Amphiphilic heteroarm star polymer synthesized by RAFT dispersion polymerization in water/ethanol solution

Supporting Information

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Materials.

2,2′-Azobis(2-methylpropionamidine)dihydrochloride (V-50, 97%) and 2-methoxyethyl acrylate (MEA, 98%) were purchased from Sigma-Aldrich. N,N′-Dimethylacrylamide (98%) was purchased from J&k. 1,6-Hexanediol diacrylate (HDDA) (90%) was purchased from Aladdin Reagent (China). n-Butyl acrylate (BA) (CP) and 2,2′-azobis(2-methylpropionitrile) (AIBN, CP), were purchased from Sinopharm Chemical Reagent Co. Ltd. AIBN was recrystallized from methanol twice. All monomers were passed through a column of Al₂O₃ to remove the inhibitor before use.

Characterization.

NMR spectra were collected on a Bruker AV 500 MHz spectrometer and chemical shifts were reported using the solvent residue as the reference.

RI-GPC: GPC measurement was performed on a Waters Alliance e2695 GPC system, equipped with a styragel guard column, a Waters styragel HR3 (molecular weight range 5.0 × 10² − 3.0 × 10³), a Waters styragel HR4 (molecular weight range 5.0 × 10³ − 6.0 × 10⁵), and a Waters styragel HR5 (molecular weight range 5.0 × 10⁴ − 4.0 × 10⁶). Detection was performed on a 2414 refractometer using DMF (HPLC grade, containing 1 mg/mL LiBr) as the eluent at a flow rate of 0.8 mL/min. The temperature of the columns was set at 65 °C and the temperature of the refractometer was set at 45 °C. Analysis of molecular weight and polydispersity index of polymers was performed using Empower 2 software against PMMA standard (molecular weight range 2.4 × 10² − 1.0 × 10⁶).

Triple-detection GPC: Measurement was performed by Malvern Instruments (China) on a Viscotec/Malvern GPC system consisting of a GPCMax auto-injector fitted to a TDA 305 triple detector array (differential RI, right angle light scattering (RALS), low angle static light scattering (LALS) and four-capillary differential viscometer detectors). The column was
Viscotek I MBMMW, DMF containing 0.02 M LiBr was used as the eluent at a flow rate of 0.7 mL/min, and the temperature of the column was controlled at 50 °C. PMMA standard was used for calibration.

Star polymer sizing was analyzed using dynamic light scattering (DLS) on a Malvern Zetasizer 3000HSA at 25 °C.

Transmission electron microscopy (TEM) imaging was performed on a Jeol 200CX microscope operating at 200 kV. The TEM samples were prepared by depositing the star polymer solution onto the copper grid with a glass capillary tube and were stained with iodine vapor in a sealed vial with a grain of iodine overnight.

Atomic force microscopy (AFM) was performed on a Shimadzu SPM-9600 operating in the tapping mode. The AFM samples were prepared by depositing the star polymer solution onto freshly cleaved mica and dried in air.

**Preparation of arm polymers.**

**Poly(N,N’-dimethylacrylamide) (PDMA)** was synthesized similarly as previously reported.\(^1\) \(M_n = 8\) kDa (RI-GPC), \(M_w/M_n = 1.10\) (RI-GPC).

**Poly(2-methoxy ethyl acrylate) (PMEA):**

\[\begin{array}{c}
\text{CH}_2\text{S}\text{SCH}_2\text{CH}_2\text{O} + \text{CH}_2\text{O} \quad \text{AIBN} \\
\text{70 °C, DMF}
\end{array}\]

PMEA was synthesized in DMF at an MEA concentration of 50% w/v at 70 °C. Chain transfer agent benzyl ethyl trithiocarbonate (0.35 g, 1.54 mmol) and MEA (20 g, 0.154 mol) were dissolved in 40 mL of DMF. The solution was degassed with nitrogen at 0 °C for 40 min before immersion into a preheated oil bath at 70 °C. After the temperature was stabilized, a degassed
solution of AIBN (5.1 mg, 0.03 mmol) in DMF was injected via a microsyringe. The polymerization was last for 3 h. The conversion of monomer was calculated to be 74%. The polymer was purified by pouring the polymerization mixture into HCl solution (pH=4) to precipitate the polymer, which was then redissolved into THF and precipitated into acid solution. The collected polymer was dried under vacuum to get 14.7 g (72% yield) of a viscous liquid. $M_n = 14$ kDa (RI-GPC), $M_w/M_n = 1.12$ (RI-GPC).

