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Copolymers of 2-hydroxy-3-(*N*-methyl-*N*-phenylamino)propyl methacrylate with methyl methacrylate and their microstructure

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Table of Contents:

1. Materials and methods.

Solvents used in the work, hexane, THF, DMF, were purified by standard procedures.[S1] Methyl methacrylate, MMA (99.5%) («Acros organics») was purified by vacuum distillation immediately before the reaction (boiling temperature 58 °C / 0.19 Torr; n_D^{20} =1.4147,). The initiator - azobisisobutyronitrile (AIBN) – was recrystallized from ethanol according to method described in.[S2]

The elemental analysis of copolymers, NMR and IR spectra were registered on the equipment of Assigned Spectral-Analytical Center of FRC Kazan Scientific Center of RAS. The elemental composition of the copolymers was determined using a vario MACRO cube organic element analyzer (Germany) .^{1}H NMR spectra were obtained on an AVANCE 600 (600 MHz) Bruker spectrometer. Chemical shifts (δ in ppm) are referenced to the solvents. IR spectra of polymer films on a KBr or NaCl plate were registered on a Tensor 27 Bruker spectrometer. The molecular weight characteristics of the copolymers were determined using size exclusion chromatography. The analysis was performed on a Tosoh EcoSEC (Japan) instrument equipped with a refractive index detector using a GMHHR-L 5 μm analytical columns connected in series. The relative molecular weights of the copolymers were determined from the refractometer data using the calibration dependences for PS standards. The obtained data were processed using the EcoSEC-WorkStation software. Stabilized THF was used as eluent. Elution rate 1 mL/min, T= 35 °C. The glass transition temperature and thermal stability of the copolymers were determined on a NETZCH STA 449 F3 simultaneous thermal analysis instrument (Jupiter, Germany); sample heating rate 10 °C/min.

2. Synthesis of Monomer and Copolymers.

2-Hydroxy-3-(*N*-methyl-*N*-phenylamino)propyl methacrylate (α-AMA, **3**) was obtained according to the procedure described in [S2]. Then α-AMA was isolated from the reaction mixture by column chromatography using chloroform/ethyl acetate eluent in a ratio of 4:1. Yield 67 %. ^{1}H NMR (600 MHz, Acetone-d_6) δ 7.17 (t, J = 7.8 Hz, 2H), 6.76 (d, J = 8.3 Hz, 2H), 6.63 (t, J = 7.2 Hz, 1H), 6.15 (s, 1H), 5.65 (s, 1H), 4.28 (s, 1H), 4.23 (dd, J = 10.6, 4.0 Hz, 1H), 4.21 – 4.17 (m, 2H), 4.15 (dd, J = 10.6, 5.4 Hz, 1H), 3.56 (dd, J = 15.0, 5.1 Hz, 1H), 3.40 (dd, J = 15.0, 6.9 Hz, 1H), 3.01 (s, 3H), 1.95 (s, 3H). IR (ν_{max}, cm^{-1}, KBr): 3462 (OH), 2928, 2823 (CH_3-O + CH_2), 2954 (CH), 2928 (CH), 2844(CH), 1719 (C=O), 3096, 1637 (–C=C–), 1600,1507, 750,694 (Ph), 1241,1170 (–COC–).

General procedure for 6 synthesis. The copolymerization reaction of MMA (**5**) and α-AMA (**3**) at different ratios of monomers was carried out in a DMF solution in the presence of 5 wt % AIBN relative to the weight of the monomers, the monomer concentration [M_1+M_2] in the DMF solution was 0.7 mol/L. Monomers, an initiator, and a solvent were loaded into a polymerization ampoule, the ampoule was degassed (1.33 Pa) by threefold freeze-thaw cycle of the reaction mixture, after which the ampoule was sealed. Copolymerization was carried out at a temperature of 70°C for 2.5 hours; then the copolymer was isolated by precipitation into water, then purified by three times reprecipitation from THF into hexane, filtered and dried in a vacuum oven, first at room temperature, then at 60 °C to constant weight.

6a: 5:**3**= 95:5 (mol%), **5** (0.442 g, 4.419 mmol), **3** (0.058 g, 0.234 mmol), AIBN (0.025 g), DMF (6.12 mL). Yield 0.238 g (47.7%). ЯМР ^{1}H (600 МГц, ацетон-d_6), δ, м.д.: 7.25 (s, 2H, Ar), 6.84 (s, 2H, Ar), 6.71 (s, 1H, Ar), 4.23 (d, H, OH-), 4.21 (1H, -O-CH_2-CH-), 4.18 (1H, N-CH_2-CH-), 4.14 (1H, -O-CH_2-CH-), 3.64 (OCH_3 of PMMA) 3.59 (1H, N-CH_2-), 3.46 (1H, N-CH_2-), 3.09 (s, 3H, N-CH_3), 1.96 (s, 3H, CH_3-C-). IR (ν_{max}, cm^{-1}, NaCl): 3600-3200 (OH), 2928, 2823 (CH_3 + CH_2), 2954 (CH), 2928 (CH), 2844(CH), 1731 (C=O), 1601,1508, 695 (Ph), 1241,1170 (–COC–). Found (%): C 60.84, H 8.34, N 0.75. Calc. (%): C 60.83 , H 8.00, N 0.65.

6b: 5:**3**= 90:10 (mol%), **5** (0.391 g, 3.912 mmol), **3** (0.109 g, 0.437 mmol), AIBN (0.025 g), DMF (5.69 mL). Yield 0.258 g (51.7 %). ЯМР ^{1}H (600 МГц, ацетон-d_6), δ, м.д.): 7.24 (s, 2H, Ar), 6.83 (s, 2H, Ar), 6.70 (s, 1H, Ar), 4.21 (1H, -O-CH_2-CH-), 4.09 (1H, N-CH_2-CH-,), 4.00 (1H, -O-CH_2-CH-), 3.62 (OCH_3 of PMMA) 3.58 (1H, N-CH_2-), 3.45 (1H, N-CH_2-), 3.09 (s, 3H, N-CH_3), 1.95 (s, 3H, CH_3-C-). IR (ν_{max}, cm^{-1}, NaCl): 3600-3200 (OH), 2928, 2823 (CH_3 + CH_2), 2954 (CH), 2928 (CH), 2844(CH), 1732 (C=O), 1601,1508, 695 (Ph), 1241,1170 (–COC–). Found (%):61.36, H 8.28, N 1.35. Calc. (%):C 61.60, H 7.97, N 1.12.

