

Determination of head addition incidence of (meth)acrylate and styrene in radical polymerization by RAFT block polymerization derivation and gradient polymer elution chromatography

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GPC curves of five series of samples with different DP

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

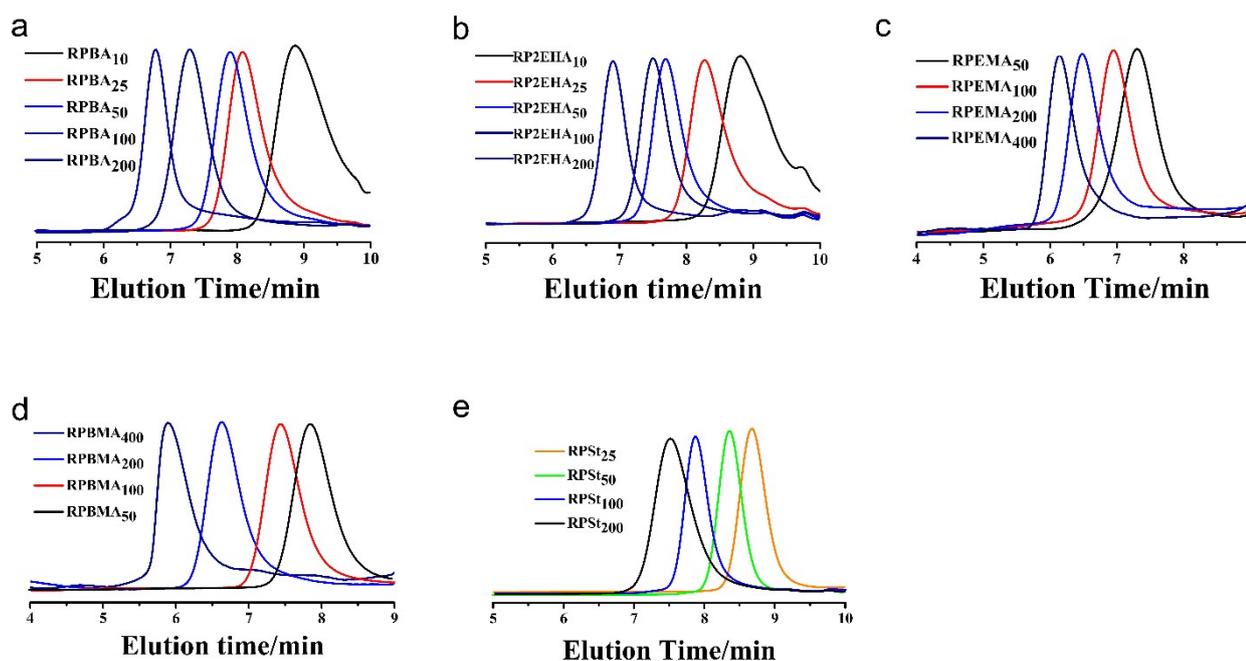


Figure S1 GPC curves of RPBA(a), RP2EHA(b), RPBMA(c), RPEMA(d) and RPSt(e) with different DP. The samples were all dissolved in THF with the concentration of 1.0 mg/ml and calibrated with PSt standards

^1H NMR spectra of six kinds of polymers with different DP

The samples exhibited same resonance signals of methine and methylene protons in backbone. Since the samples had not undergone other post-treatment processes, there were residual monomers remaining in the polymers. The signals at 5.5-7.0 ppm correspond to vinyl of monomers. There was no overlap with other peaks, so the peak area of signals in the dotted line can be used to calculate conversion.

