Photoinduced Reversible Transmittance Modulation of Rod-Coil Type Diblock Copolymers Containing Azobenzene in the Main Chain

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Supporting Information

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Experimental Section

General. 2-Cyano-5-nitrobenzotrifluoride,[1a] 4'-hydroxy-4-fluoro-3-(trifluoromethyl)azobenzene,[1b] and 4,4'-di(5-nonyl)-4,4'-bipyridine (dNbpy)[1c] were synthesized according to the literature procedures. 4-Methoxyphenol (Aldrich, ≥99%), 4-aminophenol (Aldrich, ≥99%), α-bromoisobutyryl bromide (Aldrich, ≥98%), styrene (Aldrich, ≥99%), triethylamine (TEA) (Aldrich, ≥99%), copper(I) chloride (Aldrich, ≥99%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) (Aldrich, ≥97%), potassium hydroxide (Dae Jung, ≥99%), and aluminium oxide (Aldrich, ≥99%) were used without further purification. Potassium carbonate (K_2CO_3) was dried *in vacuo* at 150 °C for 24 h prior to use. Dimethyl sulfoxide (DMSO), N,N-dimethyl formamide (DMF), and anisole were stirred in the presence of calcium hydride overnight and then distilled under reduced pressure before use. Methanol (HPLC grade), tetrahydrofuran (THF) (anhydrous grade), dichloromethane (MC) (anhydrous grade), and cyclohexane (anhydrous grade) were used without further purification.

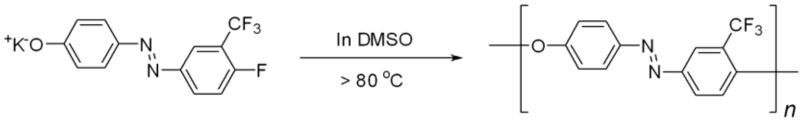
^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra of synthesized materials were recorded by using a Bruker Fourier Transform AVANCE 400 (400.13 MHz for ^{1}H and 100.62 MHz for ^{13}C) spectrometer with the residual solvent signal as an internal reference. Chemical shifts were expressed in parts per million (ppm). Molecular weights and molecular weight distributions of polymers were measured by means of gel permeation chromatography (GPC; Viscotek T60A, column; PLgel 10 μm MIXED-B). The GPC measurements were carried out with THF as eluent at a rate of 1 mL/min at 35 °C and the GPC result was calibrated with PS standards. DLS measurements were performed on a 90Plus/BI-MAS particle size analyzer (Brookhaven Instruments Corp.) at wavelength of 658 nm. The scattering angle used for the measurements was 90°. The CONTIN approximation was used to convert the diffusion coefficient into the hydrodynamic diameter (D_h). Field-emission scanning electron microscopy (FE-SEM) studies were performed on a Philips XL30S FE-SEM. Samples prepared onto silicon wafers were sputtered with gold and investigated by SEM. Field-emission transmission electron microscopy (FE-TEM) study was performed on a Tecnai G2 F30 FE-TEM (300 kV). Photoirradiation was carried out with a 200-W Super Pressure Hg lamp (Lumatec Superlite SUV-DC-P) through a lightguide and an appropriate color filter ($315 < \lambda < 390$ nm for UV light and $400 < \lambda < 500$ nm for visible light). The intensities of the UV and visible lights were ca. 6500 and 8500 mW/cm^2, respectively, at the tip of the lightguide. UV-vis absorption spectra were recorded on a JASCO V-530 spectrometer. The contact angles of resulting thin film were observed with Phoenix 300 goniometer (Surface Electro Optics Co., Ltd., Korea)

Synthesis of monomer and model compound.

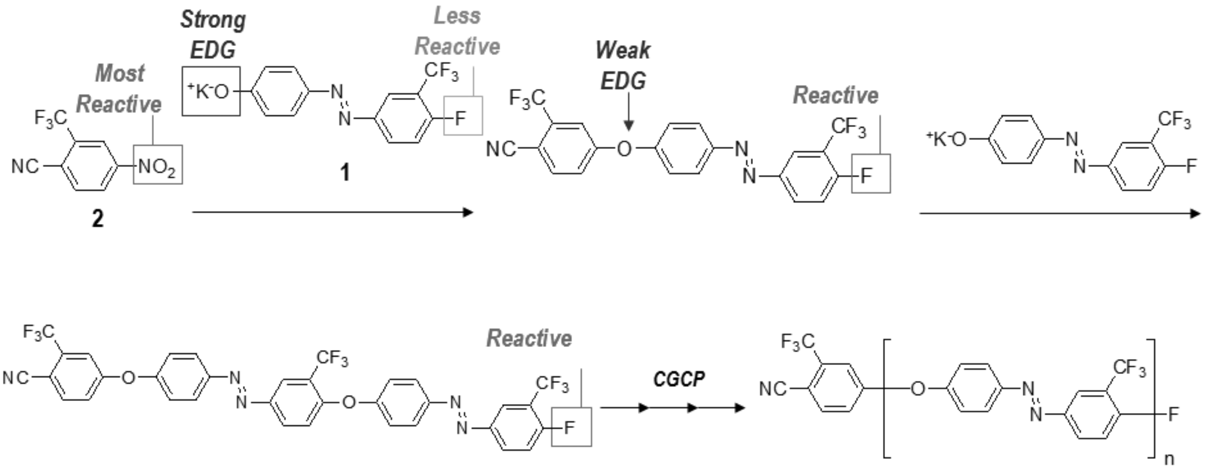
4'-Hydroxy-4-fluoro-3-(trifluoromethyl)azobenzene potassium salt. 4'-Hydroxy-4-fluoro-3-(trifluoromethyl)azobenzene (6.11 g, 21.5 mmol) and 50 mL of methanol were placed in a 250 mL flask. Potassium hydroxide (1.170 g, 20.85 mmol) was dissolved in 20 mL of methanol, and the solution was slowly added to the flask at 0 °C. The mixture was stirred at room temperature for an hour. Solvent was evaporated in a rotary evaporator, and then 100 mL of dichloromethane was added to oil-like product in the flask. The orange powder was filtered, washed with dichloromethane, and dried *in vacuo* (6.47 g, 96%); decomposed at 220 ℃ before melt. MS(Negative), m/e 283.05 (Calcd: 283.05). ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): 7.85 (m, 2H), 7.54 (d, 2H, $J = 9.1$ Hz), 7.48 (t, 1H, $J = 9.5$ Hz), 6.20 (d, 2H, J = 9.1 Hz). ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): 178.2, 156.8 (d, $J = 248.9$ Hz), 150.3, 138.4, 127.3 (br), 126.6 (d, $J = 8.2$ HZ), 122.8 (q, $J = 270.1$ Hz), 120.2, 117.9, 117.7, 117.0 (dq, $J_1 = 32.1$ Hz, $J_2 = 13.4$ Hz).