6c: 5:**3**= 80:20 (mol%), **5** (0.308 g, 3.077 mmol), **3** (0.192 g, 0.772 mmol), AIBN (0.025 g), DMF (4.98 mL). Yield 0.288 g (57.7 %). ЯМР ^{1}H (600 МГц, ацетон-d_6), δ, м.д.): 7.24 (s, 2H, Ar), 6.82 (s, 2H, Ar), 6.69 (s, 1H, Ar), 4.20 (1H, -O-CH_2-CH-), 4.09 (1H, N-CH_2-CH-,), 4.00 (1H, -O-CH_2-CH-), 3.62 (OCH_3 of PMMA) 3.57 (1H, N-CH_2-), 3.42 (1H, N-CH_2-), 3.07 (s, 3H, N-CH_3), 1.96 (s, 3H, CH_3-C-). IR (ν_{max}, cm^{-1}, KBr): 3600-3200 (OH), 2928, 2823 (CH_3 + CH_2), 2954 (CH), 2928 (CH), 2844(CH), 1731 (C=O), 1601,1508, 695 (Ph), 1241,1170 (–COC–). Found (%):C 62.06, H 8.20, N 1.81 Calc. (%): C 62.85, H 7.91, N 2.16.

6d: 5:**3**= 70:30 (mol%), **5** (0.242 g, 2.415 mmol), **3** (0.258 g, 1.038 mmol), AIBN (0.025 g), DMF (4.42 mL). Yield 0.291 g (58.3 %). ЯМР ^{1}H (600 МГц, ацетон-d6), δ, м.д.): 7.22 (s, 2H, Ar), 6.81 (s, 2H, Ar), 6.69 (s, 1H, Ar), 4.18 (1H, -O-CH_2-CH-), 4.08 (1H, N-CH_2-CH-,), 3.99 (1H, -O-CH_2-CH-), 3.61 (OCH_3 of PMMA) 3.57 (1H, N-CH_2-), 3.42 (1H, N-CH_2-), 3.05 (s, 3H, N-CH_3), 1.97 (s, 3H, CH_3-C-). IR (ν_{max}, cm^{-1}, KBr): 3600-3200 (OH), 2928, 2823 (CH_3 + CH_2), 2954 (CH), 2928 (CH), 2844(CH), 1731 (C=O), 1601,1508, 694 (Ph), 1241,1170 (–COC–). Found (%): C 63.51, H 8.27, N 2.77. Calc. (%):C 63.84, H 7.86, N 2.90.

6e: 5:**3**= 50:50 (mol%), **5** (0.143 g, 1.433 mmol), **3** (0.357 g, 1.433 mmol), AIBN (0.025 g), DMF (3.58 mL). Yield 0.340 g (68.0 %). ЯМР ^{1}H (600 МГц, ацетон-d_6), δ, м.д.): 7.21 (s, 2H, Ar), 6.78 (s, 2H, Ar), 6.67 (s, H), 4.21 (1H, -O-CH_2-CH-), 4.09 (1H, N-CH_2-CH-,), 3.99 (1H, -O-CH_2-CH-), 3.61 (OCH_3 of PMMA) 3.56 (1H, N-CH_2-), 3.40 (1H, N-CH_2-), 3.02 (s, 3H, N-CH_3), 1.96 (s, 3H, CH_3-C-). IR (ν_{max}, cm^{-1}, NaCl): 3600-3200 (OH), 2928, 2823 (CH_3 + CH_2), 2954 (CH), 2928 (CH), 2844(CH), 1731 (C=O), 1600,1508, 694 (Ph), 1241,1170 (–COC–). Found (%): C 64.75, H 8.04, N 3.78. Calc. (%): C 65.35, H 7.79, N 4.00.

6f: 5:**3**= 100:0 (mol%), **5** (0.500 g, 4.99 mmol), AIBN (0.025 g), DMF (6.60 mL). Yield 0.285 g (57.1 %). IR (ν_{max}, cm^{-1}, NaCl): 2928, 2823 (CH_3 + CH_2), 2954 (CH), 2928 (CH), 2844(CH), 1731 (C=O), 1485, 1387 (CH_3), 1241,1170 (–COC–), 549 (CH_3+ C-C).

