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One-Step Synthesis of Hollow Polymeric Nanospheres: Self-Assembly of Amphiphilic Azo Polymers Via Hydrogen Bond Formation

Taoran Zhang,[a] Cheng Jin,[a] Lingyu Wang[a] and Qinjian Yin[a*]

[a]*Key Laboratory of Green Chemistry and Technology and College of Chemistry, Sichuan University, Chengdu, 610064, China*

The preparation and characterization of CDB

We synthesized RAFT reagent CDB according to Figure 1S.

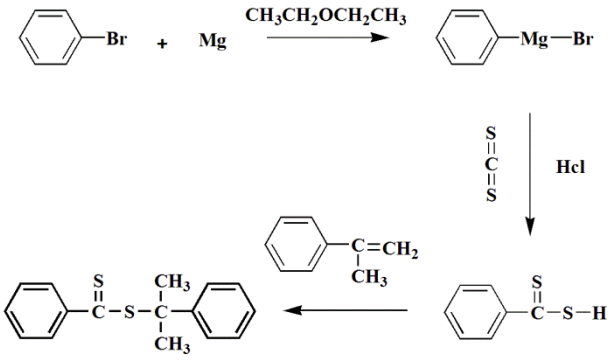

Fig 1S. Reaction scheme for synthesis of statistical RAFT reagent CDB.

^{1}H NMR spectra (Fig 2s)and ^{13}C NMR (Fig 3s) spectra were recorded by a Bruker AV II-400 NMR spectrometer at room temperature.

* Corresponding author: Tel.: +86 28 85418112; fax: +86 28 85412907. E-mail address: E-mail: changer@scu.edu.cn

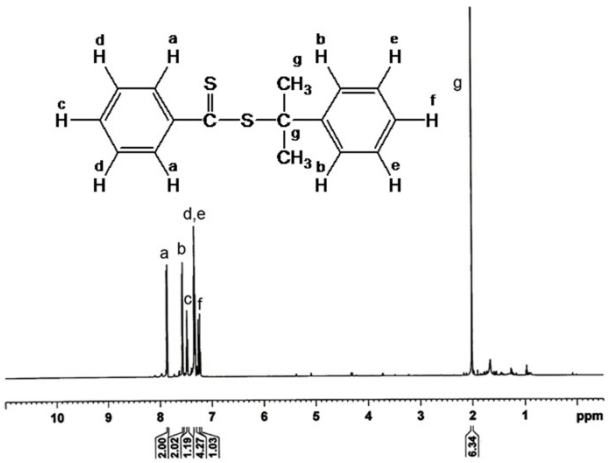

Figure S2. ^{1}H NMR spectrum for the CDB chain transfer agents in $CDCl_3$.

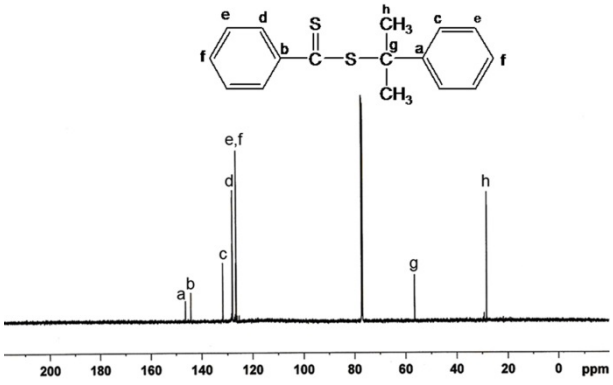

Figure S3. ^{13}C NMR spectrum for the CDB chain transfer agents in $CDCl_3$.

Fourier transform infrared (FT-IR) absorption spectra were obtained with a Bruker Tensor 27 (Figure S4).

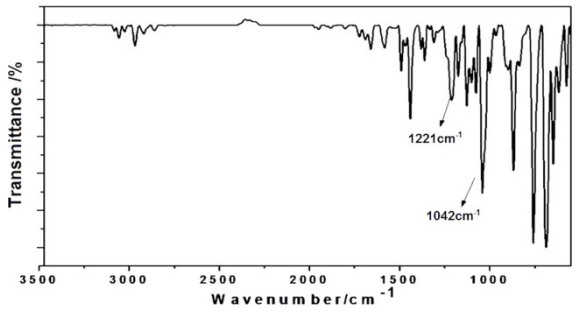

Figure S4. IR spectrum of cumyl dithiobenzoate.

The weight-average molecular weight (Mw) and number-average molecular weight (Mn) are 16803 and 13421 respectively (Figure S5).

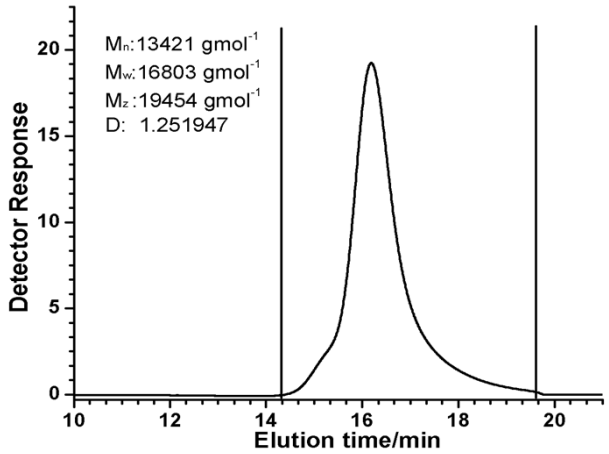

Figure S5. GPC trace for PAN-*stat*-P4VP synthesized by RAFT (DMF eluent).

Mixing a THF solution of MMR with that of PAN_{52}-*stat*-$P4VP_{101}$ produced a transparent solution, in which MMR was expected to form through hydrogen bonds between the carboxyl group and the pyridine group of PAN_{52}-stat-$P4VP_{101}$. The formation of the hydrogen bonds is supported by ^{13}C NMR and IR spectroscopy measurements. For example, the signal of the carboxyl carbon of MMR solution in chloroform shifts from 170.92 to 169.12 ppm upon addition of PAN_{52}-stat-$P4VP_{101}$ solution, which reflects that the self-association of the carboxyl is disrupted and an intermolecular hydrogen bond forms between the carboxyl hydroxyl group and the pyridyl group (Figure S6).

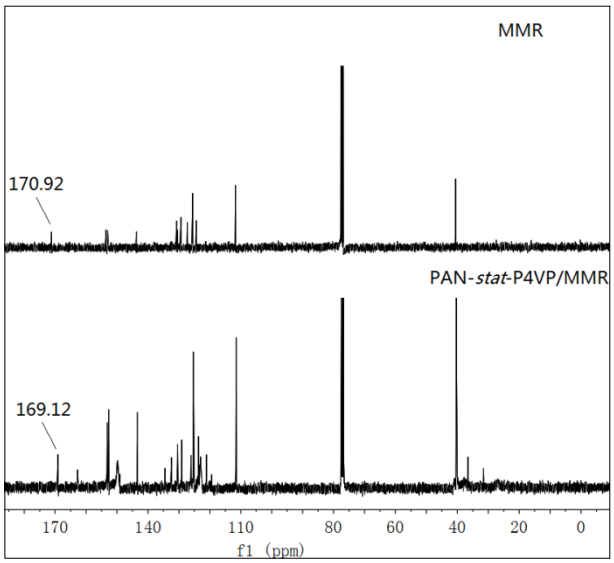

Figure S6. ^{13}C NMR results of MMR and the mixture of PAN_{52}-stat-$P4VP_{101}$/MMR_{41} in $CDCl_3$.