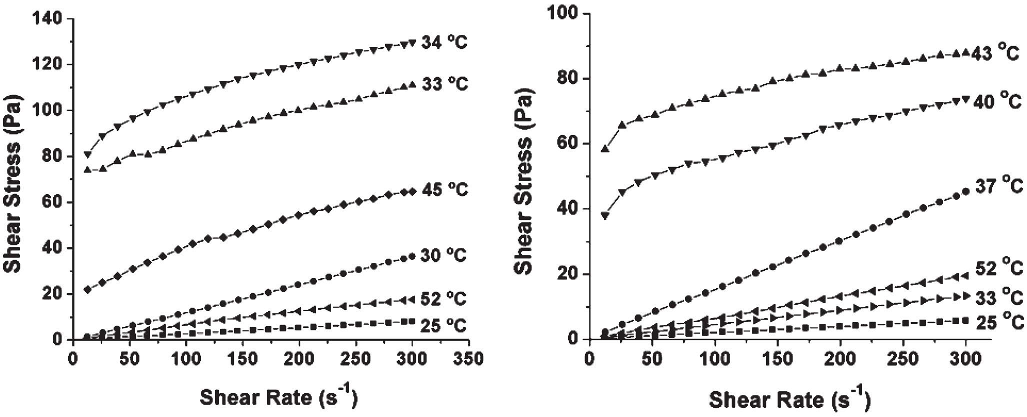
The formation of micellar gels was also evidenced by the data from frequency sweep experiments (Figures 4a and 5a). For the nonirradiated solution at 33 °C, the dynamic storage modulus G' was essentially independent of frequency (Figure 4a), while G'' varied slightly, with a minimum at an intermediate frequency. In addition, G' was about 1 order of magnitude larger than G'' in the studied frequency range from ~0.1 to ~100 s^{-1}. Similar properties were observed for the irradiated sample at 41 °C (Figure 5a). These are the characteristics of elastic solids with a cubic structure,[1−3,65] suggesting that the micelles in both solutions were packed into a cubic lattice. This is also supported by polarized light microscopy results. In the gel zones, both solutions were completely dark under a polarized light microscope with crossed polarizers, demonstrating that the gels were optically isotropic. Note that among all ordered structures only a cubic lattice is optically isotropic. In contrast to the frequency dependences of G' and G'' in the gel zones, for the nonirradiated solution at 31 °C and the irradiated solution at 37 °C, G' and G'' scaled to the second and first power of frequency, respectively (Figures 4b and 5b), which is typical for a viscoelastic fluid.[1−3,29] The fact that G' became larger than G'' in the higher frequency zone implied that the solutions contained heterogeneous assemblies, i.e., micelles at the chosen temperatures.[29]

We further studied the flow properties of both solutions under steady shear conditions. Figure 6 shows the flow curves of the 20.0 wt % aqueous solution of PEO-*b*-P(TEGEA-*co*-NBA) and the irradiated solution at various temperatures. For the nonirradiated solution at 25 °C, the shear stress σ was proportional to the shear rate $d\gamma/dt$, indicating that the solution behaved as a Newtonian liquid.



(a) (b)

Figure 5. Frequency dependences of dynamic storage modulus G' (■) and dynamic loss modulus G'' (□) of the UV-irradiated solution (a 18.9 wt % aqueous solution of PEO-*b*-P(TEGEA-*co*-AA)) at (a) 41 and (b) 37 °C. A strain amplitude of 0.2% was used in the frequency sweep experiments.