3. ^{1}H NMR and IR Spectra and Chromatograms

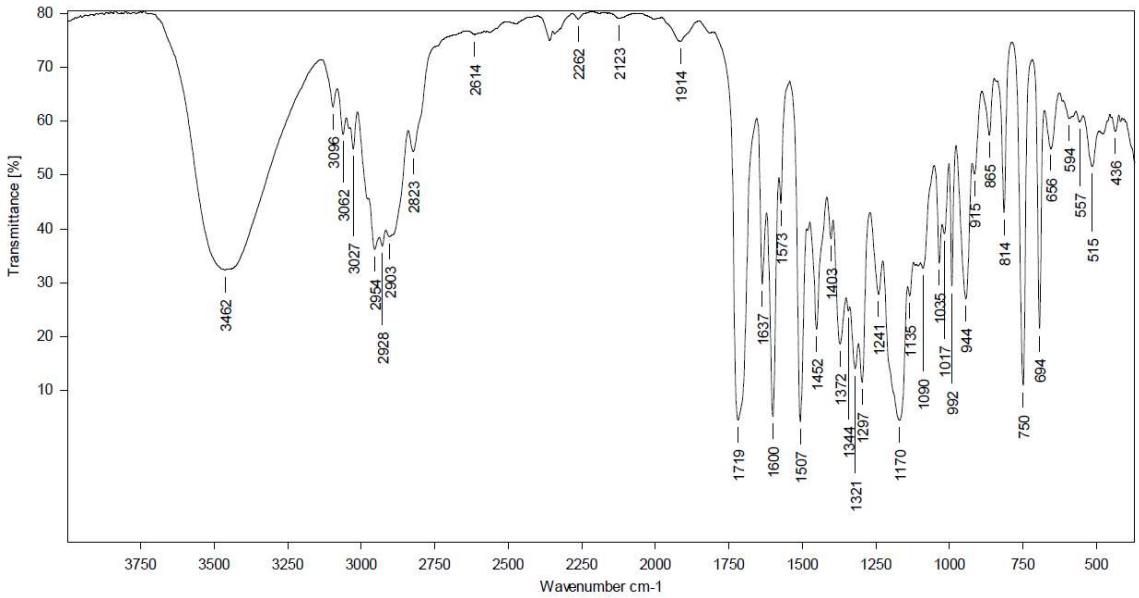

Figure S1 IR spectrum of α-AMA **3**

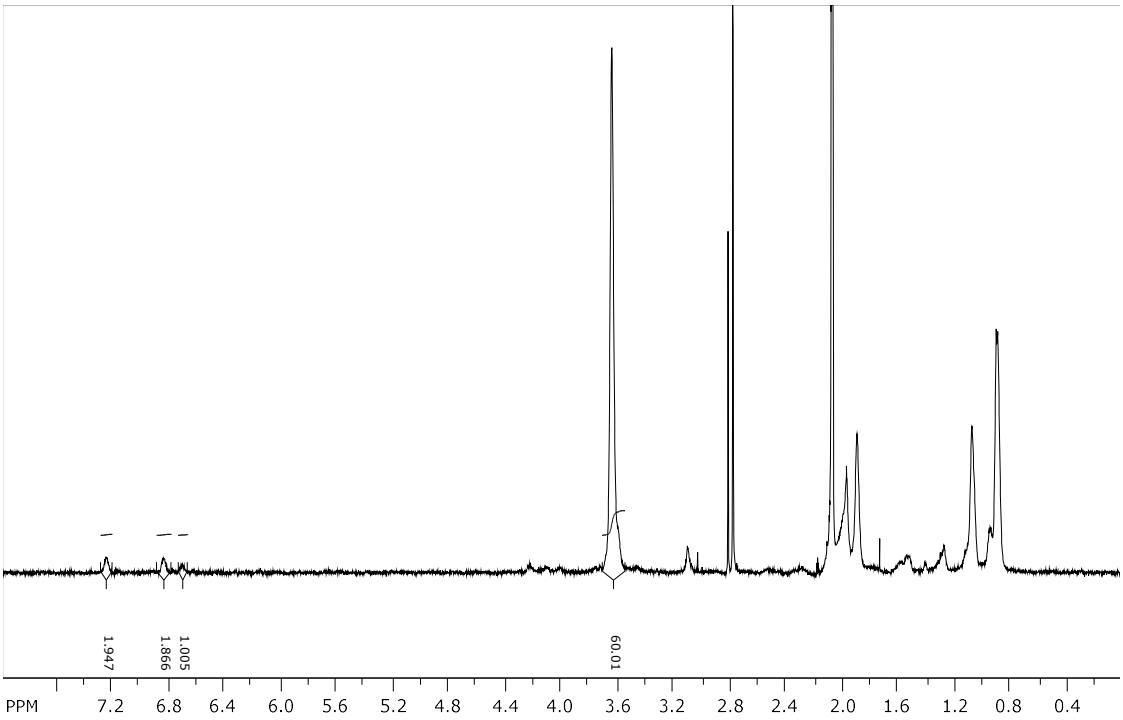

Figure S2 ^{1}H NMR of copolymer **6a**

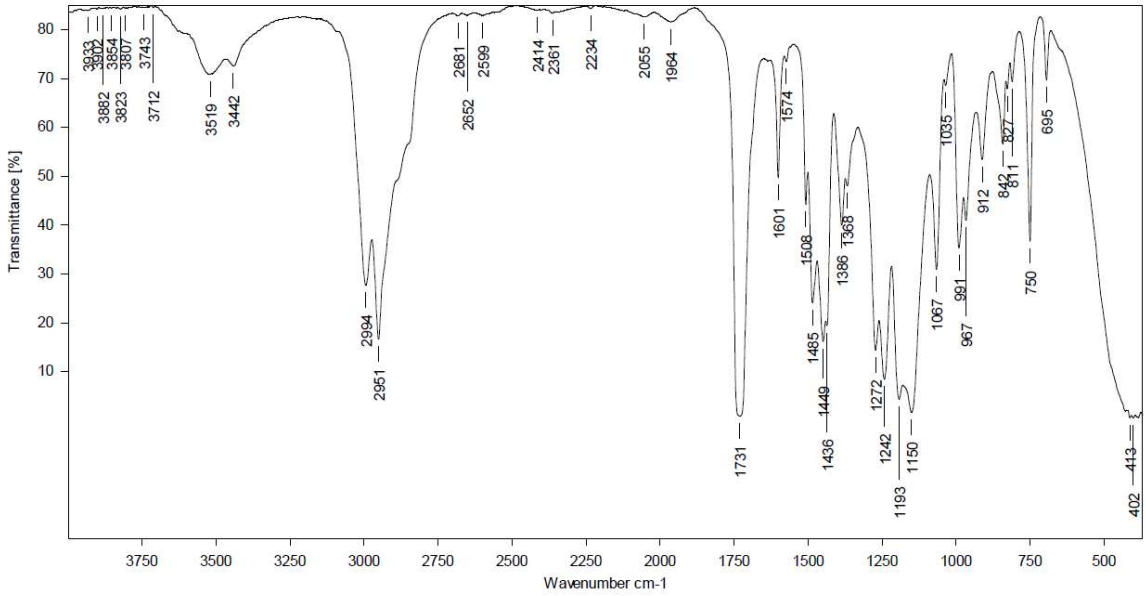

Figure S3 IR of copolymer **6a**

