

Conformational analysis of temperature switchable PNIPAM-*b*-PACMO in ionic liquid modified AuNPs: A comprehensive insight into nanocomposites formation-phase transition relationship

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Characterization of PNIPAM-*b*-PACMO block copolymer using ¹H NMR and gel permeation chromatography

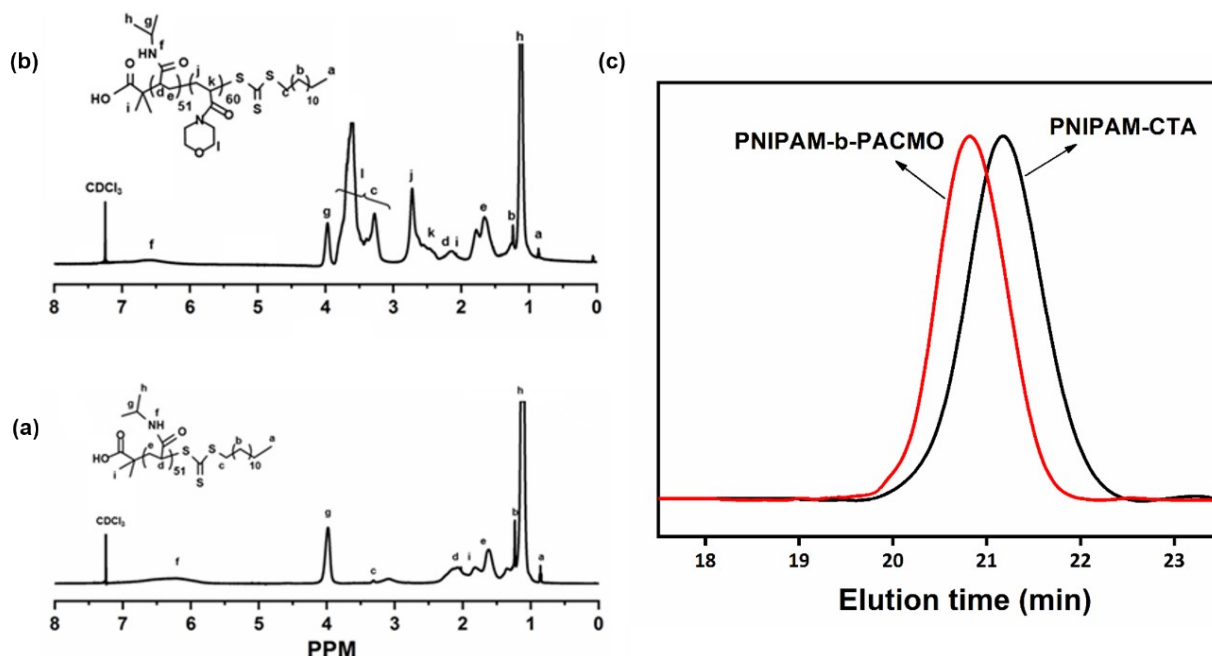


Fig. S1. ¹H NMR spectra of (a) PNIPAM-CTA, (b) PNIPAM-*b*-PACMO in CDCl₃, and (c) GPC chromatograph of PNIPAM-CTA and PNIPAM-*b*-PACMO.¹

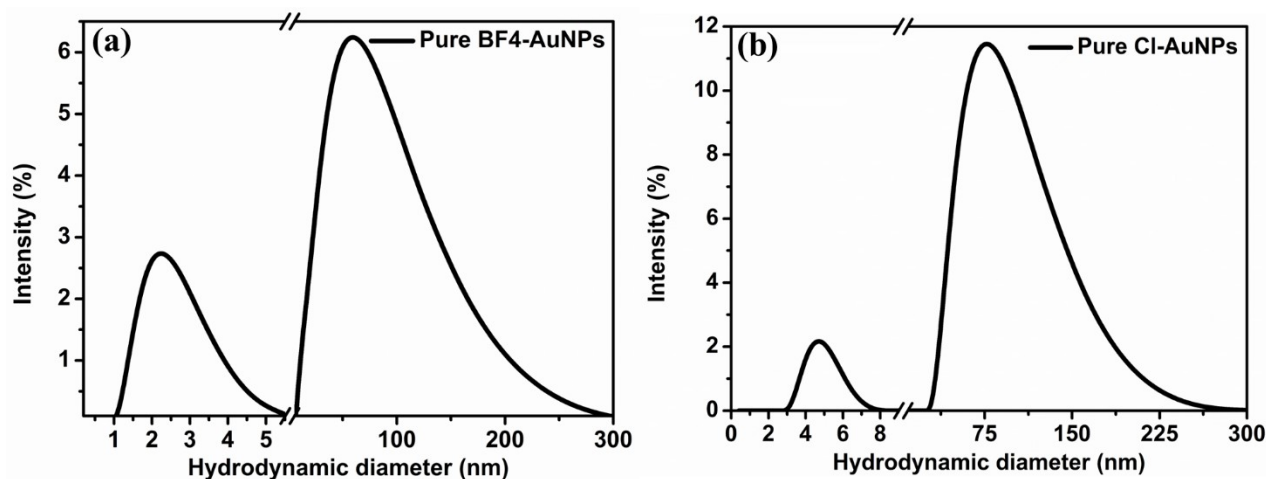


Fig. S2. DLS intensity size distribution of (a) BF₄-AuNPs, (b) Cl-AuNPs.¹

Instrumentation

UV-visible Experiments

The UV-Visible absorption spectra of PNIPAM-*b*-PACMO in the presence of different concentrations of BF₄-AuNPs and Cl-AuNPs were recorded from double beam UV-Visible spectrophotometer (UV-1800) acquired from Shimadzu co., Japan. The Instrument is having the wavelength accuracy of ± 0.3 nm along with automatic wavelength correction and the spectral bandwidth of 1.0 nm. Herein, aliquot from prepared sample solution was uniformly transferred into a quartz cuvette of 1.0 cm pathlength. The spectrum was recorded after averaging the values from three scan.