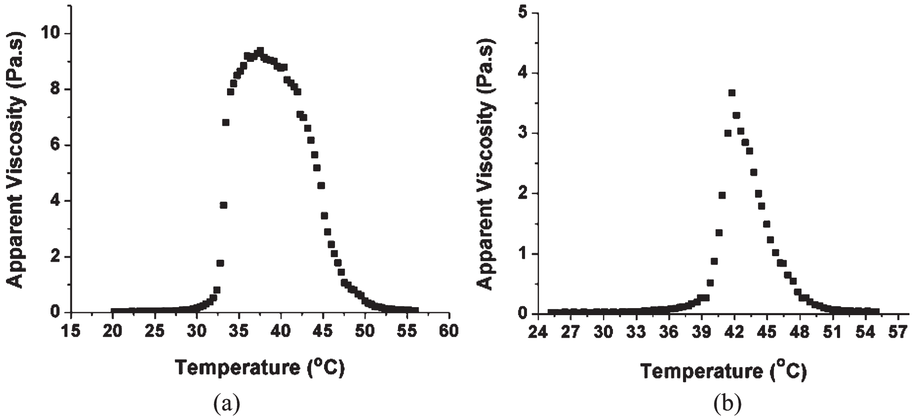
(a) (b)

Figure 6. Flow curves of (a) a 20.0 wt % aqueous solution of block copolymer PEO-*b*-P(TEGEA-*co*-NBA) and (b) the UV-irradiated solution (a 18.9 wt % aqueous solution of PEO-*b*-P(TEGEA-*co*-AA)) at various temperatures.

At 30 °C, the solution was still a Newtonian liquid, but the viscosity was slightly higher, presumably because of the presence of micelles in the solution. At 33, 34, and 45 °C, the solution exhibited a plastic flow behavior with a finite yield stress of ~70, 75, and 20 Pa, respectively. Clearly, once the initial resistance was overcome, the shear stress was essentially proportional to the shear rate. Therefore, the flow behavior can be described by the equation $\sigma = \sigma_0 + \eta\ d\gamma/dt$, where σ_0 is the yield stress and η is the viscosity. At 52 °C, the solution became a Newtonian liquid with a low viscosity (Figure 6a). Similarly, the irradiated solution exhibited a plastic flow behavior with a finite yield stress of ~40 and 60 Pa at 40 and 43 °C, respectively. Below 40 °C and above 49 °C, the polymer solution behaved as a Newtonian liquid.

Figure 7 shows the temperature dependence of apparent viscosity of the 20.0 wt % aqueous solution of PEO-*b*-P(TEGEA-*co*-NBA) before and after UV irradiation at a shear rate of 10 s^{-1}. For the solution before UV irradiation, when the temperature was below 26 °C, the viscosity was <0.040 Pa·s and there was essentially no change when the temperature was increased from 20 to 25 °C. A sharp increase in the apparent viscosity was observed when the temperature was raised to ~33 °C. After reaching the highest value, 9.38 Pa·s, at 38 °C, the apparent viscosity began to decrease with the further increase of temperature. At 56 °C, the apparent viscosity was only 0.063 Pa·s. For the irradiated solution, the apparent viscosity was very low at temperatures below 36 °C and increased rapidly at ~40 °C, where the solution turned into a gel. Upon further heating, the viscosity began to decrease; at 55 °C, the apparent viscosity was only 0.034 Pa·s. These results matched those obtained from dynamic viscoelastic measurements and the vial inversion tests. It was noticed that the highest apparent viscosity of the irradiated solution, 3.66 Pa·s observed at 42 °C, was much smaller than that of the nonirradiated solution (9.38 Pa·s at 38 °C). This is likely due to the decreased polymer concentration after UV irradiation as discussed earlier.

Sol−Gel Phase Diagrams of PEO-*b*-P(TEGEA-*co*-NBA) and PEO-*b*-P(TEGEA-*co*-AA) in Water at Moderate Concentrations. The sol−gel phase diagram of an aqueous solution of a thermosensitive diblock copolymer at low/moderate concentrations is usually a C-shaped curve,[1−3] which can be conveniently mapped out by the tube or vial inversion test. This simple method has been reported to give results in good agreement with those from rheology studies.[1−3] Our own results presented above also demonstrated this agreement. Therefore, we used the vial inversion method to determine the sol−gel phase diagrams of aqueous solutions of PEO-*b*-P(TEGEA-*co*-NBA) and PEO-*b*-P(TEGEA-*co*-AA), formed from PEO-*b*-P(TEGEA-*co*-NBA) after UV irradiation, at moderate concentrations. The results are shown in Figure 8. The lowest concentration (critical gelation concentration, CGC) of PEO-*b*-P(TEGEA-*co*-NBA) in water that can form



(a) (b)

Figure 7. Temperature dependence of the apparent viscosity of (a) the 20.0 wt % aqueous solution of PEO-*b*-P(TEGEA-*co*-NBA) and (b) the irradiated solution at a shear rate of 10 s^{-1}.