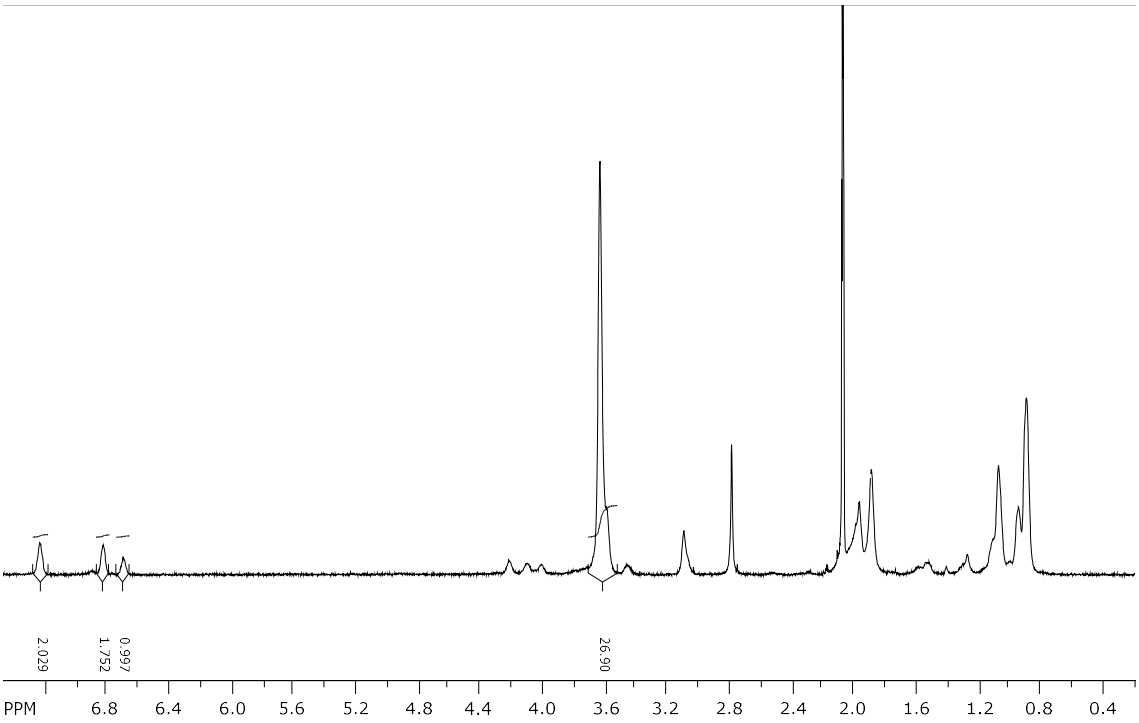

Figure S4 ^{1}H NMR of copolymer **6b**

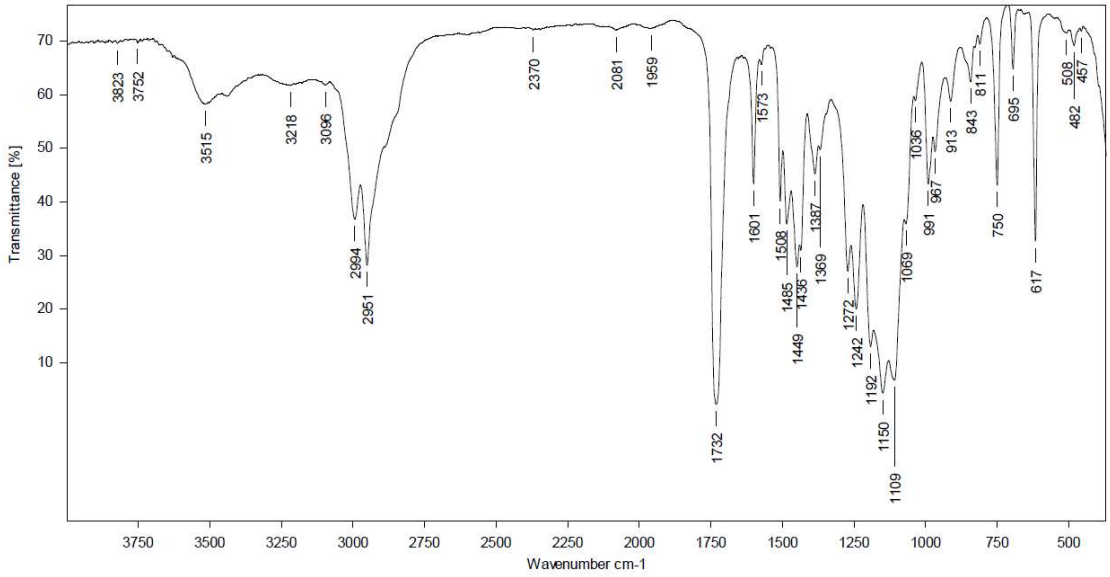

Figure S5 IR of copolymer **6b**

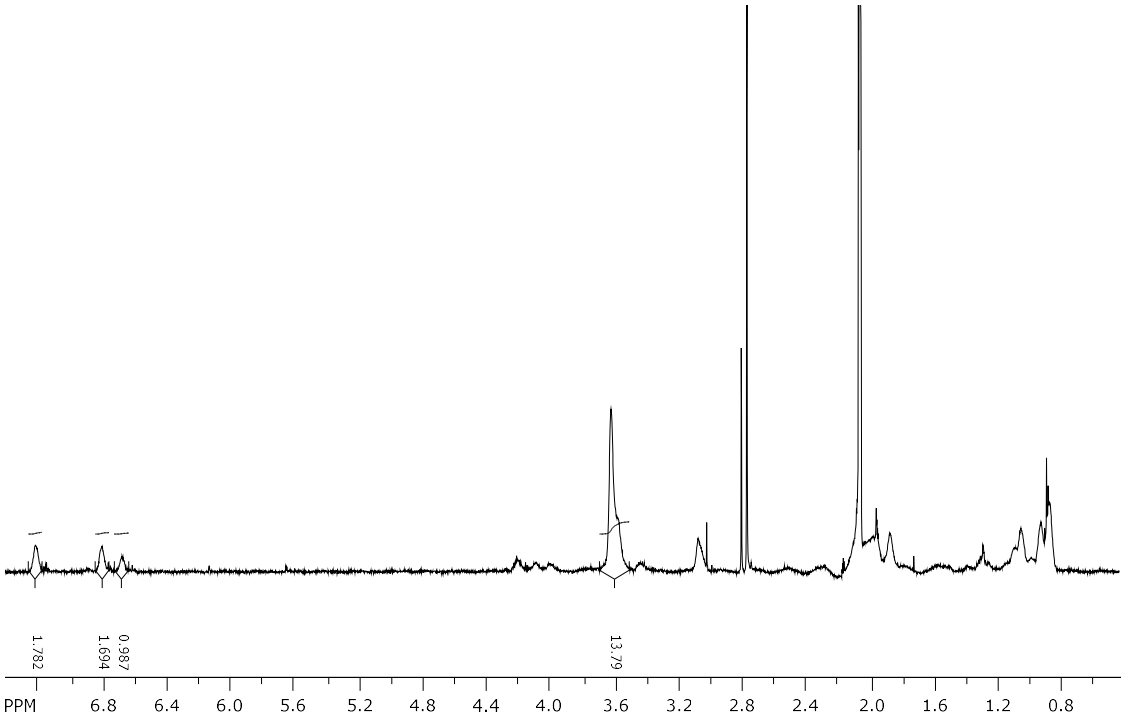

Figure S6 ^{1}H NMR spectrum **6c**

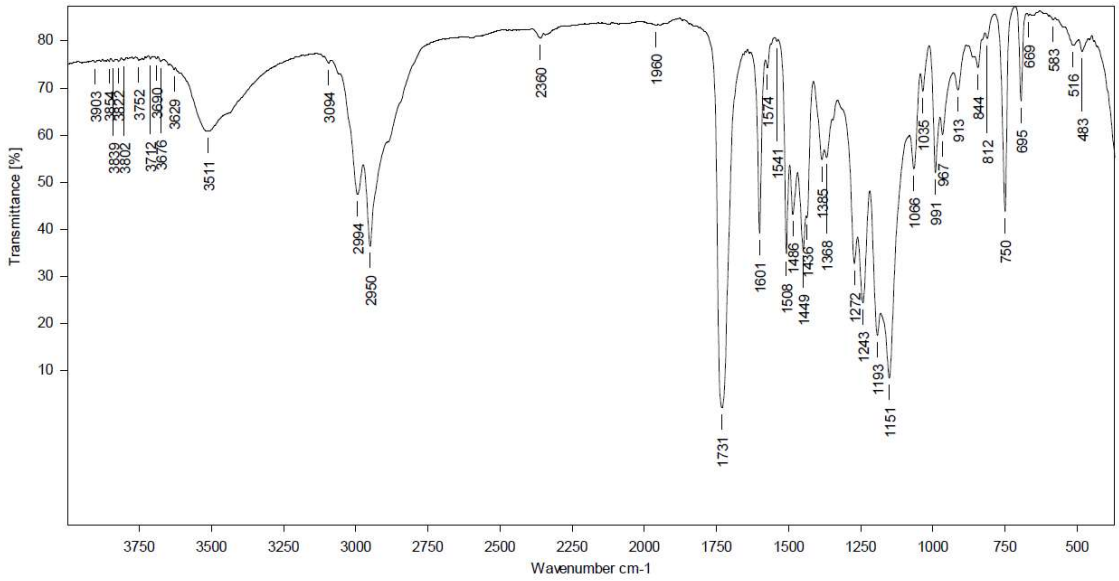

