Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for:

Determination and correlation of regioselectivity and dead dormant species from head addition in an acrylate RAFT polymerization

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1. ^{1}H NMR spectra of PBzA-BCBD samples with different DP

The samples exhibited same resonance signals of methine and methylene protons in backbone at 1.20-2.30 ppm (d and e) and that of phenyl protons (b) at 7.0-7.5 ppm. The signals at 4.8-5.0 ppm and 8.15-8.25 ppm correspond to methylene protons(c) in benzyl group and phenyl protons (a) of carbazole end group, respectively. The peak area of signals at 4.8-5.0 ppm and 8.15-8.25 ppm can be used to calculate the DP of PBzA-BCBD.

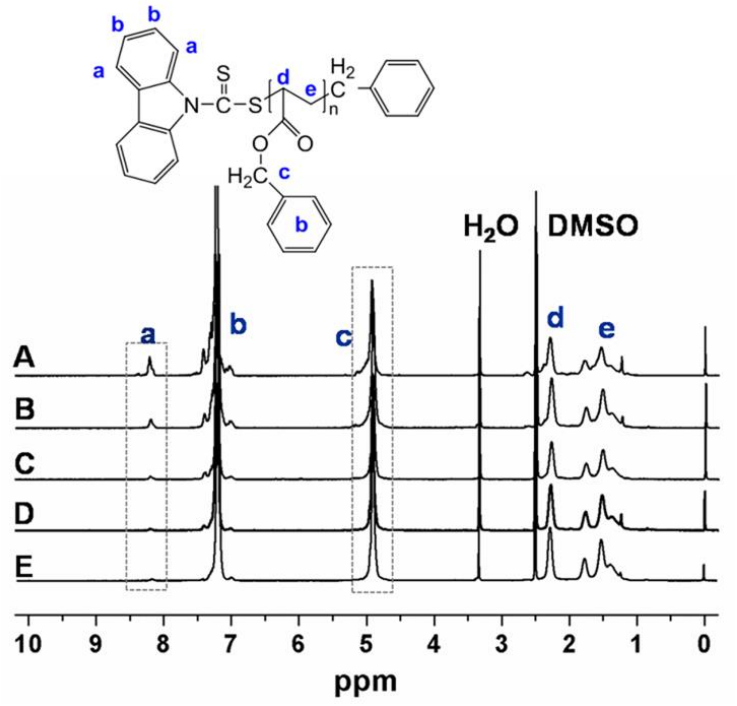

Figure S1. ^{1}H NMR spectra of $PBzA_{10}$-BCBD (A), $PBzA_{25}$-BCBD (B), $PBzA_{50}$-BCBD (C), $PBzA_{100}$-BCBD (D) and $PBzA_{200}$-BCBD (E) in DMSO

2. GPC curves of PBzA-BCBD samples with different DP

It can be found that all of samples showed symmetrical and unimodal GPC curves with narrow molar mass dispersity.

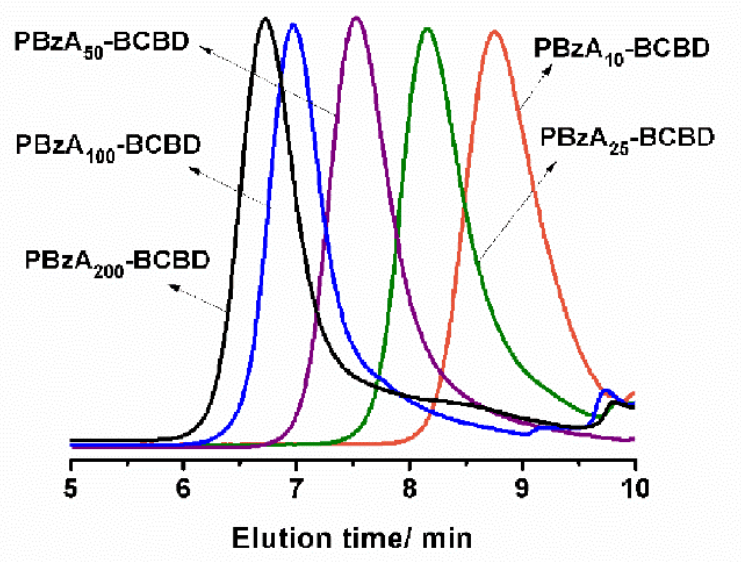

Figure S2. GPC curves of $PBzA_{10}$-BCBD, $PBzA_{25}$-BCBD, $PBzA_{50}$-BCBD, $PBzA_{100}$-BCBD and $PBzA_{200}$-BCBD. The samples were both dissolved in THF with the concentration of 1.0 mg/ml and calibrated with PSt standards

3. Impact of solvent composition on the absorption intensity of PBzA-BCBD

To determine whether solvent composition has influence on UV absorption intensity of thiocarbonylthio end group, two 0.50 mg/ml PBzA-BCBD solutions, dissolved in mixed solvent with different ratio of dichloroethane (DCE) and acetonitrile (ACN), were prepared and applied to UV-vis spectrophotometer. The first sample was dissolved in solvent DCE/ACN=83.25/16.75, which is the same composition as the eluent of homopolymer in GPEC; the second sample was dissolved in solvent DCE/ACN=33.35/66.65, which is identical to eluent of block copolymer. As shown in Figure S3, the absorption intensity of two samples showed no significant difference above 300 nm that attributes to the absorption of *N*-carbazolecarbodithioate group, indicating that the eluent composition does not influence the absorption of *N*-carbazolecarbodithioate end group, and thus the calculation method equation (9) is feasible and accurate.

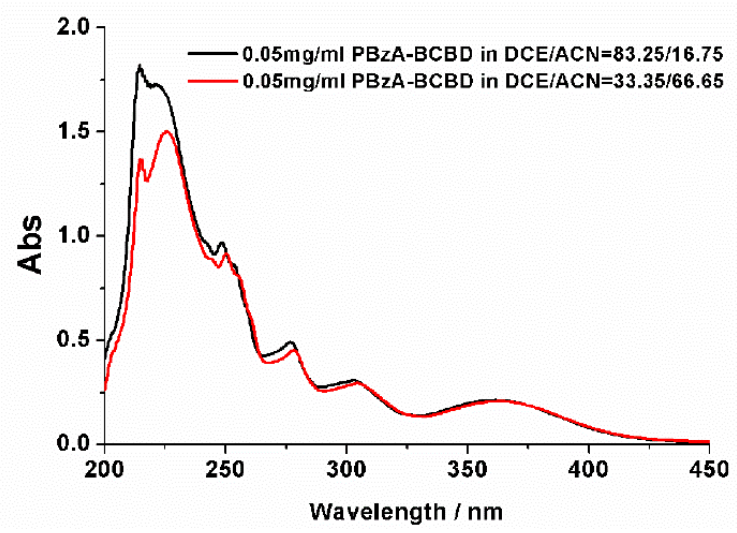

Figure S3. Ultraviolet absorption curves of PBzA-BCBD in different solvents.