Poly(ionic liquid)s-based nanogels and their reversible photo-mediated

association and dissociation

Yong Zuo, Junrui Yu, Xiaojun Liu, Peng, Cao, Pengfei Song, Rongmin Wang,* and Yubing Xiong*

Key Laboratory of Eco-Environment-Related Polymer Materials of Ministry of Education, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou, 730070, China

Correspondence to: Dr. Yubing Xiong (E-mail: yubing_xiong@163.com)

Experimental Section

1 Materials

Mono-6-deoxy-6-amino- β -cyclodextrin (6-NH₂- β -CD, purify: 98%) was purchased from Shandong Binzhou Zhiyuan Bio-Technology Co. Ltd (China). Azobisisobutyronitrile (AIBN, 98%) was purchased from Shanghai Chemical Reagent Company and recrystallized from methanol before using. Ethylene glycol dimethacrylate (EGDMA, 98%), 1-vinylimidazole (VIm, 98%) and 4-vinylbenzyl chloride were brought from Aladdin Reagent Company. The inhibitors in EGDMA and VIm were removed through distillation on vacuum. *N*,*N'*dimethlyformamide (DMF) was dried over with calcium hydride and distilled under reduced pressure. All other reagents, such as 4-phenylazo-phenol, terephthalic acid, *N*,*N'*-dicyclohexylcarbodiimide (DCC), 1hydroxybenzotriazole (HOBT), triphenylphosphorous, tributylphosphorous, methanol, acetone, diethyl ether, dichloromethane, tetrahydrofuran (THF), bis{(trifluoromethyl)sulfonyl}amide lithium (Li[NTf₂]), sodium fluoroborate, and potassium carbonate, were A.R. grade and used as received without further treatment.

2 Characterization

¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on a Brucker AM spectrometer (400 MHz) at 25 °C. The solid state ¹³C NMR spectra were recorded on a Bruker-Avance III solid state NMR spectrometer (400 MHz) at 25 °C. The 2D nuclear Overhauser effect spectra (NOESY) were recorded on a Bruker-Avance III NMR spectrometer (400 MHz) at 30 °C with D₂O as solvent. Mass spectra were recorded on Agilent 7890/5975 (USA). Fourier transform infrared (FT-IR) spectra were measured on a DIGIL FTS3000 spectrophotometer using KBr tablets. UV-vis absorption spectra were measured on a Shimadzu UV-2500PC spectrophotometer using a 1 cm path length quartz cell. X-ray photoelectron spectra (XPS) were measured on PHI-5702 energy spectrometer (USA). Thermogravimetric analyses (TGA) were measured on a Perkin Elmer TG/TGA 6300 at a heating rate of 10 °C/min. Dynamic light scattering (ALV/SP-125) equipped with an ALV-5000 multi-r digital time correlator and ADLAS DPY425 solid-state laser (output power = 22 mW at λ = 632.8 nm). All the nanogel solutions, excepting those containing β -CD dimers, were filtered through a membrane with pore size of 0.45 µm before DLS measurement. The morphology of the product was observed by scanning electron microscopy (SEM, JSM 6700F, Japan). The samples were prepared according to the standard methods.

3.1 Synthesis of 4-vinylbenzyl-triphenylphosphorous chloride (VBP-Ph)^[1]

4-vinylbenzyl chloride (1.53 g, 10.02 mmol), triphenylphosphorous (3.15 g, 12.01 mmol) and acetone (50 mL) were introduced into a clean dried round-bottom flask with a magnetic stirrer. The mixture was refluxed for 48 h under nitrogen atmosphere. Afterwards, the reaction solution was poured into diethyl ether and the precipitate was washed by diethyl ether for several times. The white solid was obtained after filtering and drying in vacuum. (3.53 g, yield: 84.86%). ¹H NMR (D₂O, 400 MHz, δ ppm): 7.63~7.41 (m, 3H), 7.40~7.30 (m, 12H), 6.90(d, 2H), 6.68(d, 2H), 6.41~6.34 (m, 1H), 5.49(d, 1H), 4.98(d, 1H), 4.43(d, 2H); ¹³C NMR (D₂O, 100 MHz, δ ppm): 137.7, 135.7, 134.1, 131.4, 130.1, 126.6, 117.6, 116.7, 115.4, 77.9. MS (ESI) *m/z*: calculated for C27H24P⁺: 379.46, found: 379.21 [M]⁺. Mp: 121.9 °C.