Figure S7 IR of copolymer **6c**

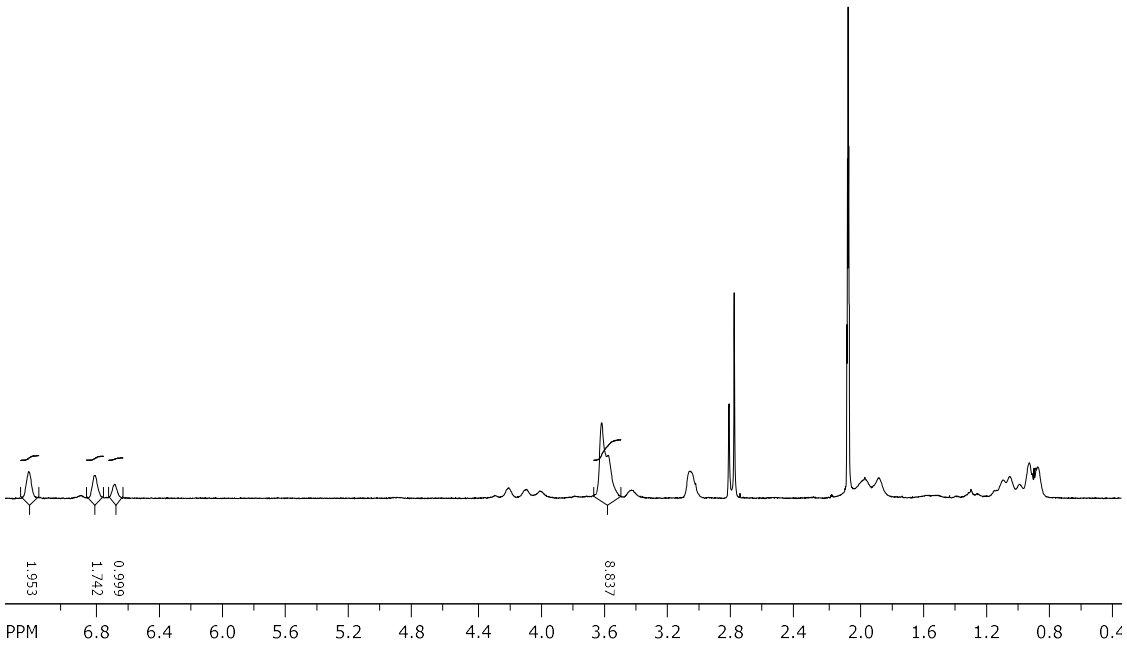

Figure S8 [1]H NMR of copolymer **6d**

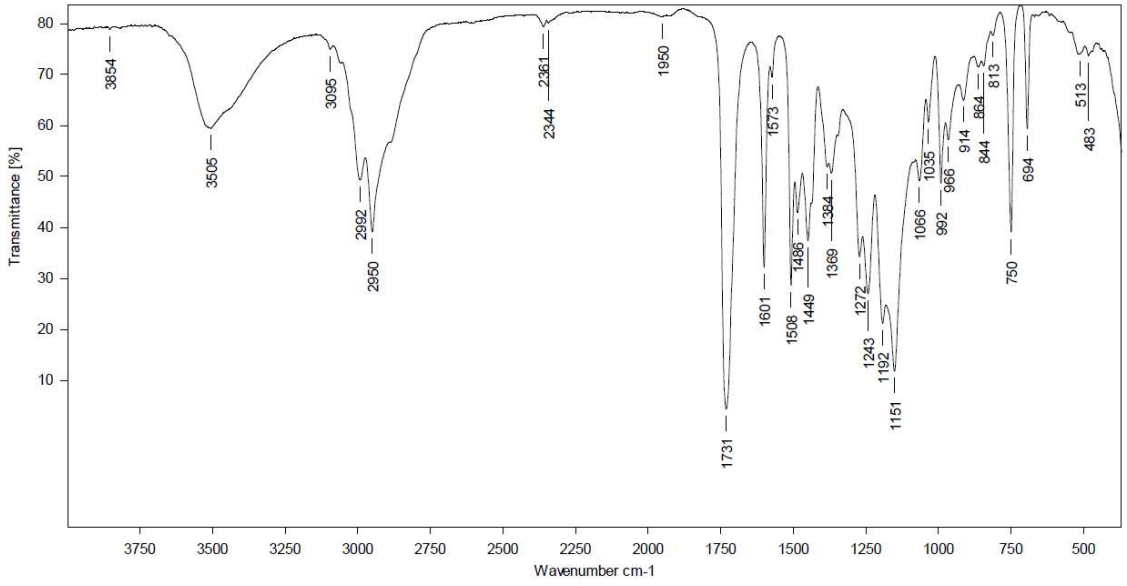

Figure S9 IR of copolymer **6d**

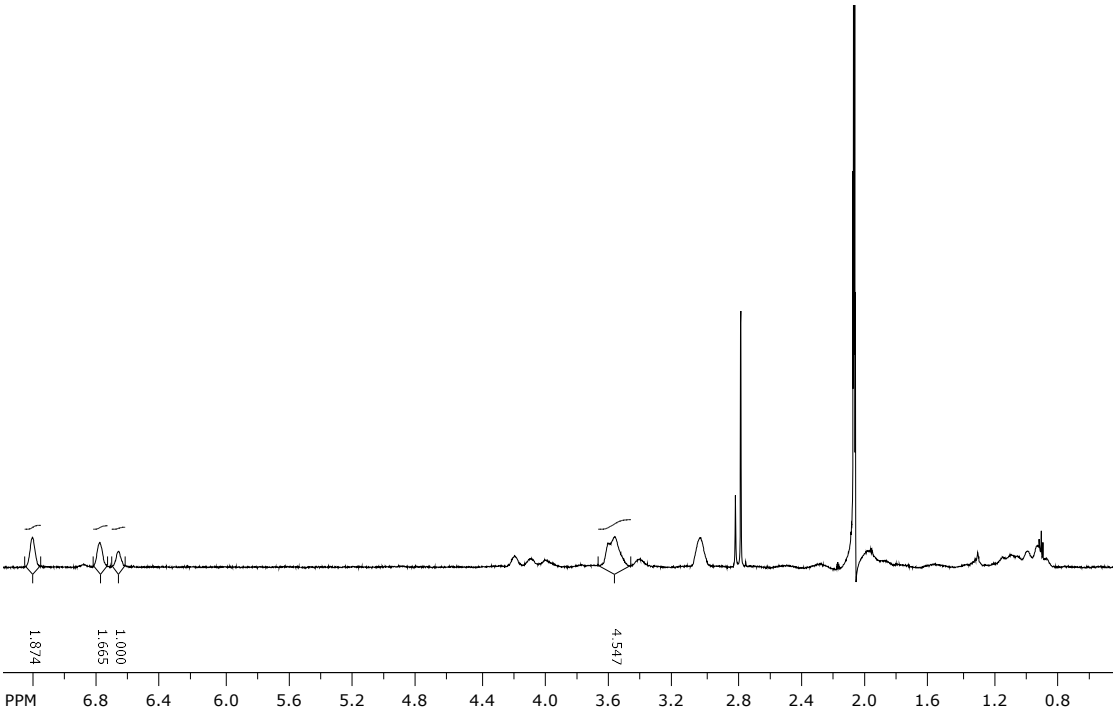

Figure S10 ^{1}H NMR of copolymer **6e**