4-Hydroxy-anisole potassium salt. The above procedure was taken for the monomer synthesis.

Synthesis of poly(arylene ether azobenzene) through chain-growth condensation polymerization. All the polymerizations were carried out under dry nitrogen atmosphere. A dried three-necked flask was equipped with a mechanical stirrer and a Dean-Stark trap connected to a water-cooled condenser. The B type initiator (2-cyano-5-nitrobenzotrifluoride, 0.0729 g, 0.342 mmol), the AB' type monomer (4'-hydroxy-4-fluoro-3-(trifluoromethyl)azobenzene potassium salt, 0.77145 g, 2.394 mmol), and DMSO (15ml, the solid content was maintained at a concentration of 5 wt%.) were placed to the flask. The reaction mixture was polymerized at 70 °C. In order to investigate the polymerization kinetics, the small portion of the reaction mixture was taken via a syringe under dry nitrogen atmosphere in certain time intervals. After the polymerization, the reaction mixture was poured into distilled water with vigorous stirring. The products were filtered and purified by reprecipitation in methanol, and dried *in vacuo* (0.597g, 86.3%).



Scheme S1. Self-initiated polymerization of the AB’ type monomer via step-growth mechanism.



Scheme S2. Chain-growth condensation polymerization of the AB’ type monomer (**1**) with the initiator (**2**).

Without any initiator, the AB’ type monomer (**1**) did not react with itself in DMSO until the reaction temperature increased over 80 °C (Scheme S1). However, the self-initiated polymerization occurred when the temperature increased above 80 °C and the polymers with a broad molecular weight distribution were obtained, because the polymerization proceeded in step-growth mechanism. To avoid self-condensation polymerization, CGCP of the AB’ type monomer was carried in DMSO at 70 °C with the initiator (**2**) as shown in Scheme S2. At 70 °C, the monomer readily reacted only with the initiator and the fluorine group became reactive enough for displacement reaction (S_NAr) because of the conversion of the strong electron-donating phenoxide group to the weak electron-donating ether bond. The polymerization proceeded in a chain-growth manner through the selective and consecutive reaction of the monomer with the growing polymer chain end group.

When the ratio of monomer to initiator was 15 ($[\mathbf{1}]_0/[\mathbf{2}]_0 = 15$) in DMSO at 70 °C, the polymers with narrow molecular weight distributions were obtained until 11 hours of polymerization, but the distributions became broad as the reaction time increased further and the shoulder peak in the high molecular weight region appeared (Figure S1). GPC profiles and ^{1}H-NMR spectra of the crude samples in certain time intervals showed that narrow polydispersity indices (PDIs) was maintained until the conversion of about 50 % (Figure S2) which means CGCP of the AB' type monomer proceeded under the reaction condition. Although a unimodal distribution was obtained from the reaction with the ratio of 8 ($[\mathbf{1}]_0/[\mathbf{2}]_0 = 8$), it was the broader than the distribution of the synthesized polymer with the ratio of 7 ($[\mathbf{1}]_0/[\mathbf{2}]_0 = 7$) (Figure S3). When the ratio of 7, the theoretical molecular weights of polymers were well matched with the experimental molecular weights obtained by ^{1}H-NMR spectra with the assumption of the quantitative initiation (Figure S4).

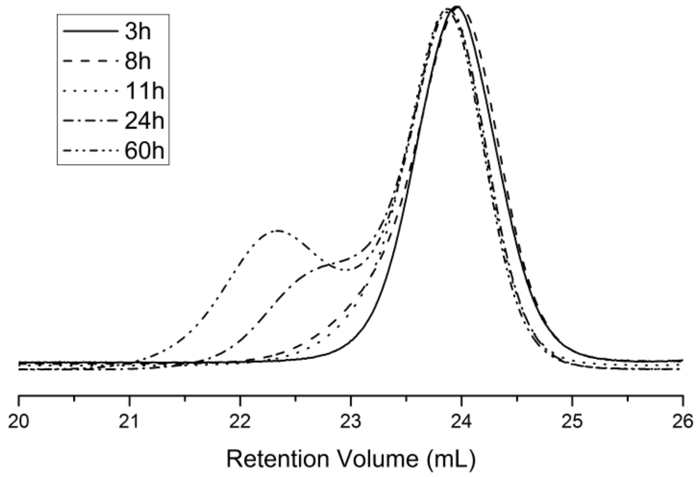
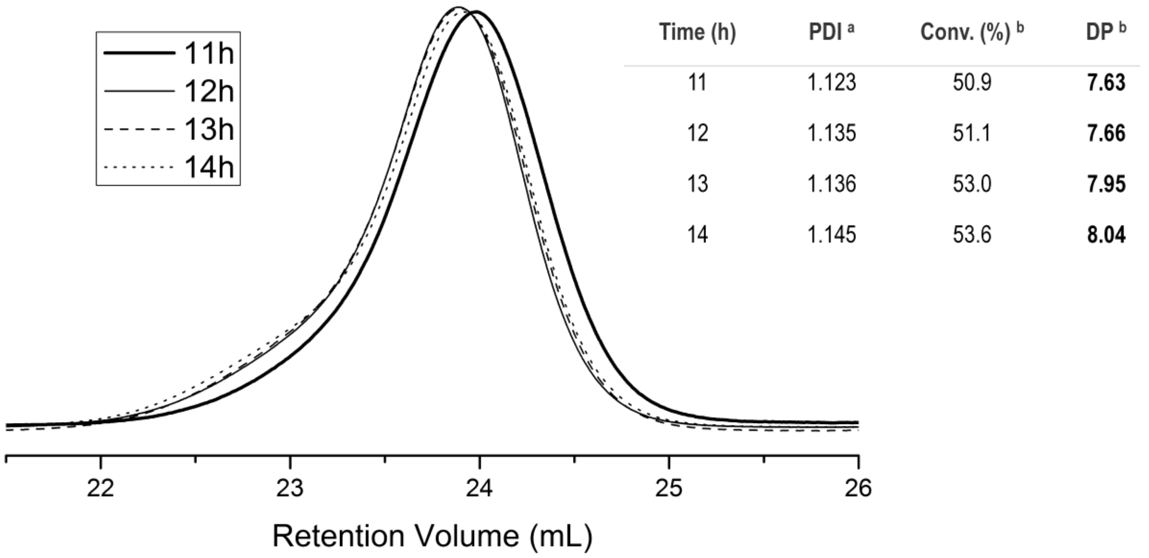


Figure S1. GPC profiles of polymers obtained in certain time intervals from the polymerization of **1** with **2** in DMSO at 70 °C ($[\mathbf{1}]_0/[\mathbf{2}]_0 = 15$).



