

## Supporting Information for

# Thermal stability of styrene/n-butyl acrylate RAFT-based copolymers

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## Experimental Procedures

### *Synthesis of homopolymers*

Polystyrene (PS), poly(*n*-butyl acrylate) (PBA) were synthesized via the RAFT polymerization using dibenzyl trithiocarbonate (BTC) as a RAFT-agent and AIBN as a radical initiator. For PS synthesis, 0.580 g of BTC (0.2 mol/L) and 0.0164 g of AIBN ( $10^{-2}$  mol/L) were dissolved in 10 ml of the freshly distilled styrene. For PBA synthesis, 0.290 g of BTC (0.1 mol/L) and 0.00164 g of AIBN ( $10^{-3}$  mol/L) were dissolved in 10 ml of the freshly distilled *n*-butyl acrylate. Then, standard manipulations were used (see EXPERIMENTAL).

### *Synthesis of copolymers*

Styrene/*n*-butyl acrylate copolymers (Cop1 – Cop6) were synthesized via the same approach. Typically, 0.7660 g of BTC (0.2 mol/L) and 0.0216 g of AIBN ( $10^{-2}$  mol/L) were dissolved in 13.2 ml of the styrene/*n*-butyl acrylate mixture of the given content (Table S1). Then, standard manipulations for the preparation of the samples for polymerization were used (see above). In all cases, copolymerization was carried out at 80 °C and was stopped at a conversion of about 80 – 90%.

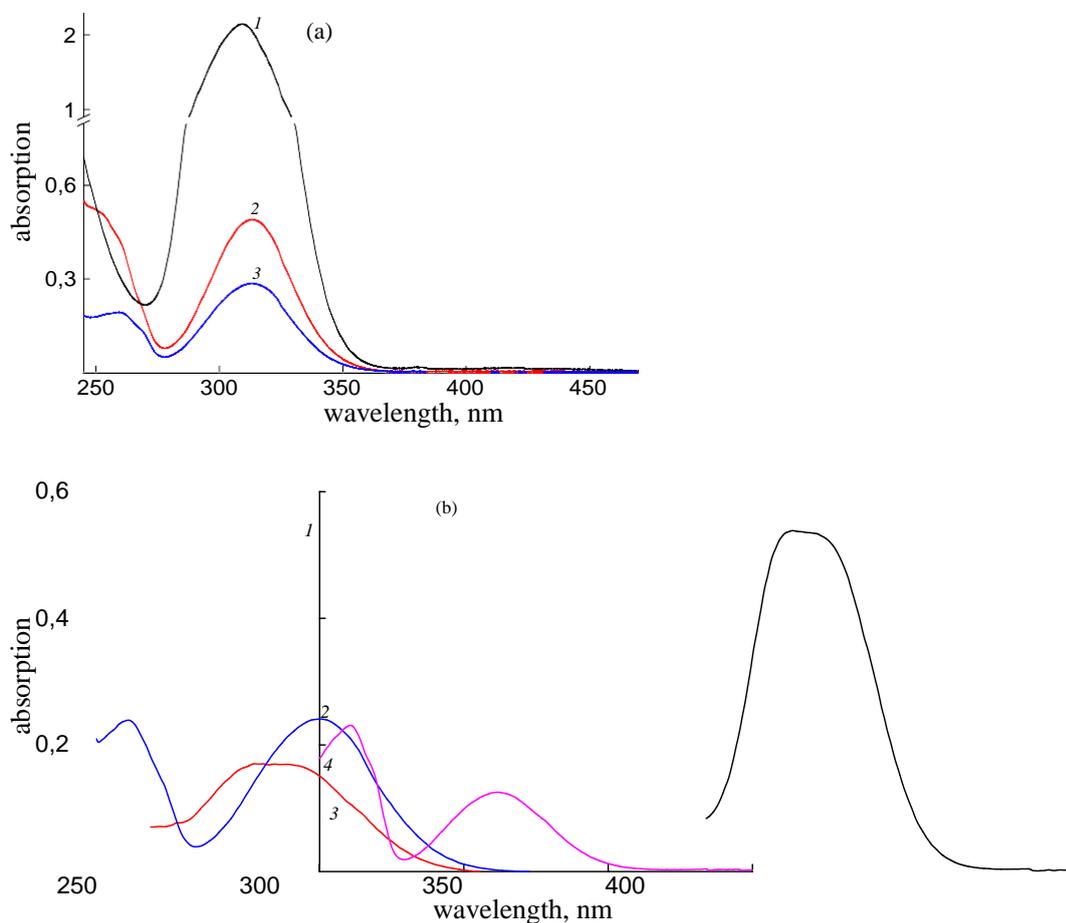
Table S1. Styrene/*n*-butyl acrylate mixtures for Cop1 – Cop6 synthesis.

