Supplementary information

RAFT-Photomediated PISA in Dispersion: Mechanism, Optical Properties and Application in Templated Synthesis

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I. Nitrogen adsorption

N_2 adsorption isotherm were obtained by using Micromeritics ASAP 2420. The samples were first outgassed at 573K during 12h and weighted to determine the real mass. After, the samples were outgassed a second time on the analysis port at 573 K during 2 h before analysis. The tubes were not backfilled with N_2 before analysis. The free volume measurements were realized after analysis in order to avoid the pollution and/or the not-reversible capture of He in the materials. The isotherms were deconvoluted with different models in order to extract the textural properties. In particular, we have used Brunauer-Emmet-Teller (BET) model[1] for the surface determination. The Rouquerol procedure[2] was used to avoid any subjectivity in evaluating the BET monolayer capacity. On the other hand, the porosity distributions were calculated by applying Density Functional Theory model (global calculation) and by Brunauer-Joyner[3] (mesoporous distribution).

II. Calculations of colloidal data

II.1 Number of particles (N_p)

$$N_p = \frac{6\tau}{\pi \rho_{PS} D_p^6} \quad (1)$$

Where

ρ_{PS}: density of polystyrene = 1.047 [g cm^3]

D_p: diameter of particles determined by TEM images using ImageJ software [nm]

τ: mass concentration of copolymer (2) [g L^{-1}]

II.2 Mass concentration of copolymer calculations (τ) :

$$\tau = \frac{Conv. \cdot m_{monomer} + m_{macro-CTA}}{\frac{m_{solvent}}{\rho_{solvent}} + \frac{m_{H_2O}}{\rho_{H_2O}}} \quad (2)$$

Where

$Conv.$: Conversion of styrene at current time []

$m_{monomer}$: initial mass of monomer [g]

$m_{macro-CTA}$: initial mass of macro-CTA [g]

$m_{solvent}$: initial mass of solvent [g]

$\rho_{solvent}$: volumetric mass density of solvent [g L^{-1}]

m_{H_2O}: initial mass of water [g]

ρ_{H_2O}: volumetric mass of water [g L^{-1}]

II.3 Polydispersity index calculations (PDI)

$$PDI = \frac{D_w}{D_n} \quad (3)$$

Where

D_w: weight-average diameter [nm]

D_n: number-average diameter [nm]

Weight-average diameter calculations (D_w) :

$$D_w = \frac{\sum {D_p}^4}{\sum {D_p}^3} \quad (4)$$

Where

D_p: diameter of particles determined by TEM [nm]

Number-average diameter calculations (D_n) :

$$D_n = \frac{\sum D_p}{n} \quad (5)$$

Where

D_p: diameter of particles determined by TEM [nm]

n : number of particles used in manual treating of TEM images with ImageJ software [-]

II.4 Mean aggregation number calculations (N_{agg})

$$N_{agg} = \frac{c(macro-CTA) \cdot N_a}{N_p} \quad (6)$$

Where

$c(macro-CTA)$: molar concentration of macro-CTA in reaction mixture [mol L^{-1}]

N_a: Avogadro constant = $6.022 \cdot 10^{23}$ [mol^{-1}]

N_p: Number of particles per 1 liter of reaction mixture [L^{-1}]

II.5 Surface area stabilized by a copolymer chain calculation (S_{agg}) :

$$S_{agg} = \frac{\pi \cdot D_p^2}{N_{agg}} \quad (7)$$

Where

D_p: diameter of particles determined by TEM [nm]

N_{agg} : mean aggregation number []

III. Additional tables

Table S1. PHEA macro-CTAs with different chain lengths

macro-CTA	*Time* h	*Conv.* %	M_n g/mol	M_w/M_n
$PHEA_{25}$-TTC	5	61	$3.12 \cdot 10^3$	1.15
$PHEA_{52}$-TTC	5	60	$6.29 \cdot 10^3$	1.17
$PHEA_{85}$-TTC	5	63	$10.14 \cdot 10^3$	1.19