![MEA conversion vs time under the polymerization condition described above. [CTA]:[MEA]:[AIBN]=1:100:0.02, [MEA]=50% w/v in DMF, 70°C.](image-url)
**Fig. S2** Pseudo first-order kinetic plot of MEA polymerization under the polymerization condition described above. \([\text{CTA}]:[\text{MEA}]:[\text{AIBN}]=1:100:0.02, [\text{MEA}]=50\% \text{ w/v in DMF, 70}^{\circ}\text{C.}

**Preparation of star polymers**

The homoarm and heteroarm CCSs were synthesized at 70 °C using BA as the spacing monomer, HDDA as the cross-linker and V-50 as the initiator. The concentration of the arm polymer(s) was maintained at 10.7 mmol/L (10% w/v for PMEA). The molar ratio of arm polymer:BA:HDDA:V-50 was 1:10:5:0.1. The conversion of arm polymer to star polymer was monitored with GPC. To quantify the arm polymer conversion, 0.2 mL of the CCS synthesis solution was withdrawn at pre-determined time intervals, the solvent of which was removed, and the left material was dissolved in 1 mL of HPLC grade DMF for GPC measurement. The arm conversion was calculated as:

\[
\text{Arm conversion} = \frac{\text{Intensity of Arm GPC peak before reaction} - \text{Intensity of Arm GPC peak at a specific reaction time}}{\text{Intensity of Arm GPC peak before reaction}}.
\]

1) **Optimization of conditions for PMEA homoarm CCS**

The solvent polarity of water/ethanol solution was optimized in order to obtain well-defined PEMA homoarm CCS. The water/ethanol solution composition was varied by increasing the
volumetric fraction of water from 20%, 30%, 40%, 50% to 60%. It was found that in 20% and 30% water/ethanol solution, no CCSs were formed. Defined CCSs were formed in 40%-60% water/ethanol solutions but some precipitate was observed in 60% water/ethanol solution due to the decreased solubility. The formation of PMEA CCS in 40% and 50% water/ethanol solution is shown in Fig. S3 and Fig. S4, respectively.

![Fig. S3](image)

**Fig. S3** PMEA homoarm CCS synthesis in 40% water/ethanol, [PMEA]=10.7 mmol/L, [PMEA]:[BA]:[HDDA]:[V-50]=1:10:5:0.1, 70°C. (A) GPC curves of CCS synthesis at different reaction times; (B) PMEA arm conversion as a function of reaction time; (C) kinetic plot of \(\ln([\text{Arm}]_0/\text{Arm})\) vs reaction time; and (D) linear fit of kinetic plot within the first 2 h of reaction.
Fig. S4 GPC curves of PMEA homoarm CCS synthesis in 50% water/ethanol at different reaction times. [PMEA]=10.7 mmol/L, [PMEA]:[BA]:[HDDA]:[V-50]=1:10:5:0.1, 70°C.

Fig. S5 Linear plot of $\ln([\text{Arm}]_0/\text{[Arm]})$ vs time for PMEA homoarm CCS synthesis within the first 30 min of reaction in 50% water/ethanol. [PMEA]=10.7 mmol/L, [PMEA]:[BA]:[HDDA]:[V-50]=1:10:5:0.1, 70°C.

(2) Preparation of PDMA homoarm CCS

Because PDMA is well soluble in water, ethanol and their mixtures of any ratios, PDMA homoarm CCS was prepared directly in 50% water/ethanol solution. Similarly, the molar ratio of
PDMA arm:BA:HDDA:V-50 was controlled at 1:10:5:0.1. The formation of PDMA CCS as a function of time is shown in Fig. S6.