Copolymer	Styrene, ml	<i>n</i> -Butyl acrylate, ml
Cop1	1.2	12.0
Cop2	2.0	11.2
Cop3	3.0	10.2
Cop4	5.0	8.2
Cop5	5.8	7.4
Cop6	11.8	1.4

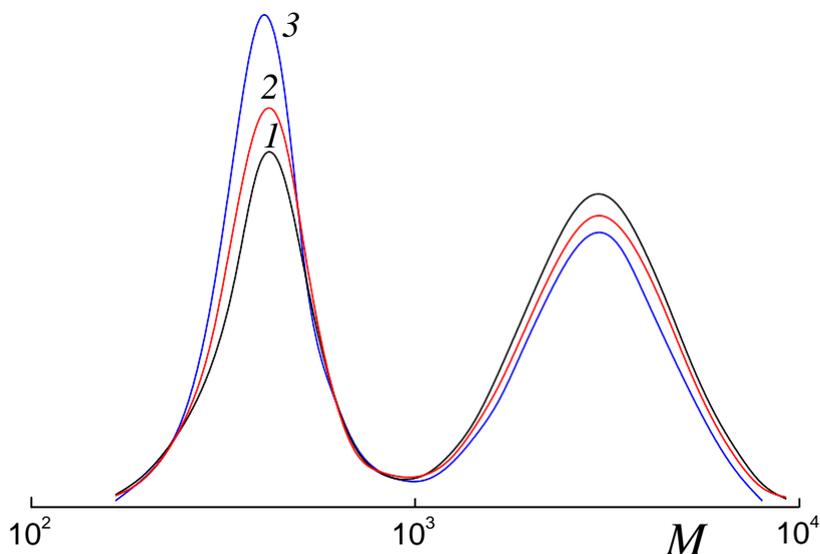
### *Synthesis of block copolymers*

PS–PBA–PS and PBA–PS–PBA block copolymers were prepared via similar synthetic approach. For PS–PBA–PS synthesis, obtained PS (0.330 g) (see *Synthesis of homopolymers*) and AIBN (0.0017 g) were dissolved in 2 ml of the freshly distilled *n*-butyl acrylate. For the synthesis of PBA–PS–PBA, PBA (0.3637 g, see *Synthesis of homopolymers*) and AIBN (0.0040 g) were dissolved in 2 ml of the freshly distilled styrene. Then, standard manipulations were used for the preparation of the samples and polymerization of reaction mixtures.

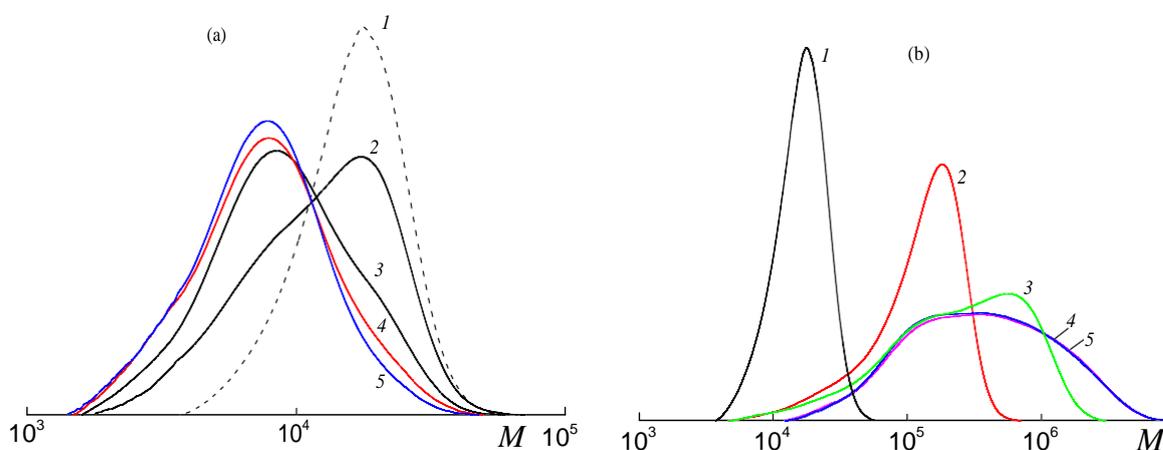
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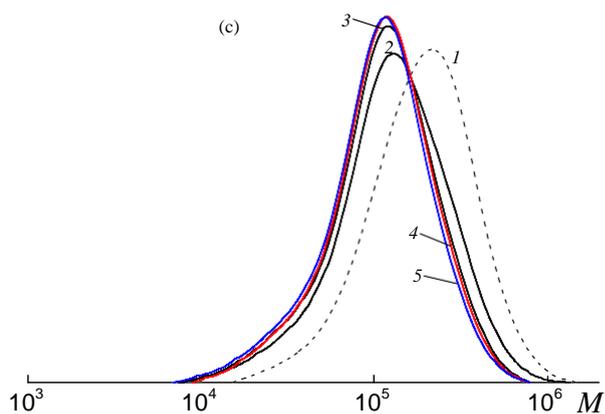