Time – time of irradiation. M_n – molecular weight determined by SEC in THF. M_w/M_n – dispersity determined by SEC in THF

Table S2. Textural and structural properties of $PHEA_{25}$-PS_{118}(**a**), $PHEA_{25}$-PS_{160}(**b**) and Pluronic F127**(c**) based carbon materials synthesized with molar ratio of phloroglucinol:glyoxylic acid:copolymer = 1:1:0.019

Name	S_{BET} $m^2\ g^{-1}$	V_t $cm^3\ g^{-1}$	V_{micro} $cm^3\ g^{-1}$	V_{meso} $cm^3\ g^{-1}$	D_p nm	$D_{p(TEM)}$ nm
$PHEA_{25}$-PS_{118}	691	1.30	0.29	1.01	~ 22	~ 22
$PHEA_{25}$-PS_{160}	702	1.57	0.34	1.23	~22	~ 29
Pluronic F127	679	0.83	0.34	0.49	6.5	~ 7

S_{BET} – total surface area determined by the BET method. V_T, V_{meso} and V_{micro} – total pore volume, mesopore volume and micropore volume. D_P – mesopore diameter calculated by the BJH method from the isotherm adsorption branch. $D_{p(TEM)}$– mesopore diameter calculated by TEM images.

IV. Additional figures

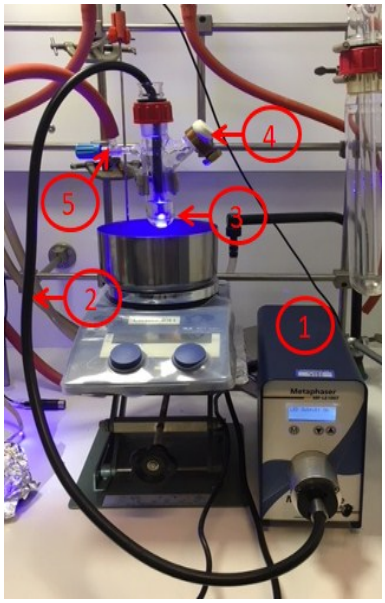

Fig. S1 Immersion-type photoreactor used in this study. (**1**) LED light source (472 nm). (**2**) Waveguide. (**3**) Double-walled Schlenk tube. (**4**) Rubber septum. (**5**) Stopcock.

