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TEMPO-mediated radical polymerization in the synthesis of poly(methyl methacrylate) macromonomer

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Experimental

Technical grade inhibitor-free methyl methacrylate (Reakhim, Russia) was distilled in vacuum under the stream of argon (b.p. 80.5 °C at 100 Torr, $n_D^{20} = 1.3984$). Styrene (pure grade, Reakhim, Russia) was purified according to standard procedure. Polyethylene glycol methacrylate (PEGMA) was synthesized as described previously [S. Zalipsky, C. Gilon and A. Zilkha, *J. Macromol. Sci. Part A – Chem.*, 1984, **A21**, 839]. 2,2,6,6–Tetramethylpiperidine-1-oxyl (TEMPO, Sigma, USA) was used as received. Azo-bis-isobutyronitrile (AIBN, Sigma, USA) was recrystallized from ethanol.

Instrumental methods

Electron Spin Resonance (ESR) spectra were recorded using RE-1307 X-range. The amount of radicals was calculated by double integration using the ESR program (version 2.3). Mn^{2+} ions in the MgO lattice were used as a reference. The spectrum of 0.1 mM TEMPO solution in MMA registered under the same conditions as the spectra of the test samples served as a standard.

The kinetics of polymerization at 120°C was studied by calorimetry on a DAK-1-1A differential automated microcalorimeter in the mode of direct registration of the rate of heat release. Kinetic calculations were performed with the known value of ΔH for the polymerization of MMA of 57 kJ mol^{-1}.

Molecular-mass characteristics of the polymers were evaluated by GPC using Waters instrument equipped with differential refractometric detector and three Ultrastyragel columns with a pore size of 10^3, 10^5 Å, and linear. GPC was performed in THF at 35 °C. Chromatogram processing was carried out on a DataModule-730 integrator. The molecular weights of the macromonomers were calculated using PMMA- standards.

Composition of the copolymers was studied using ^{1}H NMR. NMR spectra were recorded in $CDCl_3$ using Bruker DRX500 spectrometer with proton precessional frequency 500 MHz. Chemical shifts were calibrated using signals of residual protons of the solvent.

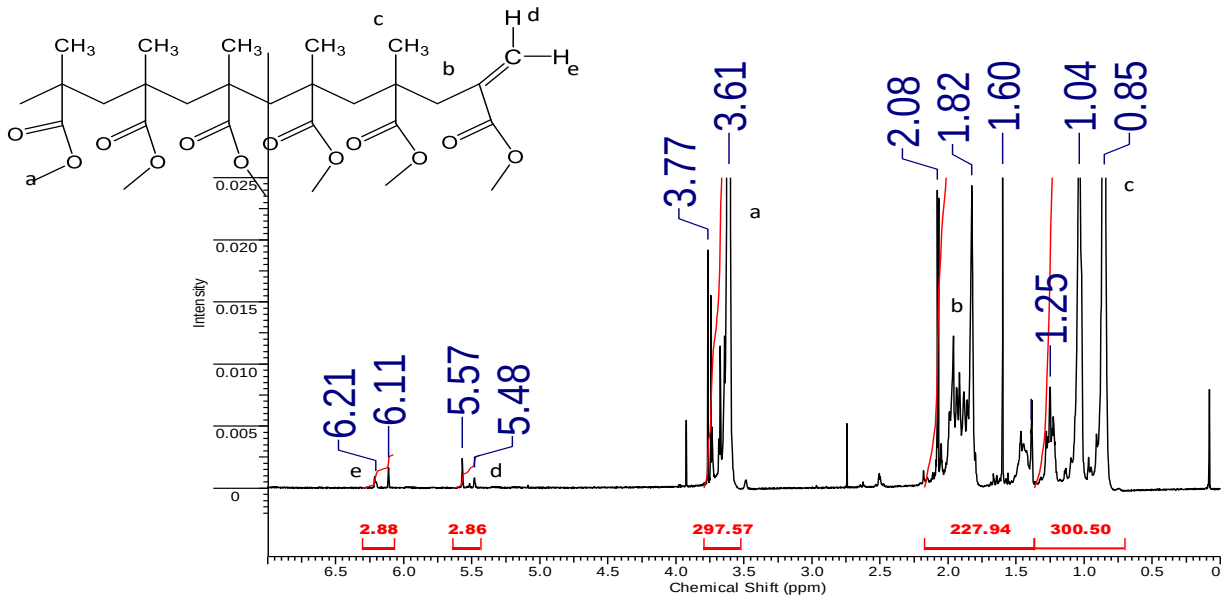

Figure S1 ^{1}H NMR spectrum of PMMA macromonomer.