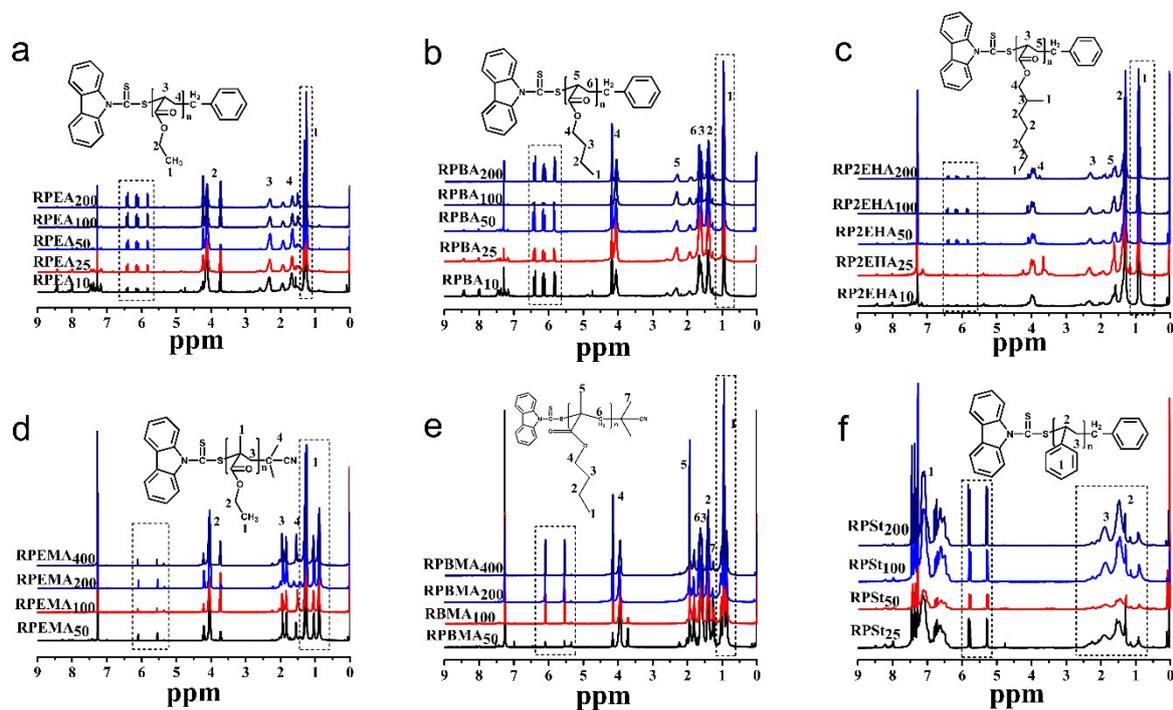


Figure S2 ^1H -NMR spectra of RPEA(a), RPBA(b), RP2EHA(c), RPBMA(d), RPEMA(e) and RPSSt(f) with different DP in CDCl_3

GPEC curves of block copolymers

According to GPEC curves of block copolymers detected at 360 nm of P2EHA-b-PMA, PEA-b-PMA, PBMA-b-PMMA, PSt-b-PBA, PEMA-b-PMA samples, Peak area of A_{360}^H and A_{360}^B can be used to calculate the content of DDS (α).