Time (h)	PDI [a]	Conv. (%) [b]	DP [b]
11	1.123	50.9	**7.63**
12	1.135	51.1	**7.66**
13	1.136	53.0	**7.95**
14	1.145	53.6	**8.04**

Figure S2. GPC profiles of polymers obtained under the same reaction condition shown in Figure S1 but with different time intervals. [a] Polydispersity indices based on PS standards. [b] Conversion and degree of polymerization determined by ^{1}H NMR spectra of the polymers.

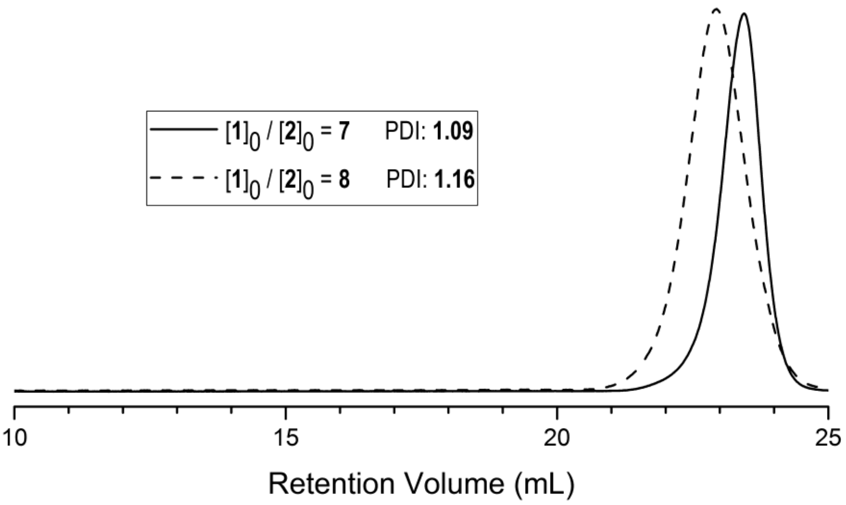


Figure S3. THF-GPC profiles of the polymers obtained by the polymerization of **1** with **2** in DMSO at 70 °C with two different ratios of the monomer to the initiator.

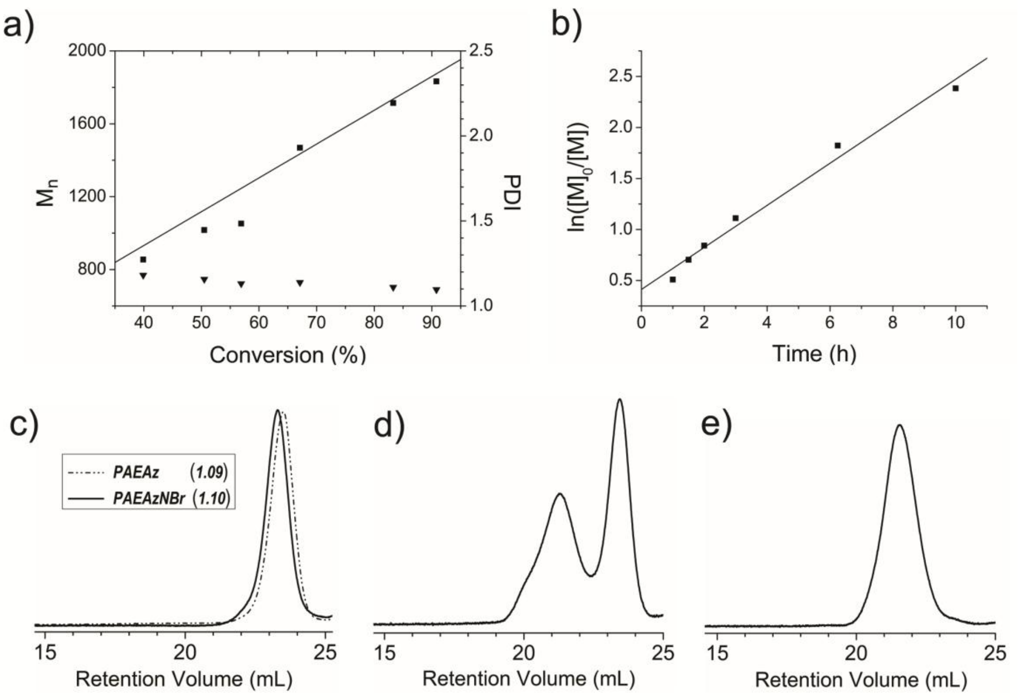


Figure S4. For polymerization with the feed ratio ($[\mathbf{1}]_0/[\mathbf{2}]_0$) of 7 in DMSO, a) Number-average molecular weight M_n (squares) and PDI (triangles) as a function of overall monomer conversion. Theoretical M_n (line) was calculated from the conversion. b) In($[M]_0/[M]$) versus time plot (squares). The line was obtained by linear regression. GPC profiles of c) **PAEAz** and **PAEAzNBr**. obtained block copolymers d) before and e) after extraction with cyclohexane.