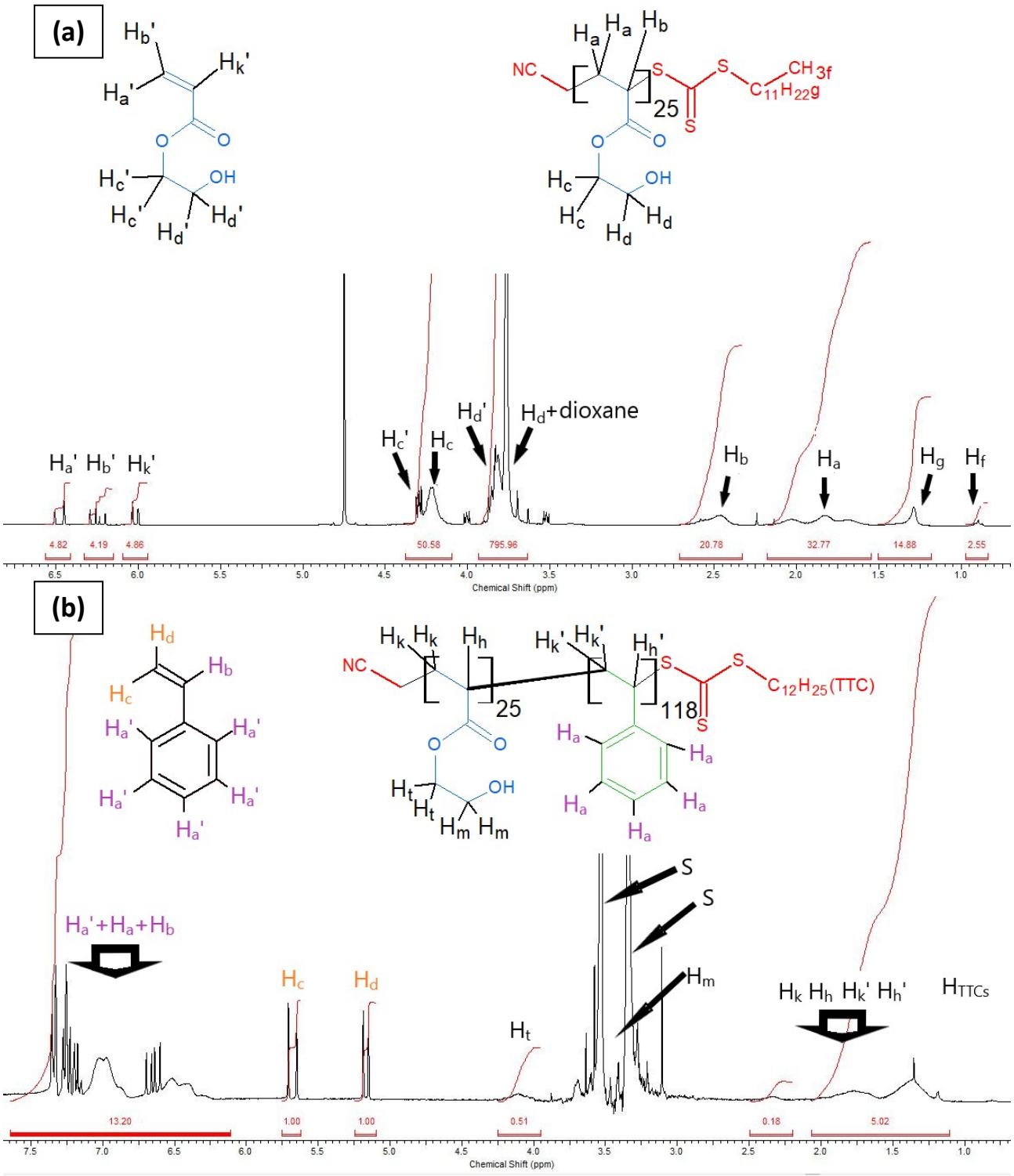

Fig. S2 (**a**) Example of ^{1}H NMR spectrum of $PHEA_{25}$-TTC. Conversion calculation :

$$Conv. = 1 - \frac{2 \cdot \left(I(H_a^{'}) + I(H_b^{'}) + I(H_k^{'})\right)}{3 \cdot \left(I(H_c^{'}) + I(H_c)\right)} \cdot 100\% = 82\ \%$$

. Experimental conditions: HEA : TTC =30 : 1; $[HEA]_0$ = 2.97 M in dioxane, blue LED (547mW cm^{-2}, 35 °C, 21 hours). (**b**) Example of ^{1}H NMR spectrum of $PHEA_{25}$-PS_{118}-TTC. Conversion calculation :

$$Conv. = 1 - \frac{5}{\left(\frac{2 \cdot \left(I(H_a^{'}) + I(H_a) + I(H_b)\right)}{I(H_c) + I(H_d)} - 1\right)} \cdot 100\% = 59\%$$

. Experimental conditions: PHEA-TTC : St =1 : 200; $[PHEA\text{-}TTC]_0$ = 7.68 mM in methanol/water mixture (8.18 g/0.43 g, 95/5 w/w %), blue LED (547mW cm^{-2}, 35 °C, 70 hours).