**Fig. S2.** The SEC curves normalized by unit area for PS after heating with AIBN in benzene solution at 80°C for 2 (1), 4 (2), and 22 h (3);  $[PS]_0 = 4 \times 10^{-3}$  mol/L and  $[AIBN]_0 = 4 \times 10^{-1}$  mol/L.

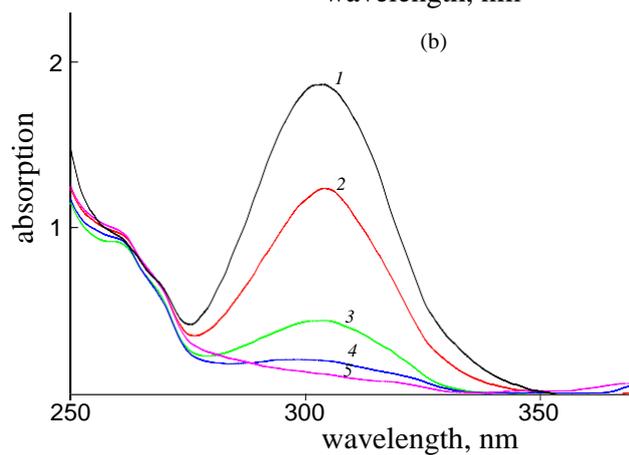
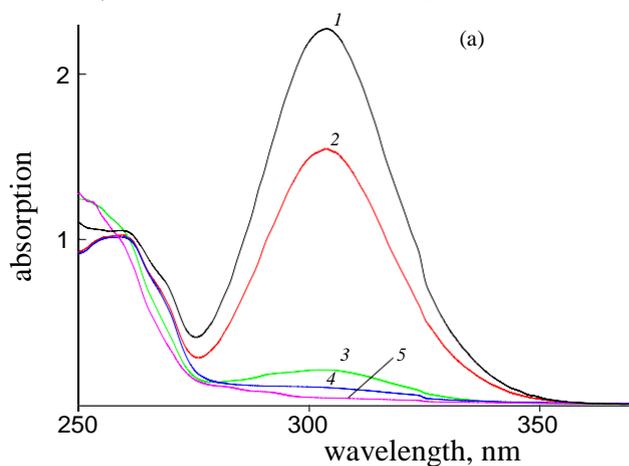


**Fig. S3.** The SEC curves normalized by unit area for (a) PS–PBA–PS ( $M_n = 2 \times 10^4$ ) before (1) and after thermal treatment in inert atmosphere at 200 °C for 6 (2), 24 (3), 48 (4) and 72 h (5); (b) chain extended polymers prepared by styrene polymerization initiated by AIBN in the presence of block copolymers treated at 200°C for 6 (1), 24 (2), 48 (3) and 72 h (4); (c) PS–PBA–PS ( $M_n = 14 \times 10^4$ ) before (1) and after thermal treatment in inert atmosphere at 200°C for 6 (2), 24 (3), 48 (4) and 72 h (5).