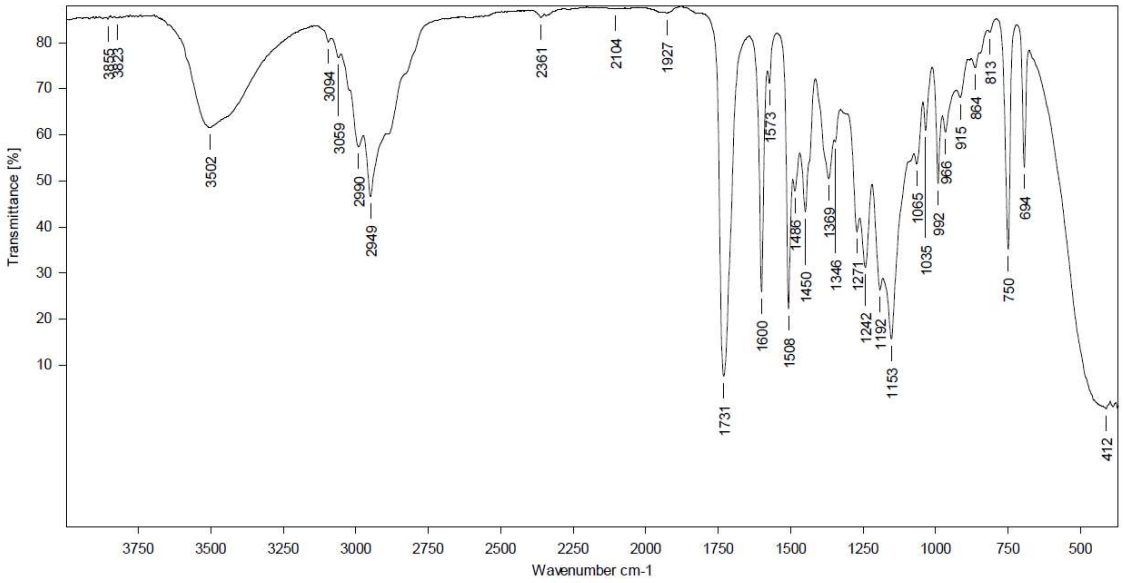

Figure S11 IR of copolymer **6e**

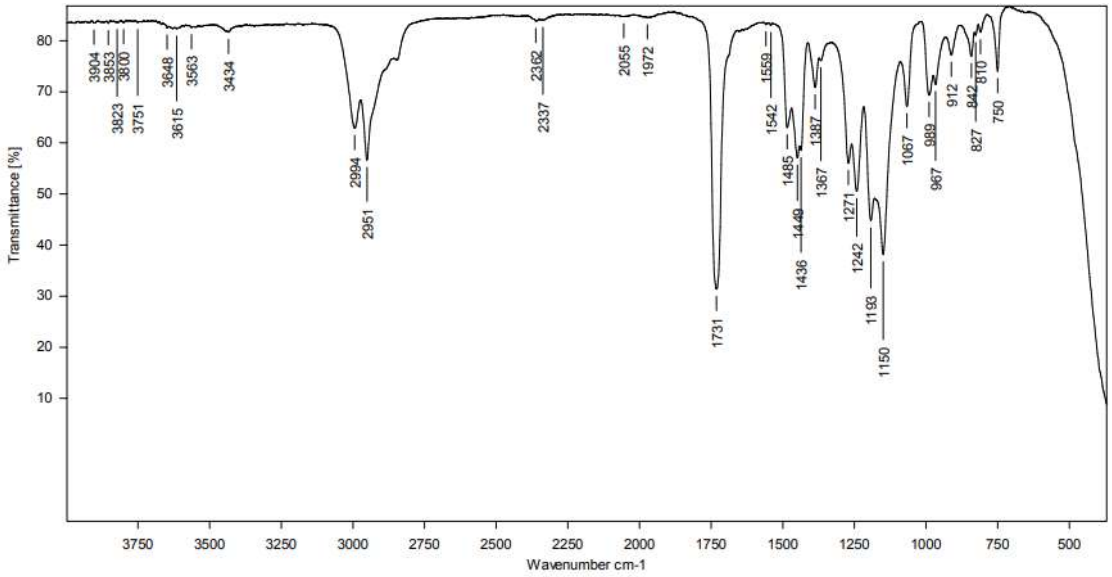

Figure S12 IR of copolymer **6f**

4. Calculation of the coefficients of relative changes in the intensity of absorption bands of hydroxyl groups and aromatic fragments in IR spectra

