

Polymerization-induced phase separation in gradient copolymers

**Mikhail Yu. Zaremski, Elena Yu. Kozhunova, Sergey S. Abramchuk,
Maria E. Glavatskaya and Alexander V. Chertovich**

Experimental

Styrene (pure grade, Reakhim, Russia) and VP (Sigma-Aldrich, Germany) were purified according to standard procedure. 4-Hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (4-hydroxy-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 4-hydroxy-TEMPO solution in cyclohexane registered under the same conditions as the spectra of the test samples served as a standard.

The kinetics of polymerization at 120°C and 130°C was studied by calorimetry on a DAK-1-1A differential automated microcalorimeter in the mode of direct registration of the heat release rate. Kinetic calculations were performed with the known value of $\Delta H_{11} = -69$, $\Delta H_{22} = -76$, and $\Delta H_{12} = -73$ kJ mol⁻¹ for styrene and VP heats of polymerization.

The IR spectra of the copolymers were measured on a Specord M-80 spectrophotometer. Samples were prepared as thin tablets in KBr. The copolymers' composition was calculated using absolute calibration from the intensity of absorption bands at 700 (Ph) and 1760 (NC=O) cm⁻¹.

Table S1 Characteristics of copolymers obtained in the styrene–VP 50:50 AIBN–4-hydroxy-TEMPO–Ac₂O system.

Polymerization time/h	Conversion (%)	M_n /kDa	M_w/M_n	F_{VP} (experimental) (%)	F_{VP} (theoretical) (%)
0.8	14	14.8	1.25	12	13
1.8	28	56.3	1.24	12	15
4.5	49	97.1	1.32	-	17.5
6	61	115	1.5	33.5	21.5
10	72	124	1.7	40	30
120	94	160	2.5	43	47

Table S2 Characteristics of copolymers used for the study of microstructure.

mol ratio S:VP in the feed	conversion (%)	M_n /kDa	M_w/M_n	$\langle F_{VP} \rangle$ (%)
60:40	95	111	1.5	37
50:50	94	160	2.5	43
40:60	94	110	2.2	57
30:70	97	61	2.2	69

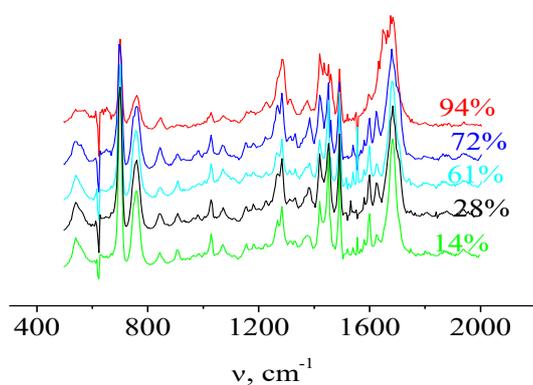


Figure S1 Changes in the IR spectra of copolymers isolated at different conversions.

MWD was analyzed using the GPC-120 PolymerLabs device. The chromatography employed under 50°C in mobile phase DMF with LiBr (0.1 %). The flow rate was 1.0 mL/min. The samples were separated with a system of 2 columns PLgel 5 μm MIXED B. The system was calibrated with monodispersed PS standards.

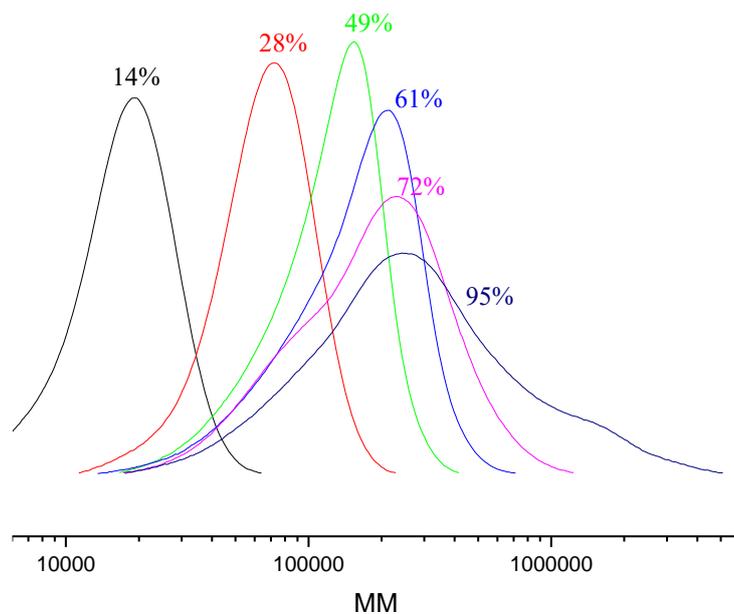


Figure S2 Typical molecular weight distributions of copolymer samples at different conversions.

Transmission Electron Microscopy (TEM) images were obtained by Leo 912 AB Omega, Karl Zeiss, microscope.

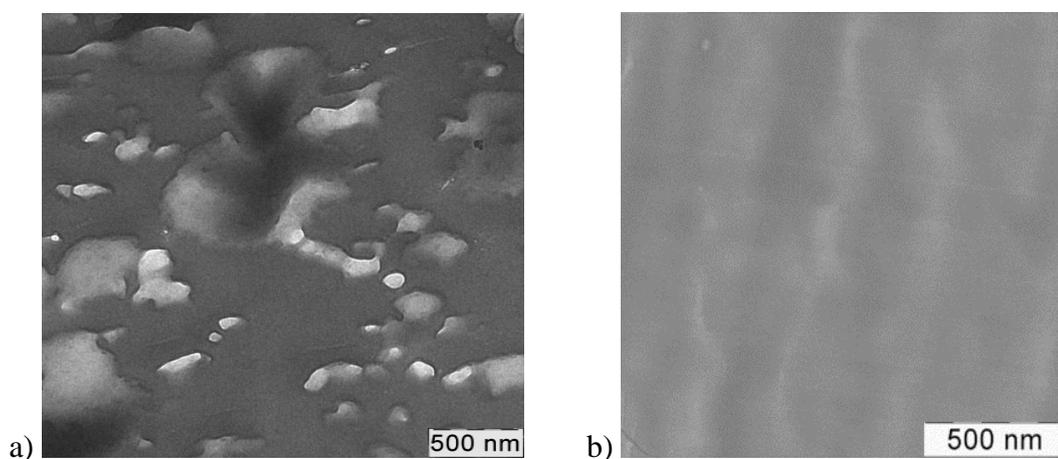


Figure S3 TEM microphotographs of ultramicrotome cuts of bulk received in the copolymerization of styrene and vinylpyrrolidone S:VP 1:1, a) statistic copolymer obtained via conventional radical polymerization (i.e., without TEMPO, conversion around 98%), b) gradient copolymer obtained via the living process with conversion ~60%.