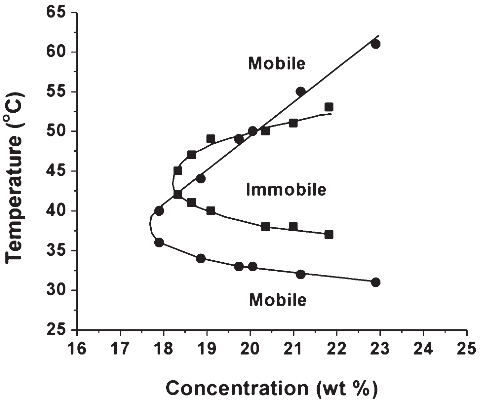


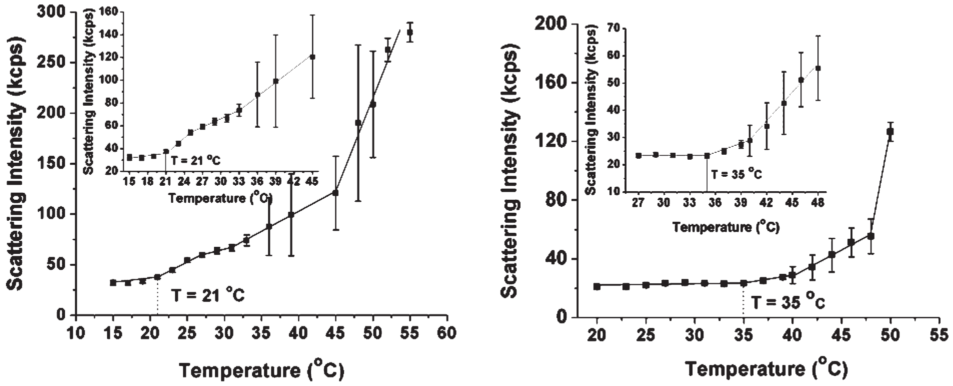
Figure 8. Sol–gel phase diagrams for aqueous solutions of PEO-*b*-P(TEGEA-*co*-NBA) (●) and PEO-*b*-P(TEGEA-*co*-AA) (■), formed from PEO-*b*-P(TEGEA-*co*-NBA) after UV irradiation at 33 °C for 6 days, at moderate concentrations.

a micellar gel was 17.5 wt %. After the cleavage of *o*-nitrobenzyl groups by UV irradiation, the CGC increased slightly to 18.3 wt %, which might result from the increased hydrophilicity of the thermosensitive block of PEO-*b*-P(TEGEA-*co*-AA). It is known that for PEO-based thermosensitive diblock copolymers the lower temperature sol–gel boundary corresponds to the enhanced micellization of the block copolymer with the increase of temperature and the ordering of spherical micelles onto a cubic macrolattice. Since this boundary was related to the LCST of the thermosensitive block, the gelation temperature did not change much with the concentration. From Figure 8, one can see that the sol–gel transition temperature for the concentration of 18.9 wt % was 34 °C, which was ~3 °C higher than that for the 22.9 wt % concentration. The upper temperature boundary is due to the negative coefficient of the PEO solubility in water.[1−3] The gel–sol transition temperature increased sharply from 40 to 60 °C with the increase of concentration from 18.3 to 22.9 wt %. After the UV irradiation, the lower boundary shifted up by ~7 °C, and the slope of the upper boundary was less steep than that for the polymer before UV irradiation.

Mechanisms of Sol-to-Gel/Gel-to-Sol Transitions of the 20.0 wt % Aqueous Solution of the Thermo- and Light-Sensitive Block Copolymer Induced by Temperature Changes and UV Irradiation. As shown in Figure 1, the 20.0 wt % aqueous solution of PEO-*b*-P(TEGEA-*co*-NBA) can undergo multiple sol–gel–sol transitions in response to temperature changes and UV irradiation. This is because the LCST transition temperature of the thermosensitive block of PEO-*b*-P(TEGEA-*co*-NBA) can be modulated by UV irradiation and the PEO solubility in water decreases with an increase in temperature.