In order to investigate the reason why CGCP of the monomer did not proceed as expected, model reactions were conducted. The synthesized polymer with the monomer to initiator ratio of 8 ($[\mathbf{1}]_0/[\mathbf{2}]_0 = 8$) was reacted with the model compound, potassium salt of 4-hydroxy anisole, which has the higher nucleophilicity than that of the monomer (Figure S5). The ^{1}H-NMR spectrum of the polymer in THF-d_8 showed clearly resolved peaks including the peaks of the end groups. The spectra in DMSO-d_6 where the polymer is partially soluble at room temperature but dissolved completely at elevated temperature also exhibit the peaks similar to those in THF-d_8 except some shifts. The peak of proton **13** remained after the model reaction at 70 ^{o}C for 24 hours, while the intensity of the peaks for **a** and **b** protons of 4-hydroxy anisole potassium salt was reduced. The GPC profiles shifted to low molecular weight region, and changed to trimodal due to the transetherification reaction between the model compound, and the backbone ether linkage of the polymer, particularly next to the initiator moiety. The transetherification produced step-growth-species containing pheoxide groups which can further react with growing polymer chains giving rise to high molecular weight polymers. We have tried to utilize other initiators which is less reactive to suppress transetherification during the polymerization. But, mono activated compounds (**I2** and **I3**) and one with amide group (**I4**) had too low reactivity to initiate reaction even at 80 °C (Figure S6).

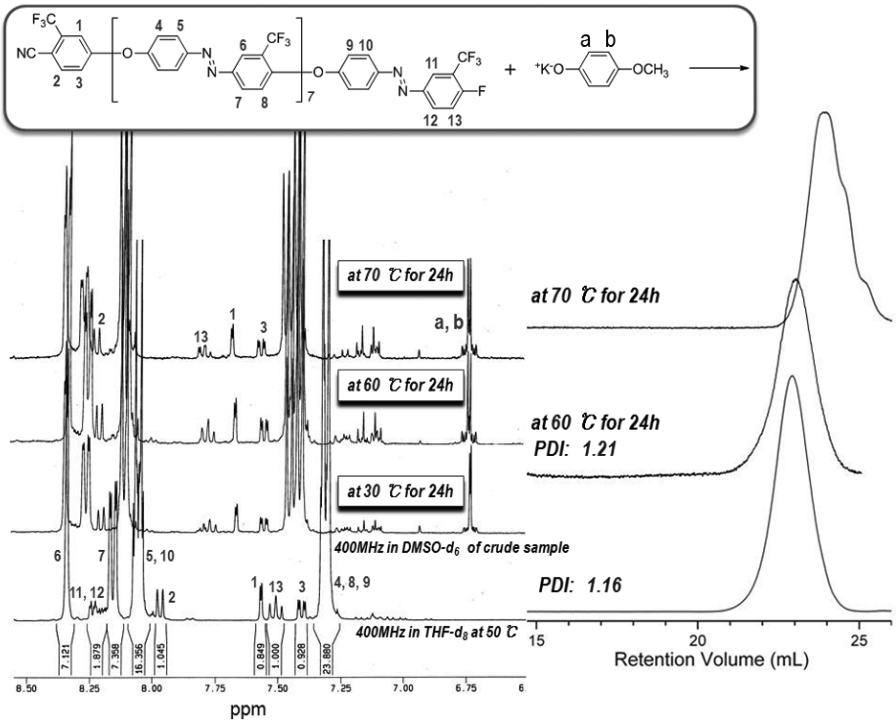


Figure S5. ^{1}H-NMR spectra and GPC profiles after model reactions at various temperatures.

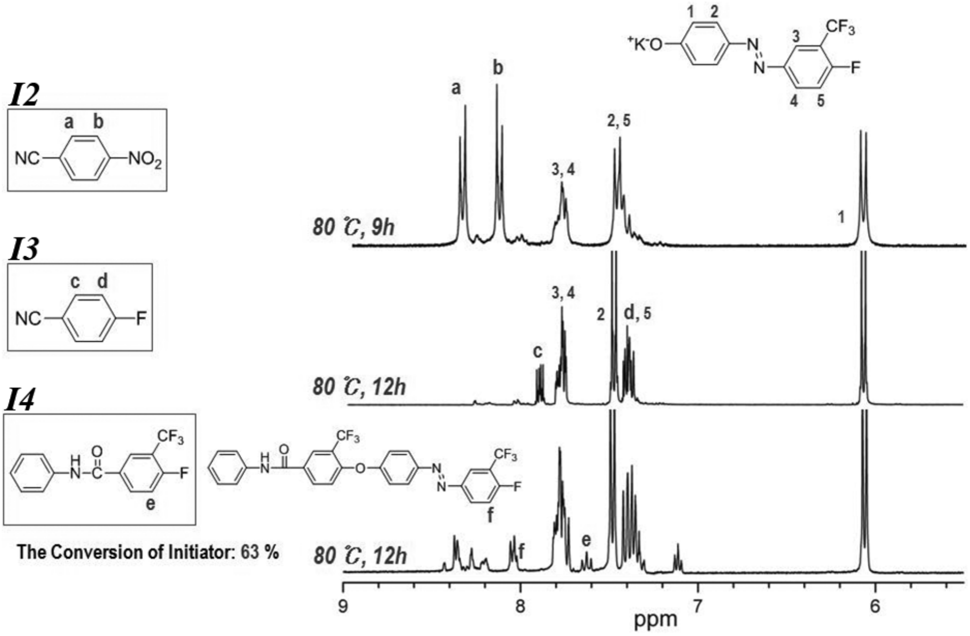


Figure S6. ^{1}H-NMR spectra after the polymerization of **1** with other initiators.

The polymer was soluble in common organic solvents except highly nonpolar solvent such as cyclohexane (Table S1). A T_g of the polymer was detected at 115 °C in the second scan of DSC curves, and 5 % weigh loss occurred at 478 °C (Figure S7).

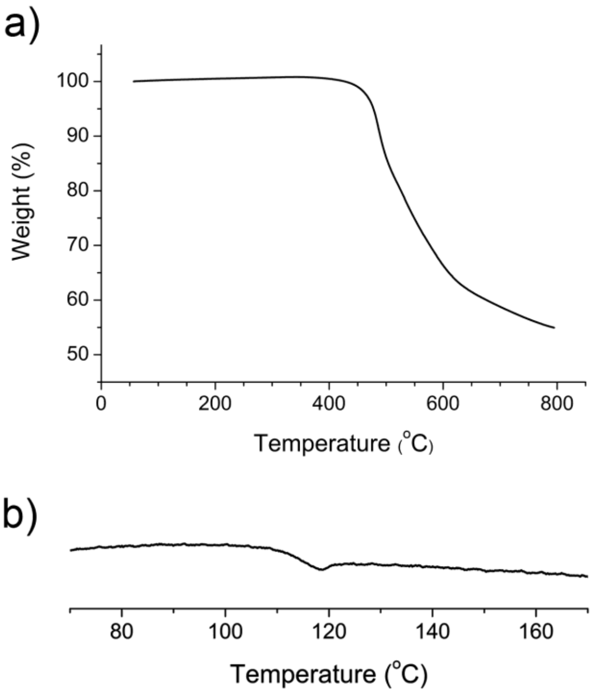


Figure S7. a) TGA thermogram and b) The second scan of DSC curves for **PAEAz** ([**1**]$_0$/[**2**]$_0$ = 7) under N_2 flow with a heating rate of a) 10 and b) 5 °C/min, respectively.

