### **Supplementary Information**

# Aryl Radical Initiators Accumulated within Layered Silicates Realize

## Polystyrene with Directly- and Regioselectively-bonded Aryl-terminal Groups

Fuminao Kishimoto<sup>†\*</sup>, Kyohei Hisano<sup>‡</sup>, Toru Wakihara<sup>†§</sup>, Tatsuya Okubo<sup>†</sup>.

<sup>†</sup>Department of Chemical System Engineering, School of Engineering, The University of Tokyo. 7-3-1

Hongo, Bunkyo-ku, Tokyo 113-8656, Japan.

<sup>‡</sup>Department of Applied Chemistry, Ritsumeikan University, 1-1-1 Nojihigashi, Kusatsu, Shiga 525-8577,

Japan.

<sup>§</sup>Institute of Engineering Innovaion, School of Engineering, The University of Tokyo. 7-3-1 Hongo, Bunkyo-

ku, Tokyo 113-8656, Japan.

\*Corresponding Author. <u>kfuminao@chemsys.t.u-tokyo.ac.jp</u> (F.K.)

#### **Experimental Procedures**

**Materials.** Saponite (SA, Na<sub>0.33</sub>Mg<sub>3</sub>(Si<sub>3.67</sub>Al<sub>0.33</sub>)O<sub>10</sub>(OH)<sub>2</sub>) was purchased from Kunimine Industries Co., Ltd. under the trade names of "Smecton SA". The cation exchange capacities of Smecton SA estimated by the Schollenberger method is 71.3 meq/100 g. The chemical composition of Smecton SA is  $1.0SiO_2 : 0.10Al_2O_3 : 0.50MgO : 0.048Na_2O$ . 2-anthrylamine, 1-pyreneamine, ethanol (99.5%), hydrochloric acid, and styrene monomer were purchased from FUJIFILM Wako Pure Chemical Corporation. 1-anthrylamine and 1-naphthylamine were purchased from Tokyo Kasei Co. Ltd., Japan. Water was purified by a Millipore Direct-Q3 Ultrapure Water System to a resistivity of 18.2 M $\Omega$  cm.

**Reaction of clays with arylammoniums.** 1-anthrylamine (1AA), 2-anthrylamine (2AA), 1-naphthylamine (NA) or 1-pyreneamine (PA) (0.2 mmol) was dissolved in ethanol (100 mL). Subsequently, 1 N HCl (100 mL) was added to the solution where the dissolved arylamines were converted to arylammoniums by protonation. Then, SA (1.0 g) were dispersed in each arylammonium solution. After stirring for 24 h at room temperature, the precipitates were collected by centrifugation, washed using deionized water and ethanol, and then dried under vacuum overnight. The obtained resultants were denoted as 1AA\_SA, 2AA\_SA, NA\_SA, or PA\_SA.

**Radical polymerization of styrene.** The styrene monomer was purified by vacuum distillation at 50 °C to remove the stabilizer (4-tert-butylcatechol). The purified styrene (40 mL) was added to a 50 mL Schleck flask, and then 1 g each of 1AA\_SA, 2AA\_SA, NA\_SA, or PA\_SA was dispersed by stirring at 80 °C under N<sub>2</sub> atmosphere. After the reaction was carried out for 24 h, the product was separated by centrifugation to remove the Saponite. The high-viscosity product (5 g) was dispersed in methanol (150 mL), and the precipitate was collected by centrifugation. This decantation was repeated twice. Subsequently, the crude product was purified by reprecipitation from tetrahydrofuran into methanol and dried under reduced pressure. The spectroscopic characteristics of the resultant polymer were measured using UV-Vis spectroscopy, excitation-emission spectroscopy, and nanosecond time-resolved emission decay measurement. The  $M_n$  (number-average molecular weight) and  $M_w$  (weight-average molecular weight) were determined by GPC (Shimadzu, LC-20AD; column, Shodex KF805; solvent: THF; flow rate, 1 mL/min; UV-Vis detector, SPD-20A; temperature, 40 °C).