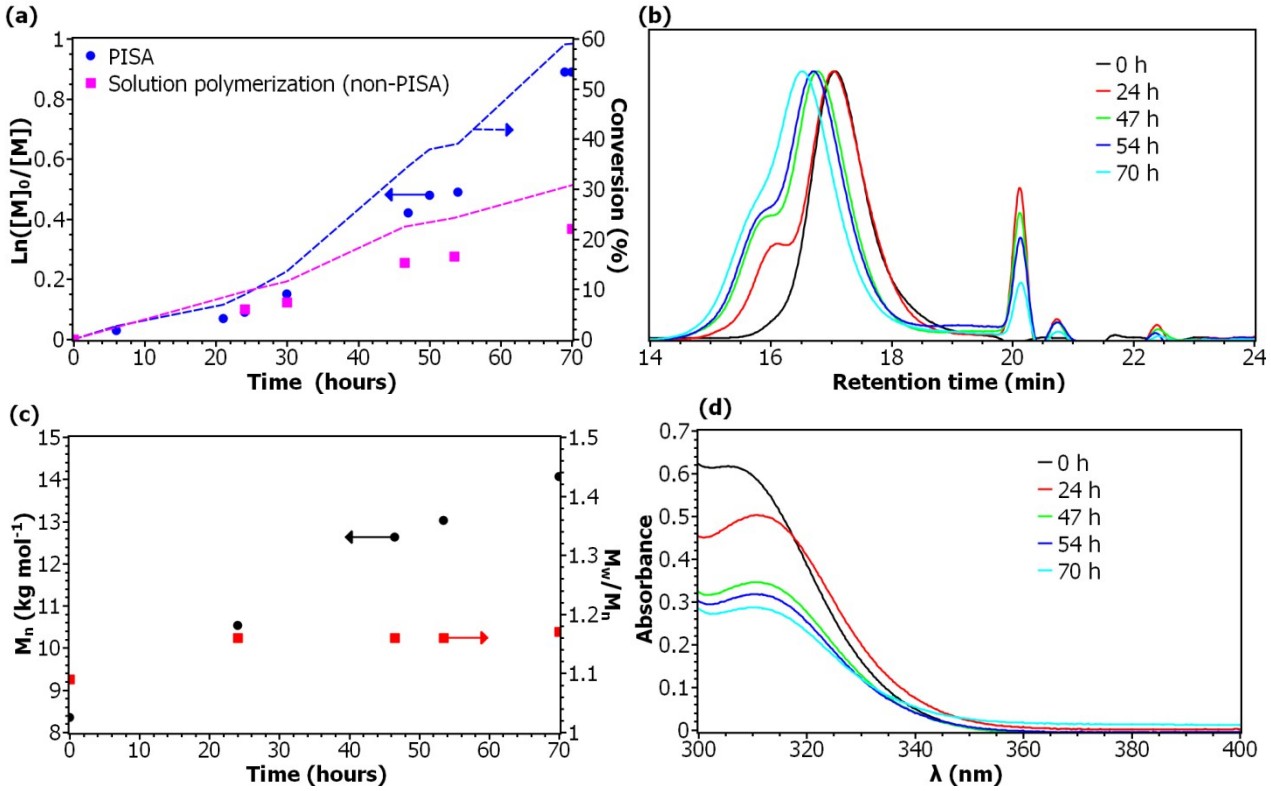

Fig. S3 (**a**) Conversion versus reaction time for the syntheses of $PHEA_{25}$-PS_{118} (PISA in dispersion) and $PHEA_{25}$-PS_{62} (solution) copolymers. (**b**) SEC chromatograms (RI detector) of $PHEA_{25}$-TTC and $PHEA_{25}$-PS_m diblock copolymers synthesized *via* RAFT photomediatedpolymerization in solution. (**c**) Evolution of M_n and polydispersity index with conversion. (**d**) UV-spectra of $PHEA_{25}$-TTC during solution polymerization.Experimental conditions: PHEA-TTC:St =1 : 200; $[PHEA\text{-}TTC]_0$ = 7.68 mM in dioxane (10.7 g), blue LED (547mW cm^{-2}, 35 °C).