As mentioned earlier, the CMT of PEO-*b*-P(TEGEA-*co*-NBA) in a 0.20 wt % aqueous solution was 25 °C, and spherical micelles with an apparent hydrodynamic diameter of ~30 nm were observed at temperatures ≥29 °C. Since the CMT of the block copolymer in the 20.0 wt % aqueous solution could be slightly different from that in a 0.20 wt % solution, we also conducted a DLS study of the concentrated solution. Figure 9a shows the scattering intensity of the 20.0 wt % aqueous solution of PEO-*b*-P(TEGEA-*co*-NBA) at a scattering angle of 90° as a function of temperature. In this experiment, the increase in scattering intensity correlates to an increase in density correlations on the length scale of $d \sim 450$ nm, where this relationship is derived from $d = 2\pi/q$ where $q = 4\pi/\lambda \sin(\theta/2)$; θ is the scattering angle, and λ is the wavelength of the scattered light. Thus, the increase in scattering intensity that is observed at 21 °C can be interpreted as an increase in aggregation and ordering due to micellization, and therefore, light scattering defines the CMT to be 21 °C, about 4 °C lower than in a 0.20 wt % aqueous solution. Note that in the studies of thermosensitive block copolymers of vinyl ethers in water Aoshima et al. found that the CMT of a block copolymer in a concentrated aqueous solution was either the same as or a few degrees lower than that in a dilute solution.[29,33,34] Additionally, the increased scattering that occurred at ~48 °C indicates further increase in density correlations on the length scale of 450 nm at this temperature.

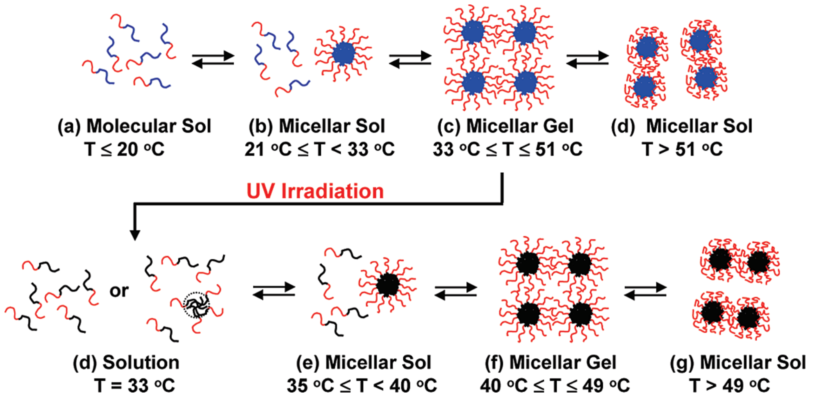
Thus, the combination of experimental results presented in this paper allows us to present a mechanism for the sol–gel/gel–sol transitions of this 20.0% solution. We believe that PEO-*b*-P(TEGEA-*co*-NBA) was dissolved molecularly at $T \leq 20$ °C as schematically illustrated in Scheme 1a. Above ~20 °C, micellization occurred with the thermosensitive P(TEGEA-*co*-NBA) block associating into the core and the PEO block forming the corona. The fraction of polymer molecules in the micelles increased with temperature. At 33 °C, the volume fraction of micelles in the solution reached a critical value and the micellar solution was transformed into a cubic-packed micellar gel (Scheme 1b). The cubic structure was manifested in the frequency independence of G' of the solution at 33 °C in the dynamic rheological measurements and the optical isotropy in the polarized light microscopy experiments.[1−3,65] Upon further heating, the PEO corona shrinks as the solvent quality decreases,



(a) (b)

Figure 9. Scattered light intensity of (a) the 20.0 wt % aqueous solution of PEO-*b*-P(TEGEA-*co*-NBA) and (b) the 18.9 wt % aqueous solution of PEO-*b*-P(TEGEA-*co*-AA) at a scattering angle of 90° as a function of temperature.[66] The data were collected from dynamic light scattering studies. The 18.9 wt % solution of PEO-*b*-P(TEGEA-*co*-AA) was obtained from the 20.0 wt % aqueous solution of PEO-*b*-P(TEGEA-*co*-NBA) after UV irradiation at 33 °C for 6 days. The insets in (a) and (b) show the enlarged plots of scattering intensity vs temperature.