3.2 Synthesis of 4-vinylbenzyl-tributylphosphorous chloride (VBP-Bu)^[2]

4-Vinylbenzyl chloride (4.03 g, 26.40 mmol), tributylphosphorous (5.36 g, 26.49 mmol) and acetone (50 mL)

were introduced into a clean dried flask with a magnetic stirrer. The mixture was refluxed for 48 h under nitrogen atmosphere. Afterwards, the reaction solution was poured into diethyl ether and the precipitate was washed by diethyl ether for several times. The white solid was obtained after filtering and drying in vacuum. (7.36 g, yield: 78.55%). ¹H NMR (D₂O, 400 MHz, δ ppm): 7.0~7.4 (m, 4H), 6.45~6.63 (m, 2H), 5.65 (d, 1H), 5.11 (d, 2H), 3.39 (t, 6H), 1.88 (s, 6H), 1.12~1.36 (m, 6H), 0.68 (t, 9H). ¹³C NMR (D₂O, 400 MHz, δ ppm): 12.8, 17.3, 17.8, 22.7, 23.5, 25.5, 26.1, 115.3, 127.2, 128.1, 130.3, 136.0, 137.4. MS (ESI) *m/z*: calculated for C₂₁H₃₆P⁺: 319.49, found: 319.30 [M]⁺. Mp: 127.3 °C

3.3 Preparation of PIL nanogels

Nanogels composed of different ionic liquids were prepared according to our previous method.^[3] The following example describes the typical synthsis of PIL-based nanogel using 100 mol% VBP-Ph and 400 mol% EGDMA based on [VAzoHIm]Br. This protocol is representative of all PIL-based nanogels syntheses. And the asprepared sample defined as 1A1P4E, in which A, P, and E are short for [VAzoHIm]Br, VBP-Ph, and EGDMA, respectively. All the samples were defined using the similar way. [VAzoHIm]Br (0.273 g, 0.60 mmol), VBP-Ph (0.249 g, 0.60 mmol) and EGDMA (0.476 g, 2.40 mmol) were dissolved in 30 mL absolute methanol, and AIBN (0.010 g, 0.061 mmol) was added followed by. Subsequently, the mixture was stirred at 70 °C for 40 h under an atmosphere of nitrogen. The reaction mixture was precipeted from diethyl ether and the crude product was washed by THF. To remove the residual monomers, the as-prepared nanogel solutions were firstly dialyzed from methanol thoroughly. Then, PIL nanogel solutions were further dialyzed from water. Finally, PIL nanogel powder was obtained by lyophilisation. (Yield: 79%)

3.4 Anion exchange of [VAzoHIm]Br

 $[VAzoHIm][NTf_2]$ and $[VAzoHIm][BF_4]$ were prepared from metathesis reaction of [VAzoHIm]Br with Li $[NTf_2]$ and NaBF₄ at room temperature. After anion exchange, ILs $[VAzoHIm][NTf_2]$ and $[VAzoHIm][BF_4]$ could dissolve in ethyl acetate instead of water (Figure S12a).

Synthesis of [VAzoHIm][NTf₂]

In a typical procedure, [VAzoHIm]Br (0.455 g, 1.00 mmol) was mixed with Li[NTf₂] (0.343 g, 1.19 mmol) in methanol (30 mL) and the mixture was stirred vigorously for 12 h at room temperature. Then, the solvent was rotary evaporated to get orange liquid. The liquid was washed by large amount of water and extracted by ethyl acetate. [VAzoHIm][NTf₂] was obtained after removing ethyl acetate and dried under vacuum overnight. (0.50 g, yield: 76.27%) Mp: 25.7 °C

Synthesis of [VAzoHIm][BF₄]

[VAzoHIm]Br (0.455 g, 1.00 mmol) was mixed with NaBF₄ (0.133 g, 1.21 mmol) in methanol (30 mL) and the mixture was stirred vigorously for 12 h at room temperature. Then, the solvent was rotary evaporated to get orange solid. The solid was washed by large amount of water and dried under vacuum at 50 °C overnight. (0.33 g, yield: 71.38%) Mp: 134.9 °C.