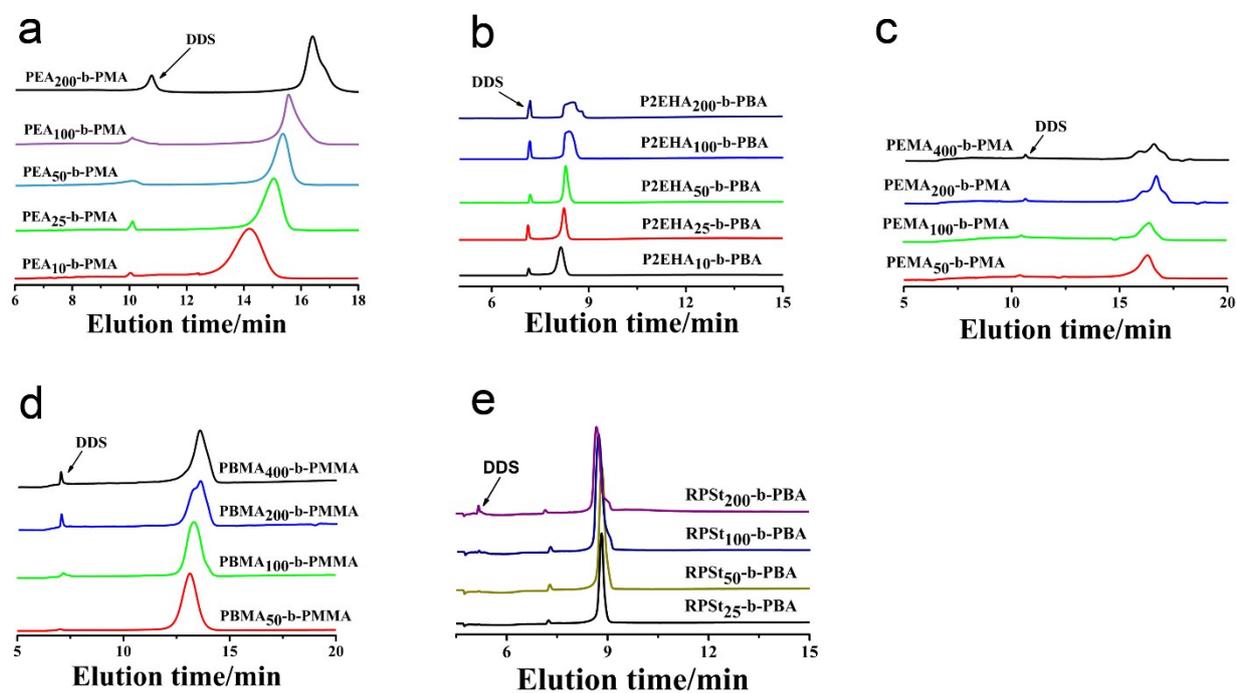


Figure S3 GPEC chromatograms detected at 360 nm of products obtained after 48 h blocking reaction of RPM1 with different DP_0 .

Block polymerization process with second monomers

The residual content of macro-RAFT agent gradually decreased as the block-derived polymerization proceeded and did not change after 24 h. When all active macro-RAFT agents were supposed to have been chain extended, the ultimate residual content of macro-RAFT agents (R_s) was attributed to DDS content, and the ultimate R_s was thought to be equal to the DDS content (α).