Table S1. Solubility of **PAEAz**.

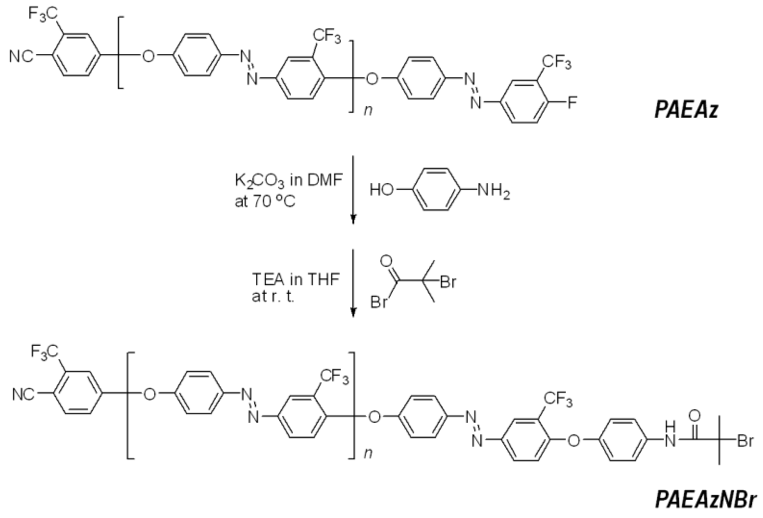
	DMSO	DMAc	DMF	NMP	THF	EA	Tol	MC	CF	DE	Bz	CyHx
PAEAz	+	+	++	++	++	++	++	++	++	++	++	--

++: soluble at room temperature, +: soluble at elevated temperature, --: insoluble; dimethylacetamide (DMAc), *N*-methylpyrrolidinone (NMP), ethylacetate (EA), toluene (Tol), dichloromethane (MC), chloroform (CF), diehtylether (DE), benzene (Bz), and cyclohexane (CyHx) for abbreviations.

End group modification of PAEAz.

The amide-linked macroinitiators (PAEAzNBr). All the reactions (Scheme S3) were carried out under dry nitrogen atmosphere. A dried three-necked flask was equipped with a mechanical stirrer and a Dean-Stark trap connected to a water-cooled condenser. **PAEAz** (0.63360 g, 0.31 mmol), 4-aminophenol (0.06746g, 0.62 mmol), K_2CO_3 (0.10730 g, 0.77 mmol), and DMF (14 mL, the solid content was maintained at a concentration of 5 wt%.) were added to the flask. The reaction mixture was heated at 70 ^oC for 3 hours. After the reaction was completed, the solution was poured into distilled water with vigorous stirring and slightly acidified. The product was filtered, washed with distilled water, and dried *in vacuo*. The product (**PAEAzNH$_2$**) was reprecipitated in methanol.

PAEAzNH$_2$ (0.62 g, 0.29 mmol) was placed into a dried 50 mL flask with triethylamine (0.5836 g, 0.58 mmol) and THF (10 mL). 2-Bromo isobutyryl bromide (0.1326 g, 0.58 mmol) was slowly added to the flask by gastight syringe. The reaction mixture was stirred at room temperature for 1 day. After the reaction was completed, the solution poured into distilled water with vigorous stirring. The precipitate was filtered, washed with distilled water and methanol, and dried *in vacuo*. The product (**PAEAzNBr**) was further purified by the reprecipitation in hexane, and the structures of the products were confirmed by ^{1}H-NMR spectra (Figure S8).



Scheme S3. End group modification of **PAEAz** for introducing ATRP initiator.

To make rod-coil type diblock copolymers, ATRP initiator was introduced into the **PAEAz**. Scheme S3 shows synthetic routes to the amide-linked macroinitiators from the **PAEAz**. The fluorine leaving group at the chain end of **PAEAz** was readily displaced with 4-aminophenol by S_NAr reaction. The peak of proton **13** in Figure S8 clearly shifted to an up field. ^{1}H-NMR spectra indicate that the displacement occurred completely. All the molecular weight distribution slightly shifted to high molecular regions, but retained narrow unimodal distribution in GPC profiles, suggesting no side reaction such as transetherification occurred (Figure S9). Subsequent reaction of 2-bromoisobutyryl bromide with **PAEAzNH$_2$** produced the macroinitiator.