**Fig. S6** GPC curves of PDMA homoarm CCS synthesis in 50% water/ethanol at different reaction times. [PDMA]=10.7 mmol/L, [PDMA]:[BA]:[HDDA]:[V-50]=1:10:5:0.1, 70°C.

Fig. S7 Linear plot of ln([Arm]₀/[Arm]) vs time for PDMA homoarm CCS synthesis within the first 30 min of reaction in 50% water/ethanol. [PDMA]=10.7 mmol/L, [PDMA]:[BA]:[HDDA]:[V-50]=1:10:5:0.1, 70°C.
(3) Preparation of PDMA-PMEA amphiphilic heteroarm CCS

PDMA-PMEA amphiphilic heteroarm CCSs were synthesized in either 40% or 50% water/ethanol under conditions similar to PMEA and PDMA homoarm CCS synthesis. The molar ratio (calculated from theoretical molecular weight) of PDMA and PMEA was maintained at 1:1, and the molar ratio of total arm polymer (PDMA+PMEA):BA:HDDA:V-50 was 1:10:5:0.1. For kinetic study, samples were withdrawn at predetermined time intervals. The heteroarm CCS synthesized in 50% water/ethanol was purified by first dialysis against acetone using dialysis tubing (MWCO 25 kDa), followed by precipitation into diethyl ether. The collected polymer was re-dissolved in THF and precipitated into ether.

![Fig. S8 GPC curves of PDMA-PMEA heteroarm CCS synthesis at different reaction times in 40% and 50% water/ethanol solutions. [PDMA+PMEA]=10.7 mmol/L, [PDMA+PMEA]:[BA]:[HDDA]:[V-50]=1:10:5:0.1, 70°C.](image-url)

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Fig. S9 PDMA-PMEA heteroarm CCS synthesis in 50% water/ethanol solution, [PDMA+PMEA]=10.7 mmol/L, [PDMA+PMEA]:[BA]:[HDDA]:[V-50]=1:10:5:0.1, 70°C. (A) Conversion of arm polymer as a function of reaction time; (C) kinetic plot of ln([Arm]₀/[Arm]) vs reaction time. The data point at 10 min was not used due to significant overlap of the formed polymers with the arm polymers.
Fig. S10 GPC curves for PDMA and PMEA arm polymers and their heteroarm CCS measured by triple-detection GPC.
Table S1  Macromolecular parameters for PDMA arm measured by triple-detection GPC.

<table>
<thead>
<tr>
<th></th>
<th>PDMA arm</th>
<th>Average</th>
<th>RSD%</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_n$ (Da)</td>
<td>6 602</td>
<td>6 425</td>
<td>1.92</td>
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<tr>
<td>$M_w$ (Da)</td>
<td>6 862</td>
<td>6 738</td>
<td>1.29</td>
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<tr>
<td>$M_w/M_n$</td>
<td>1.039</td>
<td>1.049</td>
<td>0.68</td>
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<tr>
<td>Mark-Houwink $\alpha$</td>
<td>0.731</td>
<td>0.720</td>
<td>1.07</td>
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<tr>
<td>Hydrodynamic radius $R_h$ (nm)</td>
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<td>1.754</td>
<td>0.48</td>
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<tr>
<td>$dn/dc$</td>
<td>0.0728</td>
<td>0.0731</td>
<td>0.29</td>
</tr>
</tbody>
</table>

Table S2  Macromolecular parameters for PMEA arm measured by triple-detection GPC.

