Supplemetary materials for the manuscript of I.A. Gritskova, A.A. Kuznetsov, et al. Russ. Chem.Bull. 2026 #5.

1. <u>1H NMR spectra of the St-MMA copolymer</u>

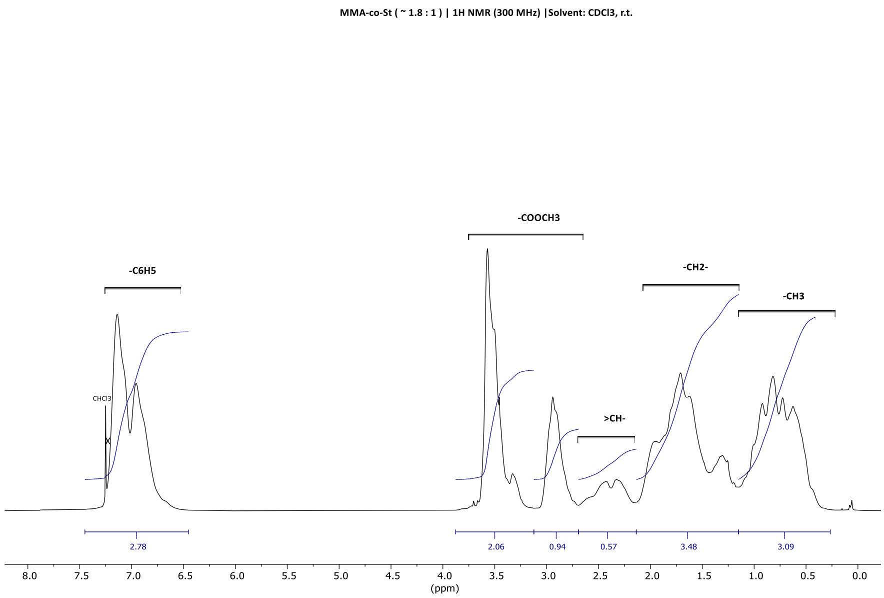

Figure S1. [1]H NMR spectrum of the CPL sample isolated by dilution of the limiting conversion at a volume ratio of St/MMA (1:2) in the initial monomer mixture. Monomer mixture/water ratio 1:4 (mol);

a surfactant concentration 0.5%- wt; potassium persulfate concentration 1.0 wt.% based on a mixture of monomers.

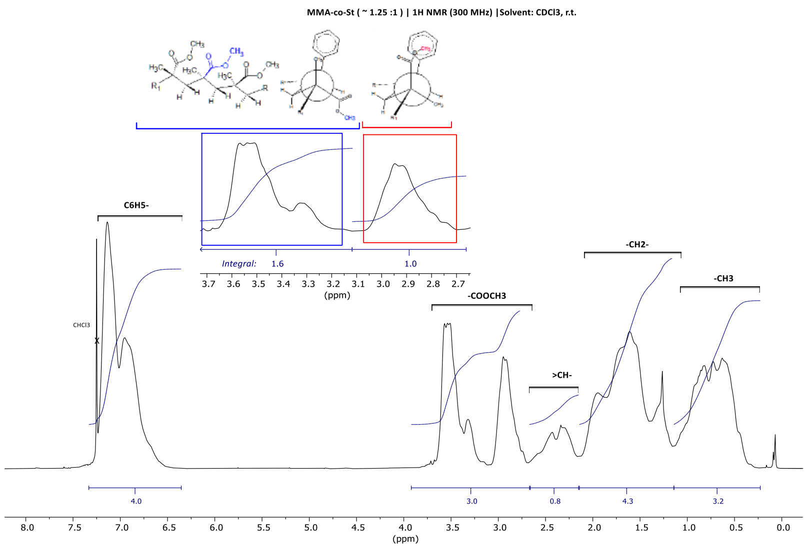

Figure S2. [1]H NMR spectrum of the CPL sample isolated after achievement of the limiting conversion at a volume ratio of St/MMA (1:1) in the initial monomer mixture. Monomer mixture/water ratio 1:4 (mol); a surfactant concentration 0.5%-wt; concentration of $K_2S_2O_8$ is 1.0 wt.% based on a mixture of monomers.

2. Calculation of the coefficient of CPL chain compositional heterogeneity Km

The CPL chain growth mechanism includes four chemical reactions (scheme D1, where M1, M2 are monomers, R1 R2 are growth radicals (Scheme D1).

Scheme D1

R1 + M1 → R1 (*k11*)

R1+ M2→ R2 (*k12)* ;

R2+ M2→ R2 (*k22*)

R2+ M1→ R1 (*k21)*

Km represents the total transient probability of a crossover growth chain occurring on the R1 and R2 radicals. The probability of the former one (R1) is expressed by the ratio of the crossover reaction rate *(k12*M2*R1)* to the sum of the reaction rates of the crossover- and homo-growth chain (*k12*M2*R1 +k11*M1*R1*). Similarly, we calculate the probability of a crossover growth on the radical R2. Then, we summarize the two transition probabilities (eq D1a) :

$$Km = \frac{k12*M2}{k12*M2+k11*M1} + \frac{k21*M1}{k21*M2+k22*M1} \qquad \text{(S1a)}$$

Taking into account notations:

r1=k11/k12, r2=k22/r12, m1= [M1]/{[M1}+[M2]}; m2=1-m1

and using the principle of stationarity in relation to the growth radicals R1 and R2:

k12 R1 M2 = k21*R2*M1 ,

after corresponding transformations, we obtain the equation D1 connecting Km with m1.

$$Km = \frac{1-m1}{(1-m1*(m1*\left(r1+\left(1+\frac{1-m1}{m1}\right)\right)} + \frac{1}{(1+r2*\frac{1-m1}{m1})} \qquad \text{(S1)}$$

3. Derivation of the equation of the balance of M1 M2 monomers and repeating units of St and MMA in the polymer system in differential form

Let us_introduce the notation: m1 = M1/M; M1, M2-concentration of monomers M1, M2; M – total concentration of monomers M=M1+M2; m1 is the mole fraction of monomer M1 in the monomer mixture; p1 is the molar fraction of M1 monomer units in the CPL chain of instantaneous composition, x is the conversion. Let's rewrite the expression for m1 in a form

$m1*M = M1$ and differentiate it to obtain eq.S2. Also, $dM1$ can be expressed in a form connected with the $p1$ (eq.S3):

$$dM1 = M*dm1 + m1*dM \qquad (S2)$$

$$p1 = dM1/dM\ ;\quad dM1 = p1*dM \qquad (S3)$$

We equate expressions (S2) and (S3):

$$M*dm1 + m1*(dM) = p1*(dM); \qquad M*dm1 = dM(p1-m1)$$

Replace M= M0(1-x)- and dM= -M0*dx, shorten M0. We obtain the equation of the material balance of the system in differential form (eq. S4), connecting $m1(x)$ and $p1$.

$$(1-x)*(dm1/dx) = (m1 - p1) \qquad (S4)$$