$\alpha = \frac{D_{3521}}{D_{2994}}$; $\alpha' = \frac{D_{1604}}{D_{2994}}$, где $D_{2994} = \log\frac{I}{I_0}$; $D_{3521} = \log\frac{I}{I_0}$; $D_{1604} = \log\frac{I}{I_0}$

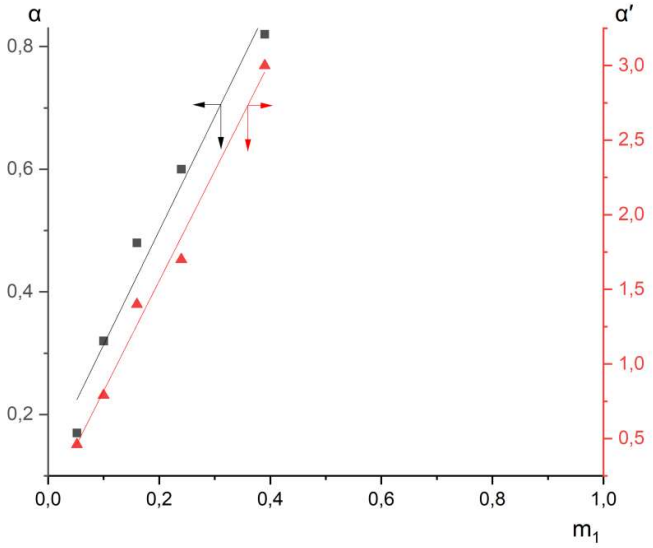

Figure S13 Dependences of α and α′ on the AMA content in copolymer (m_1)