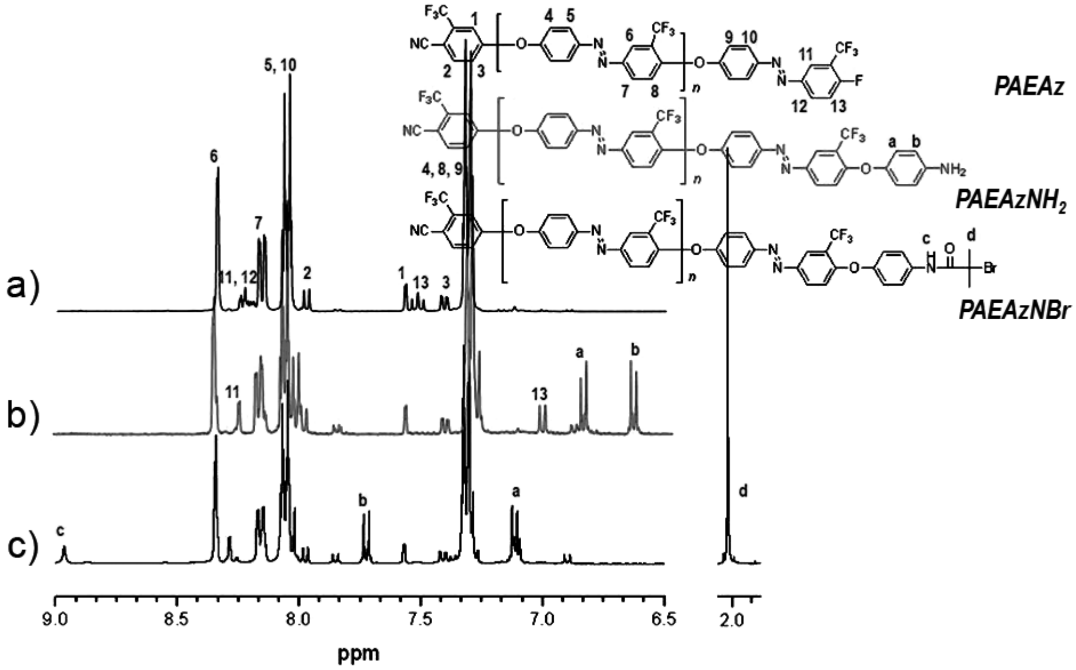


Figure S8. ^{1}H-NMR spectra of (a) **PAEAz**, (b) **PAEAzNH$_2$**, and (c) **PAEAzNBr** (400 MHz, THF-d_8, 50 ^{o}C).

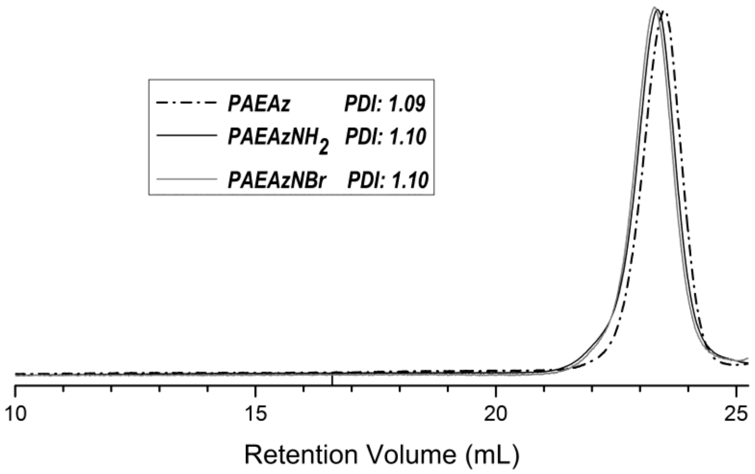


Figure S9. GPC profiles of (a) **PAEAz**, (b) **PAEAzNH$_2$**, and (c) **PAEAzNBr**.

Synthesis of diblock copolymers by atom transfer radical polymerization with macroinitiators.

P1-3. A typical polymerization procedure was described for the ATRP of styrene from the **PAEAzNBr** macroinitiator. Monomers were passed through a column filled with neutral alumina and then stored in dry argon atmosphere before ATRP. CuCl, HMTETA, anisole, and styrene were placed in a dried Schlenk flask under dried argon atmosphere. And then the mixture was degassed by “freeze-pump-thaw” (FPT) cycles. After deoxygenated anisole solution of the **PAEAzNBr** macroinitiator was added to the flask via gastight syringe under dry argon atmosphere, FPT cycles were performed three times. The flask was immersed in an oil bath heated at 110 ^{o}C. At a proper monomer conversion below 50 %, the reaction mixture was cooled in ice bath, diluted with THF, passed through a short alumina column, and then poured into methanol. The product was filtered, washed with methanol, and dried *in vacuo*. The polymer was dissolved in cyclohexane, and filtered to remove any insoluble product. Evaporation of the filtrate yielded the desired **P1-3** diblock copolymers.

ATRP of styrene with the **PAEAzNBr** macroinitiator was carried out in the various halogen exchange conditions (R-Br/CuCl) to optimize the reaction condition. In GPC curves of the crude samples taken from polymerization mixture in certain time intervals, significant amount of the unreacted macroinitiator was observed, indicating that faster initiation than propagation was not achieved (Figure S10) presumably because of the amide bond next to the initiating site. As molecular weight of the block copolymers moved to higher molecular weight region, intensities of the unreacted macroinitiator gradually decreased. To remove any unreacted macroinitiators, the block copolymer was extracted with cyclohexane where **PAEAz** is insoluble. After the extraction, GPC profile showed that the well-defined block copolymers were obtained. However, the block copolymer (*e.g.*, **P3**) having molecular weight above 20 kDa was not dissolved in cyclohexane. Therefore, **P3** was purified by reprecipitation in diethyl ether where the macroinitiator is soluble but the block copolymer is insoluble.

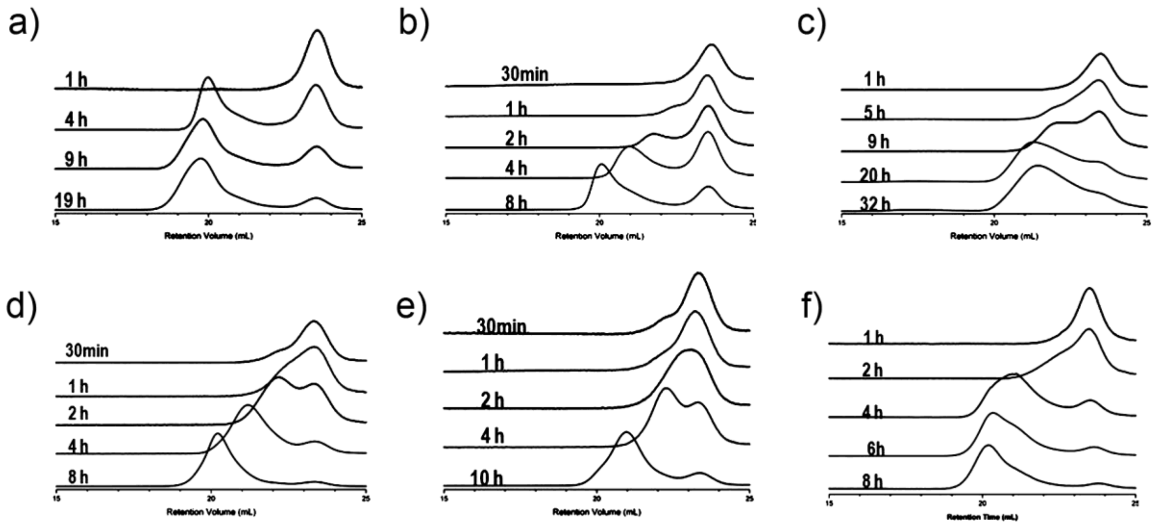


Figure S10. GPC profiles during the ATRP of styrene with the **PAEAzNBr** macroinitiator under various halogen exchange systems (R-Br/CuCl). (a) CuBr/PMDETA, 1eq. (b) CuBr/PMDETA, 5eq. (c) CuBr/dNbpy, 5eq. (d) CuCl/PMDETA, 5eq. (e) CuCl/HMTETA, 5eq. (f) CuCl/HMTETA, 2eq.