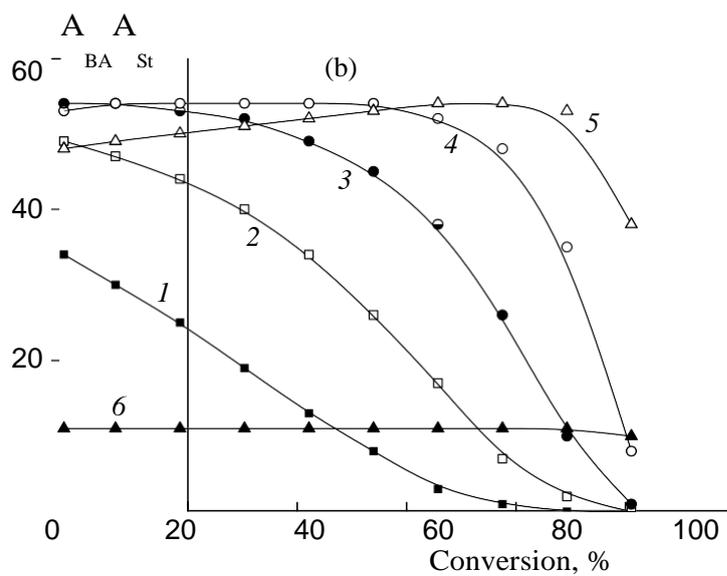
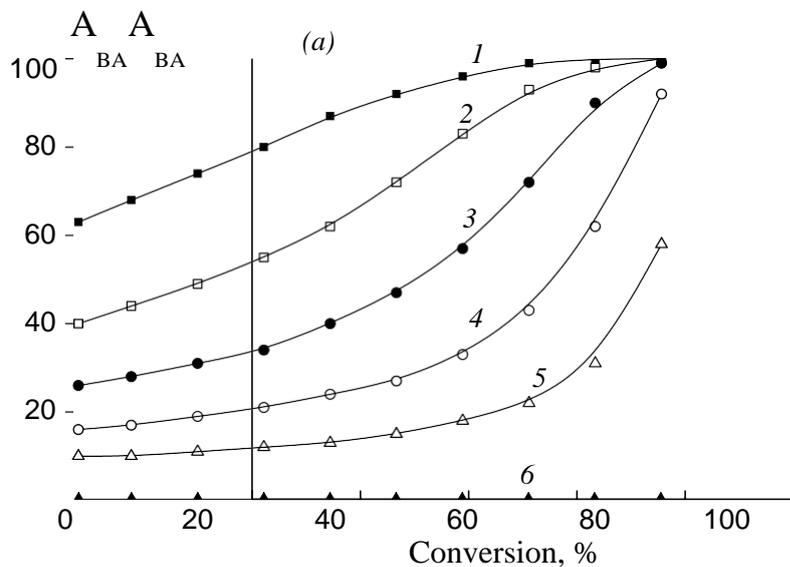