5. Chromatograms

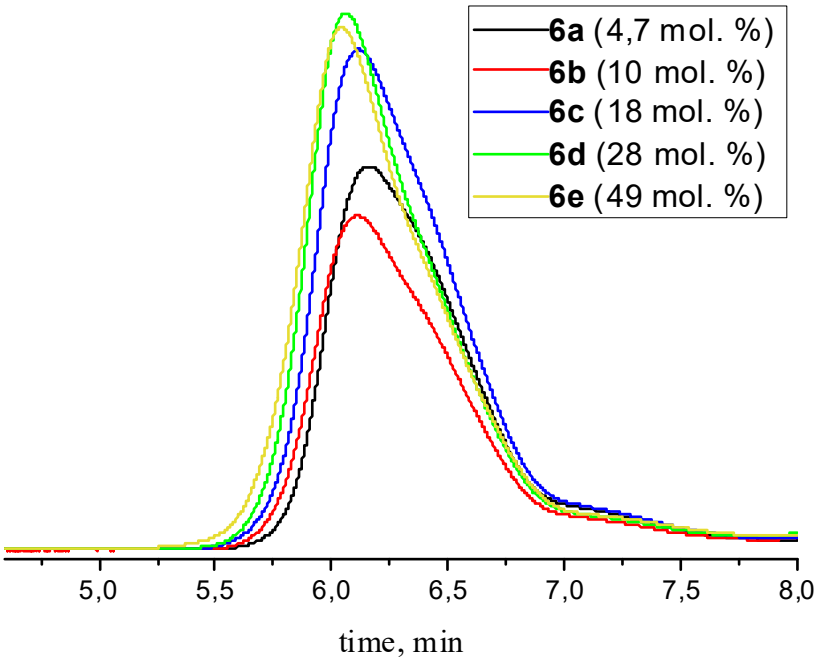

Figure S14 Chromatograms of MMA-AMA copolymers

6. Data on the compositions of copolymers and their microstructure

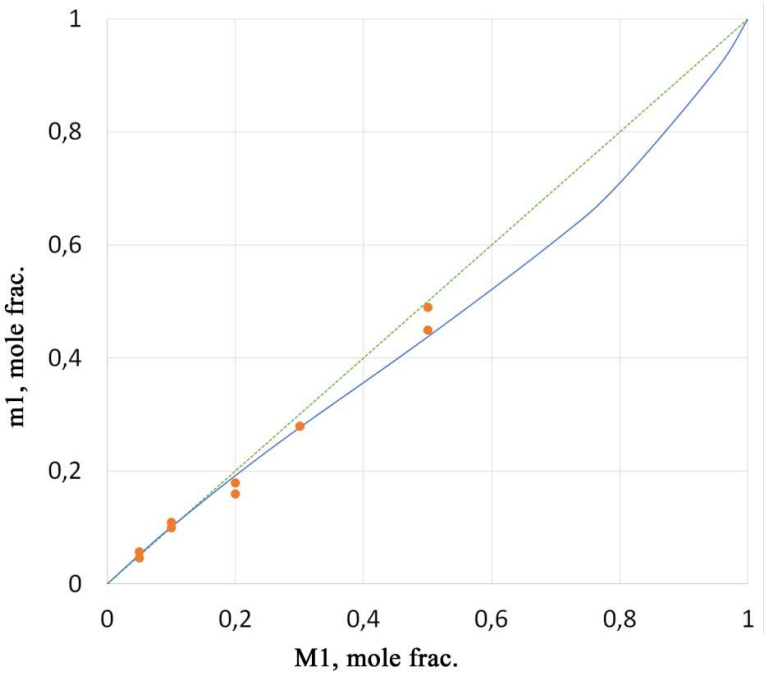

Figure S15 Theoretical dependence of the copolymers composition on the content of the initial monomer mixture at copolymerization of **6** (M_1) with **3** calculated from the copolymerization constants (blue curve). Orange dots match the experimental data

The Harwood parameter, $\underline{R}$, the probability of formation of various types of bonds, P, and the average lengths $\overline{L}_{M_1}$ and L_{M_2} of blocks of identical units were calculated using data on the composition of copolymers and the corresponding copolymerization constants r_1 and r_2 for different compositions of the monomer mixture (Table S1) according to the equations:[S3]

$$R = \frac{200}{2+r_1([M_1]/[M_2])+r_2([M_2]/[M_1])},$$

here M_1 and M_2 are **6** and **3** monomers molar concentrations in the initial mixture.

$$P_{11} = \frac{m_1 - R/2}{m_1}; P_{12} = \frac{R}{2m_1}; P_{21} = \frac{R}{2m_2}; P_{22} = \frac{m_2 - R/2}{m_2};$$

$$\overline{L}_{M_1} = \frac{m_1}{R/2}; \overline{L}_{M_2} = \frac{m_2}{R/2},$$

where m_1 and m_2 are monomers molar concentrations in a copolymer.

Table S1 Harwood parameter (R), the probability of formation of different types of bonds (P) and the average block length in copolymers ($\overline{L}_M$).

M_1, % mol	m_1, % mol	R	Probability of formation of types of bonds				Average block length	
			P_{11}	P_{12}	P_{21}	P_{22}	$\overline{L}_{M_1}$	$\overline{L}_{M_2}$
5	4.7	10.01	0.00	1.00	0.05	0.95	0.93	18.86
10	10.0	19.00	0.04	0.96	0.11	0.89	1.05	9.42
20	18.0	34.09	0.05	0.95	0.21	0.79	1.06	4.81
30	28.0	45.48	0.19	0.81	0.32	0.68	1.23	3.17
50	49.0	58.15	0.41	0.59	0.57	0.43	1.68	1.75

References

S1. A. J. Gordon and R. A. Ford, *The Chemist's Companion: A Handbook of Practical Data, Techniques, and References*, Wiley, New York, 1973.

S2. S. V. Shulyndin, T. A. Vakhonina, G. A. Estrina, B. A. Rozenberg and M. B. Zuev, *Polym. Sci., Ser. A*, 2007, **49**, 782 (*Vysokomol. Soedin., Ser. A*, 2007, **49**, 1181).

S3. H. J. Harwood and W. M. Ritchey, *J. Polym. Sci., Part B: Polym. Phys.*, 1964, **2**, 601.