<table>
<thead>
<tr>
<th></th>
<th>PMEA arm</th>
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</thead>
<tbody>
<tr>
<td>$M_n$ (Da)</td>
<td>11 652</td>
<td>10 981</td>
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<td>$M_w$ (Da)</td>
<td>12 494</td>
<td>12 050</td>
<td>2.56</td>
</tr>
<tr>
<td>$M_w/M_n$</td>
<td>1.072</td>
<td>1.097</td>
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<tr>
<td>Mark-Houwink $\alpha$</td>
<td>0.790</td>
<td>0.749</td>
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<tr>
<td>Hydrodynamic radius $R_h$ (nm)</td>
<td>2.267</td>
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<td>$dn/dc$</td>
<td>0.0373</td>
<td>0.0375</td>
<td>0.38</td>
</tr>
</tbody>
</table>
**Table S3** Macromolecular parameters for PDMA-PMEA heteroarm CCS measured by triple-detection GPC.

<table>
<thead>
<tr>
<th></th>
<th>Heteroarm CCS</th>
<th>Average</th>
<th>RSD%</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_n$ (Da)</td>
<td>259 766</td>
<td>272 828</td>
<td>266 297</td>
</tr>
<tr>
<td>$M_w$ (Da)</td>
<td>289 263</td>
<td>298 357</td>
<td>293 810</td>
</tr>
<tr>
<td>$M_w/M_n$</td>
<td>1.114</td>
<td>1.094</td>
<td>1.104</td>
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<tr>
<td>Mark-Houwink $\alpha$</td>
<td>0.556</td>
<td>0.531</td>
<td>0.544</td>
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<tr>
<td>Hydrodynamic radius</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$R_h$ (nm)</td>
<td>8.065</td>
<td>8.162</td>
<td>8.114</td>
</tr>
<tr>
<td>$dn/dc$</td>
<td>0.0504</td>
<td>0.0503</td>
<td>0.0504</td>
</tr>
</tbody>
</table>

**Calculation of arm numbers in heteroarm CCS.**

In the calculation, we assumed that conversion of BA and HDDA was 100%, which is reasonable considering the high polymerization rate and high conversion in heterogeneous polymerization systems.

The arm weight fraction in the heteroarm CCS is given by

$$
\chi_{\text{arm}} = \frac{m_{\text{PDMA conv}} + m_{\text{PMEA conv}}}{(m_{\text{PDMA conv}} + m_{\text{PMEA conv}}) + (m_{\text{BA conv}} + m_{\text{HDDA conv}})}
$$

in which, $m_{\text{PDMA conv}} = 0.5465$ g, $conv_{\text{PDMA}} = 0.74$, $m_{\text{PMEA conv}} = 1.0093$ g, $conv_{\text{PMEA}} = 0.70$, $m_{\text{BA conv}} = 0.2759$ g, $conv_{\text{BA}} = 1.0$, $m_{\text{HDDA conv}} = 0.2424$ g, $conv_{\text{HDDA}} = 1.0$.

Thus, $\chi_{\text{arm}} = 0.68$. 

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The molar ratio of PDMA and PMEA in the final heteroarm CCS was estimated from $^1$H NMR, which was 1.14:1.

According to the following equation, we calculated the number of arm in the heteroarm CCS:

$$\chi_{\text{arm}} M_{w,\text{star}} = N_{\text{PDMA}} M_{w,\text{PDMA}} + N_{\text{PMEA}} M_{w,\text{PMEA}}$$

in which, $\chi_{\text{arm}} = 0.68$, $M_{w,\text{star}} = 293810$, $N_{\text{PDMA}} = 1.14 N_{\text{PMEA}}$, $M_{w,\text{PDMA}} = 6800$, $M_{w,\text{PMEA}} = 12272$.

Thus, $N_{\text{PDMA}} = 11$, $N_{\text{PMEA}} = 10$.

Fig.S11 $^1$H NMR spectra of heteroarm CCS in (A) CDCl$_3$ and (B) D$_2$O.
**Fig. S12** 2D NOESY $^1$H NMR of PDMA-PMEA heteroarm CCS in CDCl$_3$.

**Fig. S13** DLS results of 0.2%, 0.5% and 1.0% amphiphilic PDMA-PMEA heteroarm CCS in water.
**Fig. S14** AFM micrograph and data analysis of a sample prepared from 0.1% amphiphilic heteroarm CCS in water.

Reference