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# Supporting information for

Synthesis of Poly(2-hydroxyethyl methacrylate) End-Capped with Asymmetric Functional Groups via Atom Transfer Radical Polymerization

Chengmin Hou,<sup>a,b</sup> Shudong Lin,<sup>a,b</sup> Feng Liu,<sup>a,b</sup> Jiwen Hu,<sup>a,b\*</sup> Ganwei Zhang,<sup>a,b</sup>

Guojun Liu,<sup>a,c</sup> Yuanyuan Tu,<sup>a,b</sup> Hailiang Zou,<sup>a,b</sup> Hongsheng Luo<sup>a,b</sup>

<sup>a</sup>Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou, P. R. China,

510650; <sup>b</sup>Key Laboratory of Cellulose Lignocellulosics Chemistry, University of Chinese

Academy of Sciences, P. R .China, 510650; <sup>c</sup>Department of Chemistry, Queen's University, 90 Bader Lane, Kingston, Ontario, Canada K7L 3N6.

#### The solubility of CuCl<sub>2</sub>/bpy Complex

 $CuCl_2$  (5 mg) and bpy (30 mg) catalyst complexes were mixed with 1 mL of methanol, methanol/2-butanone (m/m=3:2, 2:3, or 1:4) or 2-butanone, and 300 uL of these dissolved sample was diluted with 3 mL of corresponding solvent mixture. The solubility of these complexes was evaluated with UV-vis spectroscope by comparing ultraviolet absorption intensity of these diluted samples.

#### The solubility of PHEMA Polymer

PHEMA with DP of 80 and 800 (0.1 g) was dispersed in 1 mL of methanol, methanol/2-butanone (m/m=3:2 and 2:3) or 2-butanone under shaking once in a while over 24 h at room temperature. The solubility of PHEMA in these solvents was directly evaluated.

### **Evaluation of Polymerization Degree (DP) of PHEMA Samples**

As shown in Fig. S2, monomer conversion was calculated by  $conv. = 2*(\delta_{4,34}/2 - \delta_{5.58})/\delta_{4,34} \times 100\%$ , the polymerization degree of was calculated by  $DP = 2*(\delta_{4,34}/2 - \delta_{5.58})/\delta_{4.67}$  and molecular weight from <sup>1</sup>H NMR spectra was obtained by  $M_{n,NMR} = 130.14*DP + M_{initiator}$ .

<sup>\*</sup>Corresponding author, e-mail: <u>hjw@gic.ac.cn</u>, Fax: 011-86-020-85232307, Phone: 86-020-85232307.



*Fig. S1* <sup>1</sup>H NMR spectra of a) propargyl 2-bromoisobutyrate (PBiB), b) 3-(trimethylsilyl)propargyl 2-bromoisobutyrate (TMSPBiB), and c) 3-(triisopropylsilyl)propargyl 2-bromoisobutyrate (TiPSPBiB).



Fig. S2 <sup>1</sup>H NMR spectra of unpurified PHEMA with peaks assignment.



Fig. S3 <sup>1</sup>H NMR spectra of purified PHEMA.



*Fig. S4* the solubility of a) CuCl<sub>2</sub>/bpy in methanol (sample 1), methanol/2-butanone at 3:2 (sample 2), methanol/2-butanone at 2:3 (sample 3), methanol/2-butanone at 1:4 (sample 4) and 2-butanone (sample 5); the solubility of PHEMA with molecular weight of b) 10400 g/mol and c) 104000 g/mol in methanol (sample 1), methanol/2-butanone at 3:2 (sample 2), methanol/2-butanone at 2:3 (sample 3), and 2-butanone (sample 4).



**Fig. S5**. The relationship of  $Ln(K_p^{app})$  and 1/T based on Arrhenius equation.



*Fig.* S6 The <sup>1</sup>H NMR spectra of purified TMS-C=C-PHEMA-Br and block copolymers PHEMA-b-PBA and MPEG-b-PHEMA.

*Table S1* The total solubility parameter ( $\delta$ ), dispersion solubility parameter ( $\delta_D$ ), hydrogen bonding solubility parameter ( $\delta_H$ ) and polar solubility parameter ( $\delta_p$ ) of methanol, methanol/2-butanone at 3:2, 2:3 and 1:4 (m/m) and 2-butanone with those of PHEMA polymer.

$f_{MEK}$ /%	f <sub>MeOH</sub> /%	$\delta/(cal/cm^3)$	$\delta_d/(cal/cm^3)$	$\delta_p/(cal/cm^3)$	$\delta_h/(cal/cm^3)$
		1/2	1/2	1/2	1/2
0	100	14.49	7.42	6	10.9
40	60	12.402	7.56	5.36	7.54
60	40	11.358	7.63	5.04	5.86
80	20	10.314	7.7	4.72	4.18
100	0	9.27	7.77	4.4	2.5
PHEMA		11.38	7.75	5.76	7.22