Fluorescence Experiments

Fluorescence intensity measurements of the sample solutions are ascertained by using a Cary Eclipse fluorescence spectrofluorometer (Varian optical spectroscopy instruments, Mulgrave, Victoria, Australia) containing an intense xenon flash lamp as the light source. The emission spectra are recorded with a PMT voltage of 720 V and slit width of 10/10 nm. By mixing a fixed concentration of polymer (5 mg/mL) and increasing concentration of BF₄-AuNPs, Cl-AuNPs from 2 to 10 nM at a constant temperature of 25 °C, the ongoing interactions between BF₄-AuNPs, Cl-AuNPs and PNIPAM-*b*-PACMO are studied.

Dynamic Light Scattering (DLS) measurements

To assess the hydrodynamic diameter (nm) of PNIPAM-*b*-PACMO in the presence of different concentrations of BF₄-AuNPs and Cl-AuNPs, the Zetasizer Nano ZS90 dynamic light scattering (DLS) instrument (Malvern Instruments Ltd., UK) is used. The instrument is

equipped with a fixed wavelength of 633 nm and 4 Mw He-Ne lasers. A quartz sample cell containing 1.0 ml of a filtered sample is sealed with a Teflon- coated screw cap to protect from air and dust. The Brownian motions of particles are detected by DLS and correlated to the particle size. The data collected was analysed using the Malvern Zetasizer software version 7.01. The temperature dependent studies are also performed on the above-said instrument.

Fourier Transform Infrared Spectroscopy (FTIR) measurements

All the Fourier transform spectrum are acquired by an Is 50 FT-IR (Thermo- Fischer scientific) spectrometer. The two ZnSe windows and bubble free samples are placed into an IR cell. Inside the sample chamber, a chromel alumel K-type thermocouple was provided for monitoring of temperature. Each IR spectrum reported here is an average of 240 scans using a spectral resolution of 4 cm⁻¹. Before the sample spectra, a background spectrum is collected. Furthermore, for each sample containing PNIPAM-b-PACMO, the deuterium oxide (D₂O) spectrum was used as background.

Zeta Potential Experiments

Zeta potential measurements were also performed on Zetasizer Nano ZS90 instrument using DTS1070 disposable cuvettes. The data collected was analyzed using the Malvern Zetasizer software version 7.01

Scanning Electron Microscopy (SEM)

Scanning electron microscope reveals the detailed surface characteristics and 3-dimensional structure of the sample under consideration. Freeze dried samples were used to explore the morphology of polymer and the complex formed by polymer and IL-modified AuNPs on the instrument JEOL Japan Mode: JSM 6610LV with an EHT voltage of 10.00 kV and tungsten as the electron source.

Transmission Electron Microscope (TEM)

Morphological characterization of PNIPAM-b-PACMO and PNIPAM-b-PACMO in the presence of BF₄-AuNPs, Cl-AuNPs is carried out using TECNAI 200 kV (Fei, electron optics) equipped with digital imaging and 35 mm photography system. For a better understanding of ongoing interactions among BF₄-AuNPs, Cl-AuNPs and PNIPAM-b-PACMO, images were taken.

Atomic Force Microscopy (AFM)

For recording the AFM images, Witec GmbH AFM (Germany) instrument was utilized. A freshly cleaved mica sheet was employed for the preparation of sample slides and 10 μ L samples were drop casted on the mica sheet which was then air-dried. All the images were apprehended in the tapping mode with a cantilever. The resonance frequency was set at 80 kHz while the force constant was kept 40 N/m. The captured images were then processed and flattened with the help of project FOUR software provided by Witec GmbH, Germany.

Table S1. Variation in hydrodynamic diameter (nm) of PNIPAM-*b*-PACMO in IL-modified AuNPs obtained from DLS at room temperature (25 °C).

Concentration of IL-modified AuNPs (nM)	Hydrodynamic diameter (nm)	
	BF ₄ -AuNP	Cl-AuNP
0	7.07±0.02	7.07±0.02
2	8.20±0.01	8.35±0.01
4	8.73±0.01	10.90±0.01
6	9.60±0.01	12.51±0.01
8	12.66±0.01	13.23±0.01
10	13.50±0.01	15.83±0.01

Table S2. Phase transition temperature of PNIPAM-*b*-PACMO in IL-modified AuNPs obtained from temperature dependent DLS studies.

Concentration of IL-modified AuNPs (nM)	LCST (°C)	
	BF ₄ -AuNP	Cl-AuNP
0	37.1±0.1	37.1±0.1
2	34±0.1	37.5±0.1
4	36±0.1	41.6±0.1
6	37±0.1	45.4±0.1
8	38±0.1	51.2±0.1
10	40±0.1	53.9±0.1

Table S3. Variation in Zeta potential (mV) of PNIPAM-*b*-PACMO in IL-modified AuNPs at room temperature (25 °C).

Concentration of IL-modified AuNPs (nM)	Zeta potential (mV)	
	BF ₄ -AuNP	Cl-AuNP
0	-2.06±0.01	-2.06±0.01
2	2.96±0.01	34.6±0.03
4	3.42±0.01	38±0.03
6	5.09±0.02	38.9±0.04
8	5.21±0.02	41±0.05
10	5.9±0.02	45±0.05

References

1. S. Mor, S. Kumar, K. Ramesh, R. Umapathi, K. Kumar, M. Safarkhani, K. T. Lim, Y. S. Huh, P. Venkatesu, *J. Ind. Eng. Chem.*, 2024, **137**, 225–234.

