Materials are appeared on: New Journal of Chemistry

Supporting information for

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

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The solubility of CuCl\textsubscript{2}/bpy Complex

CuCl\textsubscript{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 \textmu L of these dissolved sample was diluted with 3 mL of corresponding solvent mixture. The solubility of these complexes was evaluated with UV-vis spectroscopy 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
\[ \text{conv.} = 2 \times \left( \frac{\delta_{4.34}}{2 - \delta_{5.58}} \right) / \delta_{4.34} \times 100\%, \]
the polymerization degree of was calculated by
\[ DP = 2 \times \left( \frac{\delta_{4.34}}{2 - \delta_{5.58}} \right) / \delta_{4.67} \]
and molecular weight from \textsuperscript{1}H NMR spectra was obtained by
\[ M_{n,\text{NMR}} = 130.14 \times DP + M_{\text{initiator}}. \]

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Fig. S1 $^1$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 $^1$H NMR spectra of unpurified PHEMA with peaks assignment.

Fig. S3 $^1$H NMR spectra of purified PHEMA.
Fig. S4 the solubility of a) CuCl$_2$/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 $^1$H NMR spectra of purified TMS-C≡C-PHEMA-Br and block copolymers PHEMA-\textit{b}-PBA and MPEG-\textit{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.

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<th>f\textsubscript{MEK}/%</th>
<th>f\textsubscript{MeOH}/%</th>
<th>$\delta$/(\text{cal/cm}^3)(^{1/2})</th>
<th>$\delta_D$/(\text{cal/cm}^3)(^{1/2})</th>
<th>$\delta_H$/(\text{cal/cm}^3)(^{1/2})</th>
<th>$\delta_P$/(\text{cal/cm}^3)(^{1/2})</th>
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