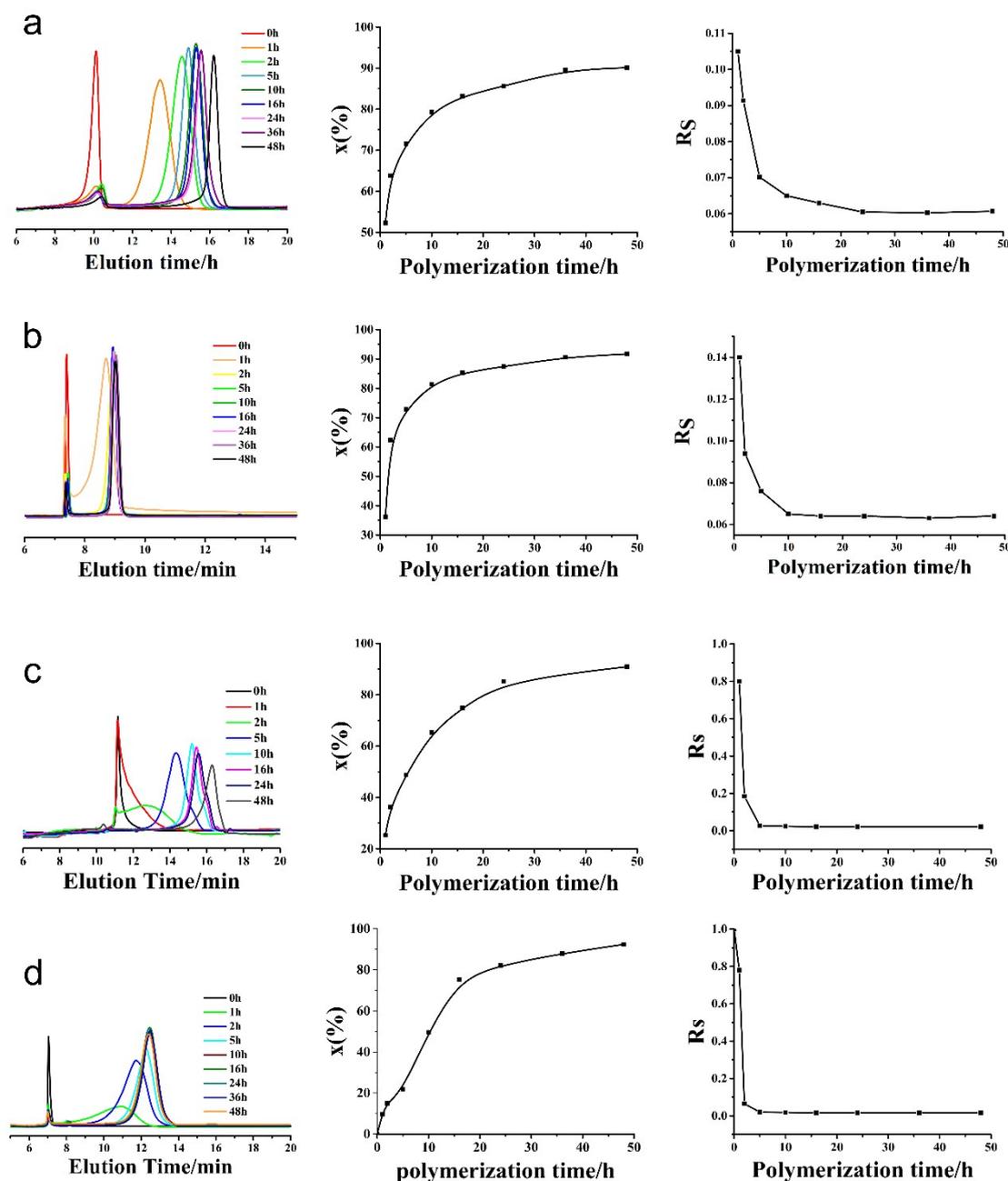


Figure S4 GPEC detected at 360 nm of block polymerization products, conversion of second monomer, and residual ratio of macro-RAFT agents (R_s) at different chain extension reaction times.

- (a) chain extension reaction of RPEA₅₀ with MA
- (b) chain extension reaction of RP2EHA₅₀ with BA
- (c) chain extension reaction of RPEMA₁₀₀ with MMA
- (d) chain extension reaction of RPBMA₁₀₀ with MMA

GPEC spectra of collected dead polymers RPBA₅₀

The collected dead homopolymers RPBA₅₀ were analyzed by GPEC using the selected elution procedure for RPBA. The chromatogram detected at 360 nm only showed a single peak at 7.3 min.

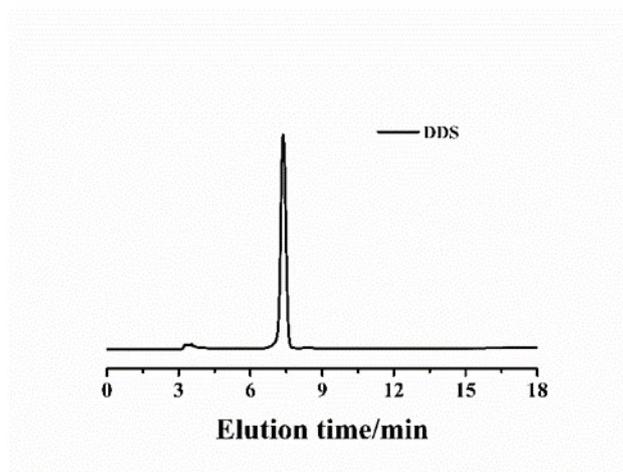


Fig. S5 GPEC spectra of collected dead polymers RPBA₅₀ detected at 360 nm.