3.5 Anion exchange of PIL nanogels

The procedures of anion exchange of PIL nanogels with $Li[NTf_2]$ and $NaBF_4$ were both conducted in absolute methanol, and 1A1P4E was representative of all the PIL nanogels. $NaBF_4$ (0.05 g) was added into 1A1P4E nanogel solution (15 mL, solvent: absolute methanol) in a vial and the mixture was stirred vigorously at room temperature. After 12 h, the precipitation was observed in the bottom of vial and the Tyndall effect of top solution was almost vanished. In addition, the filtered precipitation can be redispersed in acetonitrile or acetone. (Figure S12b)



Figure S1 ¹H NMR spectrum (400 MHz) of terephthalic acid bridged β -CD dimer in DMSO- d_6 at 298 K.



Figure S2 ¹H NMR spectrum (400 MHz) of Azo-Hex in CDCl₃ at 298 K



Figure S3 ^{13}C NMR spectrum (100 MHz) of Azo-Hex in CDCl3 at 298 K



Figure S4 ¹H NMR spectrum (400 MHz) of [VAzoHIm]Br in DMSO-d₆ at 298 K



Figure S5 ¹³C NMR spectrum (100 MHz) of [VAzoHIm]Br in DMSO- d_6 at 298 K



Figure S6 ¹H NMR spectrum (400 MHz) of VBP-Ph in D₂O at 298 K



Figure S7 $^{\rm 13}C$ NMR spectrum (100 MHz) of VBP-Ph in D2O at 298 K



Figure S8 ¹H NMR spectrum (400 MHz) of VBP-Bu in D_2O at 298 K



Figure S9 13 C NMR spectrum (100 MHz) of VBP-Bu in D₂O at 298 K



Figure S10 Solid state ¹³C NMR spectrum (400 MHz) of PIL nanogel (1A1P4E) obtained by freeze-drying the dialysis solution.



Figure S11 Representative photographs of PIL nanogels before and after dialysis. From left to right are 1A1P3E, 1A1P4E, 2A1P4E, 1A1B4P in methanol, dialysis solution of 1A1P3E, 1A1P4E, 2A1P4E, 1A1B4P in water, and inclusion complex solution of PIL nanogel and β -CD dimer, respectively.



Figure S12 Photographs of [VAzoHIm]Br in water (a) and 1A1P4E in methanol (b) in the presence of $NaBF_4$ or $Li[NTf_2]$.

Table S1 Content	of carbon	hydrogen	and nitroge	n in PII r	nanogels after	dialvsis
	01 641 8011,	11,010,000,000			anogeis arter	anaryono

Entry	Azo-IL:PIL:EGDMA	C %	H %	N %
1P4E	0:1:4	62.67	6.74	0
1A1P3E	1:1:3	60.64	6.32	0.44
0.5A1P4E	0.5:1:4	60.78	6.49	0.27
1A1P4E	1:1:4	60.96	6.60	0.39
2A1P4E	2:1:4	61.04	6.14	0.51



Figure S13 XPS survey scan of PIL nanogel (2A1P4E) obtained by freeze-drying the dialysis solution.



Figure S14 TGA curves of PIL nanogels with various feed ratio



Figure S15 Time dependent UV-vis absorption spectra of PIL nanogel (2A1P4E) in water treated by heating at 55 °C after UV light irradiation. The concentration of Azo units in nanogel solution is 5.3×10^{-5} mol·L⁻¹.



Figure S16 Standard work curve of [VAzoHIm]Br solution in water obtained by the absorbance at 353 nm. The equation of the fitting line, which is absorbance related to Azo unit concentration, is y = 14.62x-0.03, and correlation coefficient R² = 0.9996.

Entry	Azo-IL:VBP-Ph:	D _h (nm)	PDI	D _h (nm)	PDI
	EGDMA	before illum.	before illum.	after illum.	after illum.
0.5A1P3E	0.5:1:3	22.7	0.16	25.4	0.20
0.5A1P4E	0.5:1:4	44.7	0.34	61.9	0.16
1A1P3E	1:1:3	19.6	0.25	24.1	0.13
1A1P4E	1:1:4	41.2	0.22	48.9	0.36
2A1P3E	2:1:3	17.2	0.20	15.6	0.30
2A1P4E	2:1:4	39.0	0.16	32.8	0.27

Table S2 Hydrodiameter and PDI of nanogels in methanol before and after UV irradiation

D_h = the average hydrodynamic diameter, PDI: polydispersion index. The UV illumination duration is 60 min.