Scheme 1. Schematic Illustration of Thermo- and Light-Induced Multiple Sol-to-Gel/Gel-to-Sol Transitions of the 20.0 wt % Aqueous Solution of PEO-*b*-P(TEGEA-*co*-NBA) under Different Conditions



which results in the breakup of the gel to a sol, where the increase in light scattering suggests that particles are micelle aggregates. This makes sense, as the relatively poor solvent quality of the water for both the core and corona of the micelle would imply that the micelles will aggregate to minimize PEO−water contacts. Further scattering experiments are planned to more thoroughly detail the structure of the particles in this high-temperature sol. Regardless, the structural change causes the release of the structural constraint and the conversion of the gel to a micellar sol (Scheme 1c).

We reported in an earlier study that at a carefully chosen temperature UV irradiation can dissociate the micelles into the unimers.[48] In the present work, we irradiated the micellar gel at 33 °C to cleave the *o*-nitrobenzyl groups. After 6 days, ~ 95% of *o*-nitrobenzyl groups were cleaved, and the gel became a free-flowing liquid with an apparent viscosity of 0.026 Pa·s at 33 °C (Figure 7). Note that the apparent viscosity of the solution before UV irradiation was 3.84 Pa·s at 33 °C, which was nearly 150 times higher than the apparent viscosity of the irradiated solution at the same temperature. The CMT of a 0.20 wt % aqueous solution of PEO-*b*-P(TEGEA-*co*-AA), formed from the PEO-*b*-P(TEGEA-*co*-NBA) after UV irradiation, was 35 °C. Figure 9b shows the plot of scattering intensity of the irradiated solution versus temperature. It appears that the scattering intensity began to increase slightly at 35 °C. As describe above, the scattering at one angle cannot provide sufficient information to characterize the state of PEO-*b*-P(TEGEA-*co*-AA) in the irradiated solution at 33 °C. However, it is very likely that the block copolymer was either in the unimer state or in the early stage of the micellization transition zone at 33 °C. For the latter case, some polymer chains might form interchain clusters or ill-defined micellar aggregates,[29] but a significant amount of PEO-*b*-P(TEGEA-*co*-AA) should be in the unimer state (Scheme 1d). Future scattering experiments will be completed to more thoroughly characterize the structure of these systems. Note that the thermosensitive block P(TEGEA-*co*-AA) of the resultant block copolymer contained ionizable carboxylic acid groups; the LCST of P(TEGEA-*co*-AA) and thus the CMT of PEO-*b*-P(TEGEA-*co*-AA) could be tuned by adjusting the pH.[57] With the further increase of temperature, the solution underwent sol−gel−sol transitions (Scheme 1e,f), similar to the thermo-induced phase transitions of the solution before UV irradiation. From the results of rheology and polarized light microscopy studies, the gel at 41 °C was composed of cubic-packed micelles.