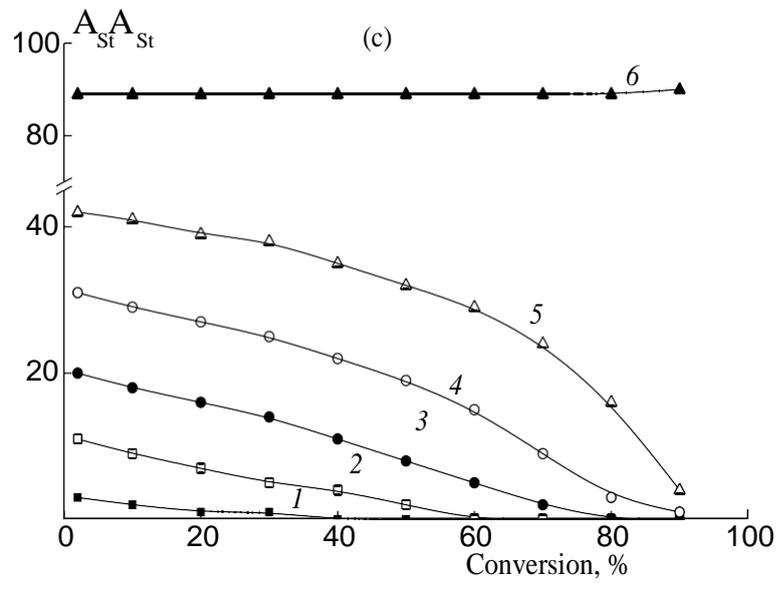


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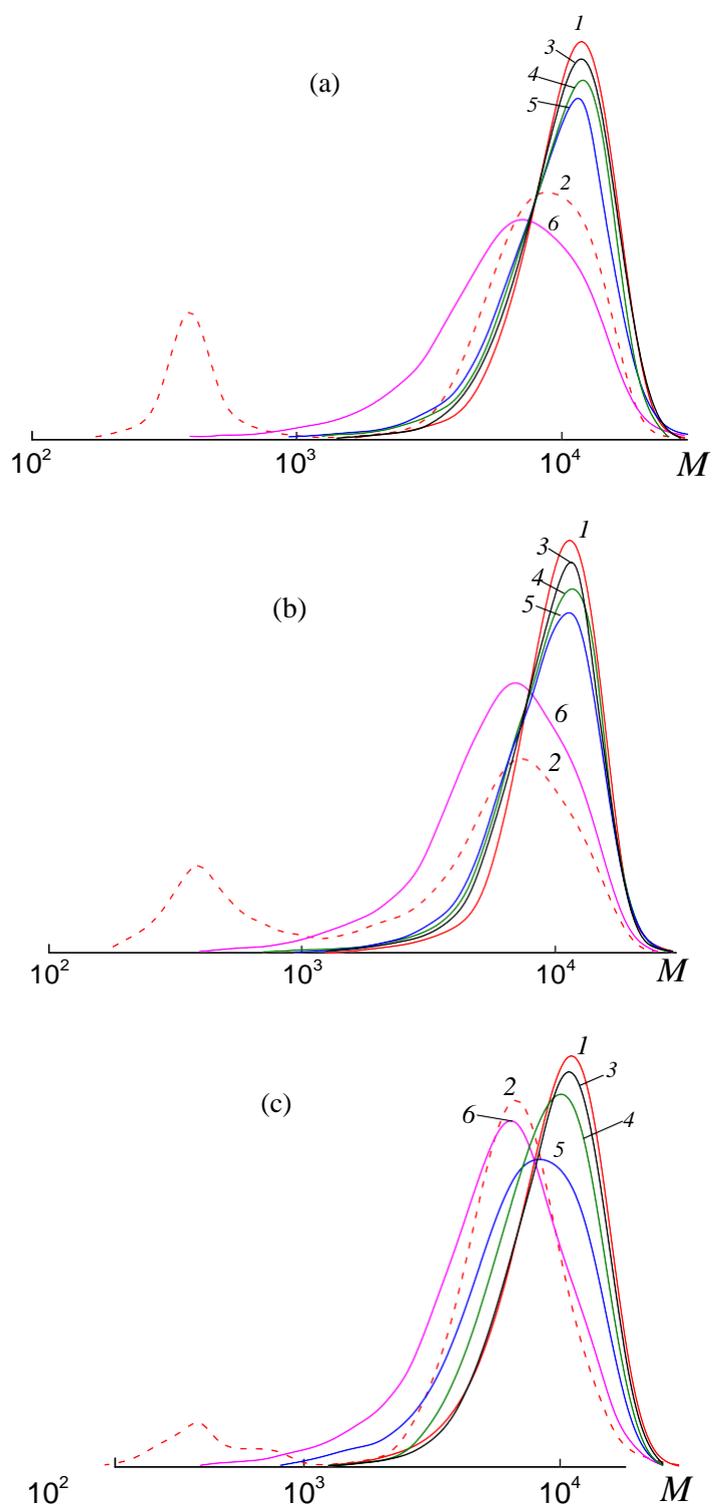


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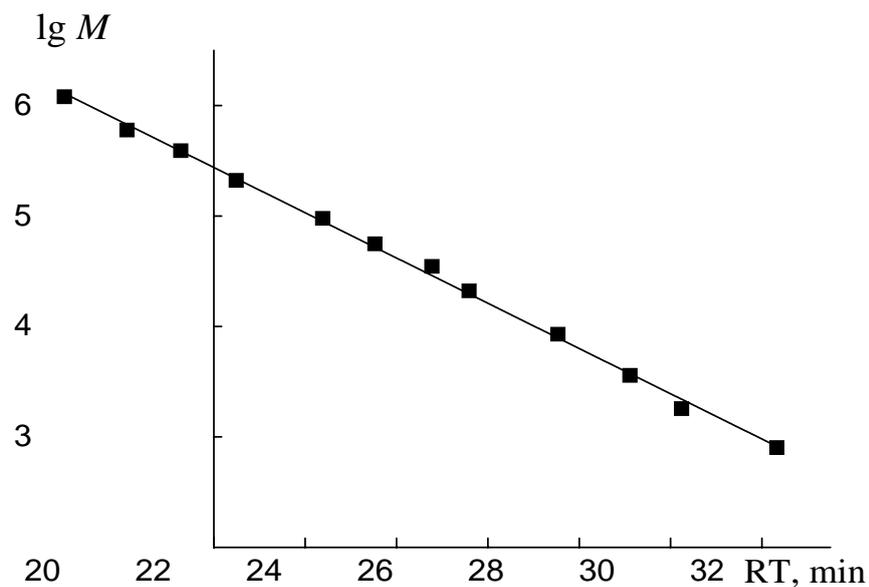




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