Figure S17 Hydrodiameter of 1A1P4E in water upon alternative UV and visible light irradiation.

Determination of association constant for trans-Azo-based IL and cis-Azo-based IL with β -CD by UV-vis spectra method^[4,5]

As shown in Figure S18 and S19, association constants between *trans*-[VAzoHIm]Br or *cis*-[VAzoHIm]Br and β -CD in water were determined by following the UV absorptions at 350 nm and 440 nm, respectively. The concentration of [VAzoHIm]Br was 2.5×10⁻⁵ M. Upon addition of excess β -CD, the absorbance of *trans*-Azo or *cis*-Azo group increased. With an assumption of a 1:1 stoichiometry, the inclusion complexation of β -CD (H)

with *trans*-[VAzoHIm]Br or *cis*-[VAzoHIm]Br (G) is expressed by the following equation: $H + G \leftrightarrow H \cdot G$

We employed the usual double reciprocal plot according to the modified Benesi-Hidebrand equation:

$$\frac{1}{\Delta A} = \frac{1}{K_a \Delta \varepsilon[G][H]} + \frac{1}{\Delta \varepsilon[G]}$$

Where G, H, K_a represents guest (*trans*-[VAzoHIm]Br or *cis*-[VAzoHIm]Br), host (β -CD), association constant respectively. ΔA denotes the absorbance difference before and after host molecules are added. $\Delta \varepsilon$ denotes the difference of the molar extinction coefficient between the host and host-guest complex at the same wavelength. The association constant K_a is calculated by the equation:

$$K_a = \frac{b}{k} = 4.96 \times 10^3 M^{-1}$$
 (for *trans*-[VAzoHIm]Br/β-CD system)
$$K_a = \frac{b}{k} = 4.80 \times 10^2 M^{-1}$$
 (for *cis*-[VAzoHIm]Br/β-CD system)

Where k is the slope value of line plot, and b is the intercept of the line plot.

As shown in Figure S20 and S21, association constants K_n between PIL nanogel containing *trans*-Azo units or *cis*-Azo units and β -CD in water were determined via the same method as [VAzoHIm]Br. The concentration of Azo units in nanogel was 3.0×10^{-5} M.

$$K_n = \frac{b}{k} = 8.77 \times 10^3 M^{-1}$$
 (for *trans*-nanogel/β-CD system)
$$K_n = \frac{b}{k} = 1.07 \times 10^3 M^{-1}$$
 (for *cis*-nanogel/β-CD system)



Figure S18 UV absorption of *trans*-[VAzoHIm]Br upon stepwise addition excess β -CD. The concentration of *trans*-[VAzoHIm]Br was 2.5×10⁻⁵ M.



Figure S19 UV absorption of *cis*-[VAzoHIm]Br upon stepwise addition excess β -CD. The concentration of *cis*-[VAzoHIm]Br was 2.5×10⁻⁵ M.



Figure S20 UV absorption of PIL nanogel containing *trans*-Azo units upon stepwise addition excess β -CD. The concentration of *trans*-Azo units in nanogel was 3.0×10⁻⁵ M.



Figure S21 UV absorption of PIL nanogel containing *cis*-Azo units upon stepwise addition excess β -CD. The concentration of *cis*-Azo units in nanogel was 3.0×10^{-5} M.

Reference

- [1] Y. Xiong, H. Wang, R. Wang, Y. Yan, B. Zheng and Y. Wang, Chem. Commun., 2010, 46, 3399.
- [2] Y. Xiong, Y. Wang, H. Wang, and R. Wang, *Polym. Chem.*, 2011, **2**, 2306.
- [3] Y. Xiong, J. Liu, Y. Wang, H. Wang and R. Wang, *Angew. Chem. Int. Ed.*, 2012, **51**, 9114.
- [4] Y. Wang, N. Ma, Z. Wang and X. Zhang, Angew. Chem. Int. Ed., 2007, 46, 2823.
- [5] R. Dong, Y. Liu, Y. Zhou, D. Yan and X. Zhu, *Polym. Chem.*, 2011, **2**, 2771.