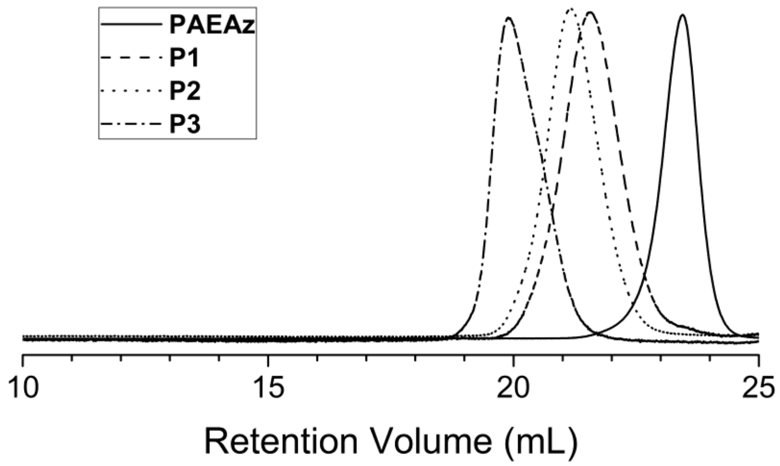


Figure S11. THF-GPC profiles of **PAEAz** and the well-defined block copolymers (**P1-3**).

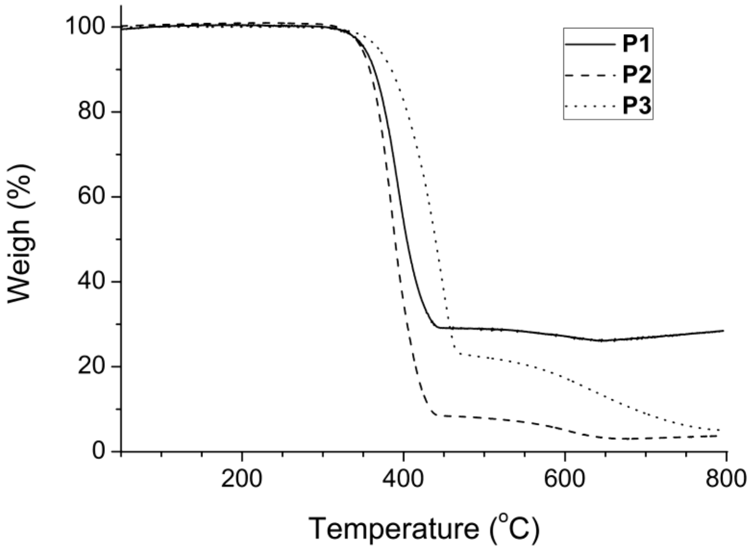


Figure S12. TGA thermograms of **P1-3** under N_2 flow with a heating rate of 10 °C/min.

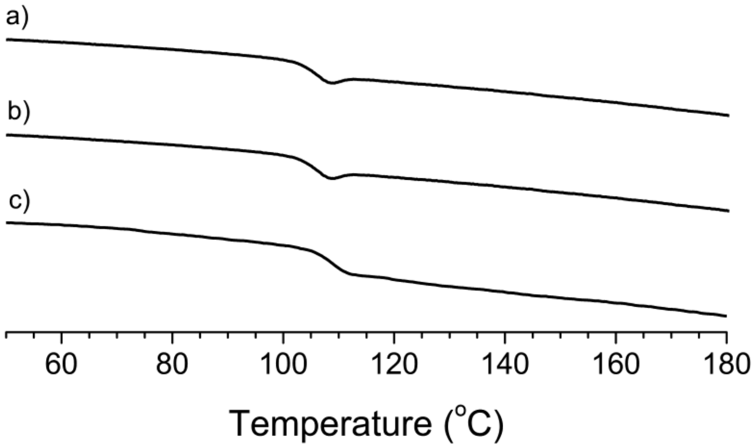


Figure S13. The second scan of DSC curves of **P1-3** under N_2 flow with a heating rate of 5 °C/min.

Preparation of micellar aggregates.

Micellar aggregates of **P1** and **P2** were prepared by adding cyclohexane with stirring into 1 % (w/v) solution of THF followed by dialysis against cyclohexane to remove THF. To investigate the effect of photoirradiation on the self-assembled block copolymer micelle in cyclohexane, DLS and UV-vis spectra measurements of the solution irradiated by UV and visible light were conducted. For the preparation of FE-TEM and FE-SEM specimens, small amount of the diluted solutions was drop cast on a carbon-coated copper grid and silicon wafer, respectively.

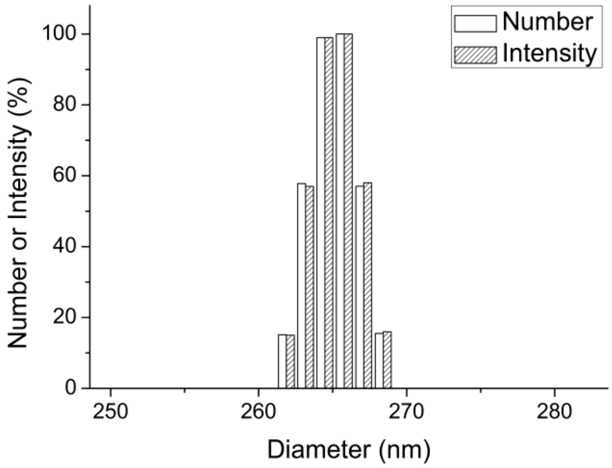


Figure S14. a) DLS plots of the self-assembled block copolymer micelles of **P1** prepared in cyclohexane. The blank and patterned columns are the number and intensity MSD values, respectively. (PDI: 0.005)