Conclusion

We demonstrated that a 20.0 wt % aqueous solution of a thermo- and light-sensitive hydrophilic block copolymer, PEO-*b*-P(TEGEA-*co*-NBA), can undergo multiple sol−gel−sol transitions under different conditions in response to temperature changes and UV irradiation. The solution was a free-flowing Newtonian liquid with a low viscosity at low temperatures. Upon gradually heating to 33 °C, the solution was transformed into a transparent gel, which exhibited a plastic flow with a finite yield stress under a steady shear condition. The gel flowed under its own weight when the temperature reached 50 °C. At 33 °C, the 20.0 wt % solution was irradiated with 365 nm UV light; the gel was converted to a free-flowing, deep-red liquid. ^{1}H NMR spectroscopy analysis showed that $\sim$95% *o*-nitrobenzyl groups were cleaved. The irradiated solution underwent similar thermo-induced sol−gel−sol transitions except that the sol-to-gel and gel-to-sol transitions shifted to 40 and 48 °C, respectively. Dynamic rheological measurements showed that G' was essentially independent of frequency for the gel at 33 °C before UV irradiation and 41 °C after UV irradiation, suggesting that both gels were composed of cubic-packed micelles, which was also supported by the results from polarized light microscopy studies. The sol−gel/gel−sol transition temperatures determined from rheological measurements were in good agreement with those from visual inspection. The phase diagrams of the block copolymer in water before and after UV irradiation at moderate concentrations were mapped out by the vial inversion method. While the upper boundary did not change much, the lower temperature boundary shifted up by $\sim$7 °C after UV irradiation. The principle used in this work, that is, the sol−gel transition temperatures can be tuned by modulating the LCST of a thermosensitive block via a second external stimulus, can be extended to other block copolymer systems. For example, by incorporating ionizable carboxylic acid groups into the thermosensitive block of a block copolymer, the LCST transition temperatures can be reversibly and precisely tuned by changing the pH,[57] making it possible to precisely control sol−gel−sol transitions.

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(63) It should be noted here that by visual inspection and dynamic light scattering we did not observe any insoluble cross-linked polymer in a 0.2 wt % aqueous solution that was made by diluting the irradiated sample. To further investigate if chain degradation or cross-linking occurred during the UV irradiation, we conducted two control experiments. In the first one, we made a 21.9% aqueous solution of PEO-*b*-PTEGEA ($M_{\mathrm{n,GPC}}$ = 20.9 kDa and PDI = 1.12) that contained *o*-nitrobenzyl alcohol (concentration: 4 mg/mL) to mimic the 20.0 wt % aqueous solution of PEO-*b*-P(TEGEA-*co*-NBA). The solution was irradiated at 30 °C for 6 days with 365 nm UV light from the same UV lamp used for the 20.0 wt % aqueous solution of PEO-*b*-P(TEGEA-*co*-NBA). There were no any changes in the ^{1}H NMR spectrum and in the molecular weight and molecular weight distribution from GPC analysis. The sol-to-gel transition temperature of this solution after UV irradiation was 41 °C, which was identical to that before UV irradiation. In the second experiment, we irradiated a 19.5 wt % aqueous solution of $\mathrm{PEO_{113}}$-*b*-P($\mathrm{TEGEA_{89}}$-*co*-(2-(*o*-nitrobenzyloxy)ethyl acrylate)$_{10}$) ($\mathrm{PEO_{113}}$-*b*-P($\mathrm{TEGEA_{89}}$-*co*-$\mathrm{EGNBA_{10}}$), $M_{\mathrm{n,SEC}}$ = 20.4 kDa, PDI = 1.13) at 30 °C for 6 days with the same UV lamp. ^{1}H NMR spectroscopy analysis showed that the photocleavage was complete. There were essentially no changes in the molecular weight and molecular weight distribution from GPC analysis. Thus, we can conclude from these experiments that the chain degradation or cross-linking of the block copolymer did not occur during the UV irradiation.

(64) Contrary to the report by Li et al. in ref 15 that the soft gel zone could not be located by the tube inversion method, our block copolymer solution did not flow in the tilted/inverted vial in the temperature range of 45−51 °C before UV irradiation and of 45−49 °C after UV irradiation, presumably because our vial had a smaller inner diameter and the gel could support its own weight.

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(66) Each data point in these two plots represents the average of 300 values of scattered light intensity collected at a scattering angle of 90° over a period of 5 min at a constant temperature (one value per second). The fluctuation of scattered light intensity for each data point is the standard deviation. Note that the gel is a nonergodic system and the scattering intensity is position-dependent. Therefore, we changed the sampling position of the DLS tube randomly every 15 s. Clearly, the fluctuation of scattering intensity before the sol-to-gel transition temperature is extremely small. The sol-to-gel and gel-to-sol transitions can also be seen from the changes in the magnitude of the fluctuation of scattered light intensity.