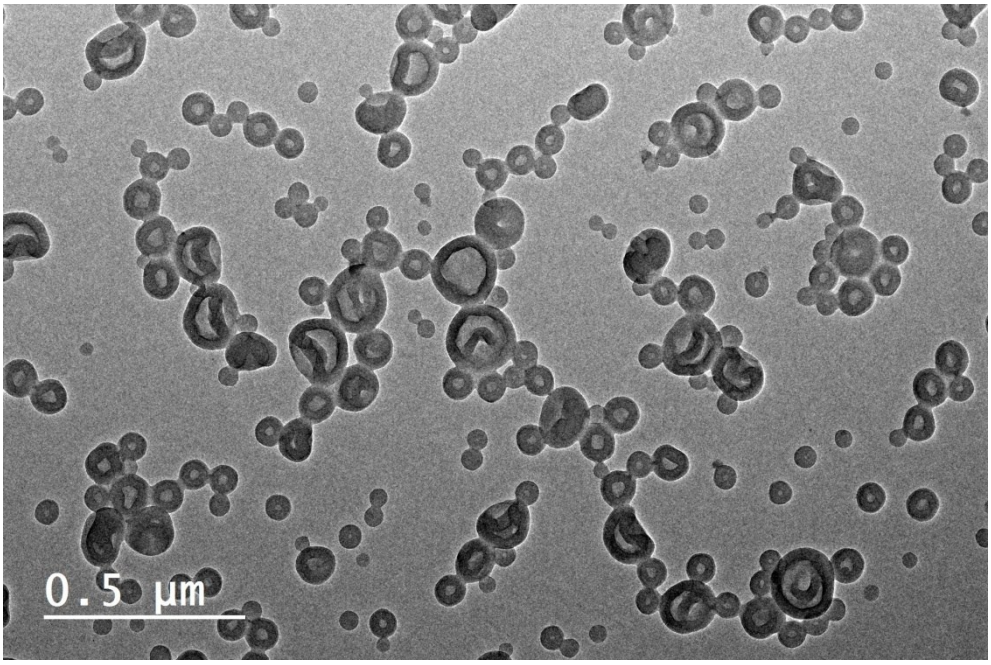

Fig. S4 TEM image of vesicular nano-objects based on $PHEA_{17}$-PS_{136} copolymer synthesized *via* dispersion PISA of St.

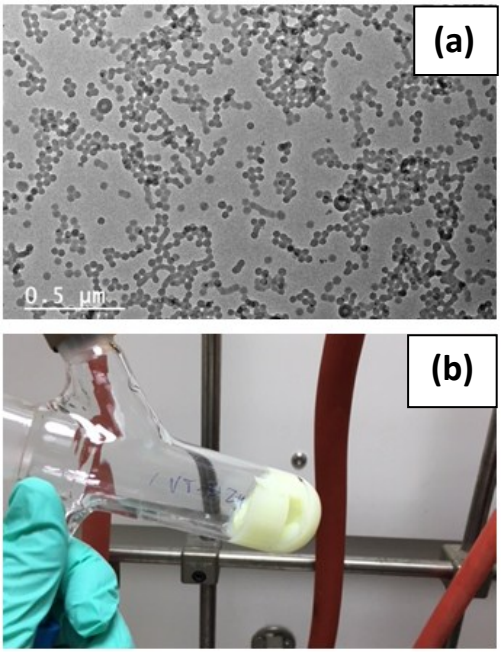

Fig. S5 (**a**) TEM image of $PHEA_{25}$-PS_{118} latex after addition of a shot of divinylbenzene (DVB). (**b**) Gelation was observed within 24 h of irradiation. Experimental conditions: DVB (20 mg) was added in the reaction mixture of $PHEA_{25}$-PS_{118} (5 g).