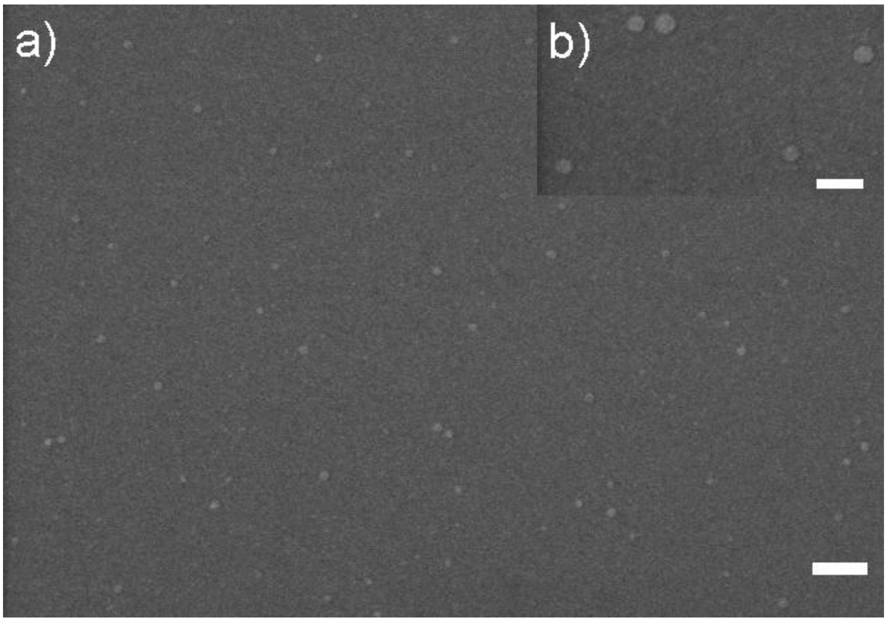


Figure S15. SEM images on a Si wafer of the self-assembled block copolymer micelle of **P1** prepared in cyclohexane; a) with scale bars of 400 nm. b) with scale bars of 200 nm.

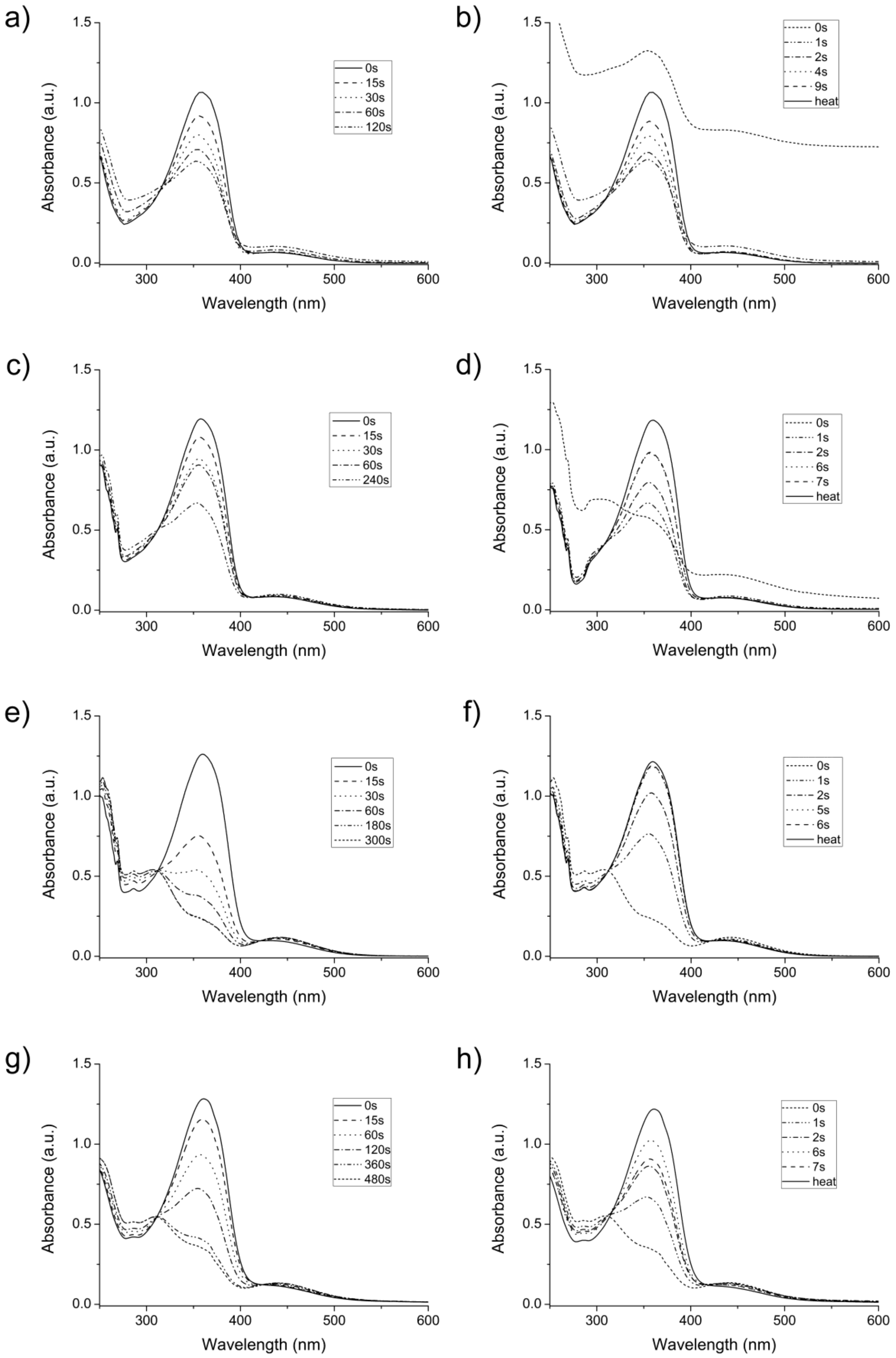


Figure S16. UV-vis spectral changes of of the self-assembled block copolymer micelle; of a) and b) **P1**, c) and d) **P2** in cyclohexane, e) and f) **P2**, g) and h) **P3** in THF.

References

1 (a) M. Seo, G. Seo, S. Y. Kim, *Angew. Chem. Int. Ed.*, 2006, **45**, 6306; (b) Y. J. Kim, M. Seo, S. Y. Kim, *J. Polym. Sci. Part A: Polym. Chem.*, 2010, **48**, 1049; (c) J. Qiu, T. Pintauer, S. G. Gaynor, K. Matyjaszewki, B. Charleux, J.-P. Vairon, *Macromolecules*, 2000, **33**, 7310.