**Characterizations.** XRD patterns were recorded using an X-ray diffractometer (Ultima IV, Rigaku), with monochromated Cu K $\alpha$  radiation. CHN elemental analysis was conducted using a CE-440F (Systems Engineering). ESR spectra were recorded on a JES-FA200 (JEOL) X-band electron paramagnetic resonance spectrometer. The ESR measurements were performed at RT. Approximately 50 mg of powdered samples were packed in quartz sample tubes ( $\varphi = 5$  mm), where the height of the packed samples was ~6 mm. Each spectrum was normalized by signals attributed to the manganese marker (Mn<sup>2+</sup>). The number of radicals in the measured sample was estimated by a comparison method with 2,2,6,6-tetramethylpiperidine-1-oxyl dissolved in toluene (1 mmol/L). UV–Vis absorption spectra were recorded on a V–670 (JASCO). Emission-excitation spectra were obtained using a fluorescence spectrophotometer FP–8500 (JASCO). The

luminescence decay curves were obtained by applying a time-resolved emission spectrometer (Quantaurus-Tau C11367-01, Hamamatsu Photonics K.K.). The samples were photoexcited using a sub-nanosecond pulsed light emitting diode ( $\lambda = 280$  or 405 nm) with a frequency of 1 MHz. The emission light was monochromated using a band path filter (fwhm = 10 nm) and Czerny-Turner-type spectrograph.

**Computation** All of the computations were performed using DFT with the B3LYP hybrid functional and a 6-31+G(d,p) (for C, H, N, O, and F atoms) basis set in the Gaussian 03 package. The input files were generated using GaussView, Version 6. The optimized geometry for the arene radical cations was found by DFT calculations using the same basis set. Stationary points were characterized by vibrational frequency calculations, and we confirmed that the structures were the minima on the potential energy surface. Then, time-dependent density functional theory (TD-DFT) calculations of the optimized molecules in the water solvent were carried out with the same hybrid functional and basis set to obtain further insight into the photophysical properties of the complex.



Figure S1. XRD patterns of 1AA\_SA before and after polymerization reaction.



**Figure S2.** GPC chromatograms for the purified NA\_PS measured at  $\lambda = 254$  nm (dashed line) and  $\lambda = 320$  nm (solid line). The inset is an enlarged chromatogram within a 5 to 10-min retention time.



**Figure S3.** GPC chromatograms for the purified PA\_PS measured at  $\lambda = 254$  nm (dashed line) and  $\lambda = 340$  nm (solid line).

Sample	Wavelength (nm)	Peak No.	Retention time (min)	M <sub>n</sub>	$M_{\rm w}/M_{\rm n}$	Peak area ratio (%)
		#1	7.67	102,000	1.8	0.7
1AA_PS	254	#2	10.6	1,000	1.2	92.4
		#3	11.2	500	1.0	6.9
	382	#1	7.39	143,000	2.0	34
		#2	11.3	600	1.1	66
		#1	7.65	103,000	1.9	2.1
2AA_PS	254	#2	10.5	1,000	1.2	94.1
		#3	11.2	500	1.0	3.8
	382	#1	7.51	126,000	2.4	34
		#2	10.7	1,000	1.1	66

 Table S1. Molecular weights of the resultant polymers.

**Table S2.** Molecular weights of the NA\_PS.

Sample	Wavelength (nm)	Peak No.	Retention time (min)	M <sub>n</sub>	$M_{\rm w}/M_{\rm n}$	Peak area ratio (%)
		#1	7.86	72,000	2.0	3.4
NA_PS	254	#2	10.6	1,000	1.1	93.7
		#3	11.2	500	1.0	2.9
	320	#1	8.37	64,000	2.5	45
		#2	10.6	1,000	1.1	55

# **Table S3.** Molecular weights of the PA\_PS.

Sample	Wavelength (nm)	Peak No.	Retention time (min)	M <sub>n</sub>	$M_{\rm w}/M_{\rm n}$	Peak area ratio (%)
PA_PS -	254	#1	7.86	15,000	1.3	6.3
		#2	10.6	3,000	1.1	82.7
		#3	11.2	500	1.0	9.4
	340	#1	9.26	12,000	1.2	9.5
		#2	9.97	2,000	1.2	86.0
		#3	11.2	500	1.0	4.5