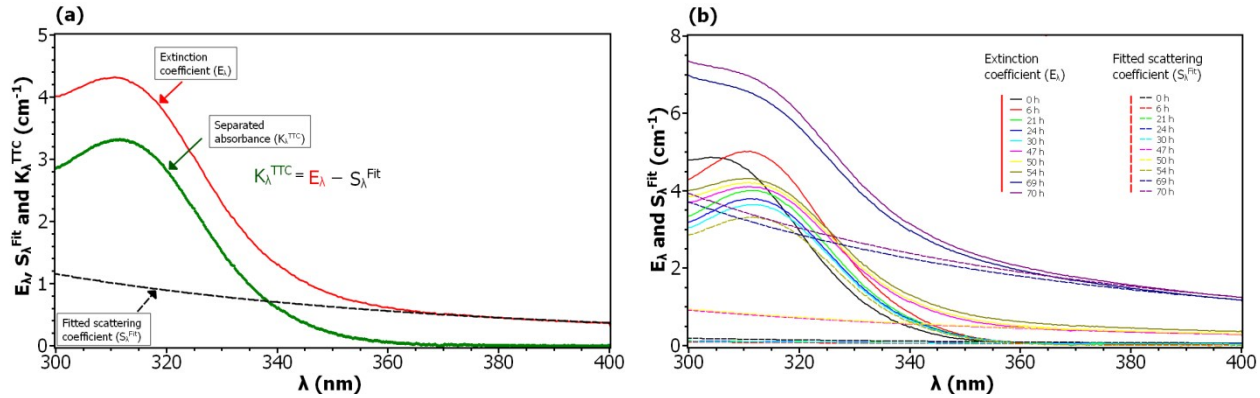

Fig. S6 (**a**) Example of the fitting of scattering coefficient (S^{Fit}_{λ}) for 54 h of irradiation. (**b**) Summary of the fitting of scattering coefficient (S^{Fit}_{λ}).

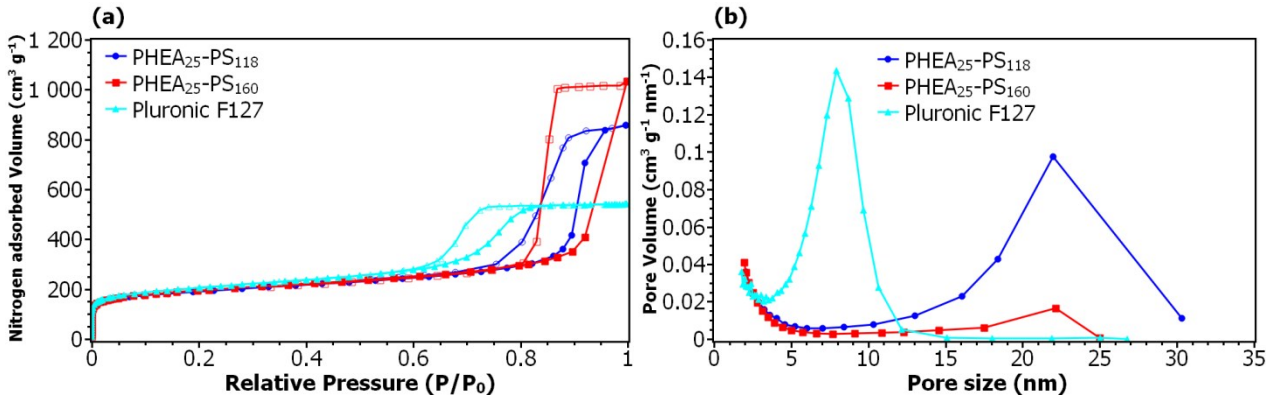

Fig. S7 (**a**) Nitrogen adsorption/desorption isotherms and (**b**) pore size distribution by the BJH method of $PHEA_{25}$-PS_{118}(blue), $PHEA_{25}$-PS_{160}(red) and Pluronic F127(cyan) based carbon materials synthesized with molar ratio of phloroglucinol:glyoxylic acid:copolymer = 1:1:0.019.

V. References

1 S. Brunauer, P.H. Emmett,E. Teller,*J Am. Chem. Soc.,* 1938*, **60**,* 309.

2 J. Rouquerol, P. Llewellyn, F. Rouquerol, *Stud. Surf. Sci. Catal.,* 2007,**160**, 49.

3 E.P. Barrett, L.G. Joyner, P.H. Halenda, *J Am. Chem. Soc.*, 1951, **73**, 373.