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Concentration dependence of quadratic nonlinear-optical characteristics of azo-functionalized methacrylic copolymers

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1. Materials and methods

The solvents used in the work, including hexane, THF, DMF and cyclohexanone, were purified using standard procedures.[S1] 4-Nitrobenzenediazonium tetrafluoroborate was prepared using a published method,[S2] and sodium acetate was used without prior purification.

Elemental analysis of the copolymers, as well as recording of NMR and IR spectra, were carried out using the equipment of the Assigned Spectral-Analytical Center of the 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 recorded on Bruker AVANCE-600 (600 MHz) and Bruker AVANCE 400 (400 MHz) spectrometers. Chemical shifts (δ, in ppm) are given relative to solvents. IR spectra of polymer films on KBr or NaCl plates were recorded on a Bruker Tensor 27 spectrometer. Molecular weight characteristics of the copolymers were determined by size exclusion chromatography (SEC). The analysis was carried out on a Tosoh EcoSEC instrument (Japan), equipped with a refractometric detector, using 5 μm GMHHR-L analytical column. The relative molecular weights of the copolymers were determined from refractometry data using calibration curves for polystyrene standards. The obtained data were processed using the EcoSEC-WorkStation software. Stabilized THF was used as the eluent. The elution rate was 1 ml min^{-1} at T = 35 °C. Ultraviolet-visible (UV-VIS) and electronic spectra of the chromophore-containing copolymers were recorded on an ECOVIEW UV-6100 spectrometer in THF at a concentration of about 2.5×10^{-2} g dm^{-3} using 10-mm quartz cuvettes or as films on a cover glass. The spectra were recorded at a scan rate of 480 nm min^{-1} using a spectral slit width of 1 nm. The glass transition temperature and thermal stability of the copolymers were determined using a NETZCH STA 449 F3 simultaneous thermal analysis instrument (Jupiter, Germany) at a sample heating rate of 10 °C min^{-1} in Ar.

2. Synthesis of chromophore-containing polymers

Synthesis and characteristics of polymers **1a-e** were published earlier.[S3]

General procedure for the synthesis of copolymer 2. A solution of aniline-containing copolymer **1** in THF was placed in a flat-bottomed flask equipped with a magnetic stirrer. The calculated amount of 4-nitrobenzenediazonium tetrafluoroborate was added with stirring. Equal amounts of sodium acetate were then added after 10 and 20 min. The reaction was carried out with vigorous stirring at room temperature for 8 h. After the reaction time, the polymer was purified by dissolution with THF, followed by precipitation in hexane repeated three times. The isolated polymer was dried in a vacuum oven to constant weight.

2a: **1a** (0.165 g, 1.532 mmol), 4-nitrobenzenediazonium tetrafluoroborate (0.022 g), sodium acetate (0.013 g), THF (5.25 ml). Yield 0.169 g (95.91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.33 (s, 2H, Ar), 7.94 (s, 4H, Ar), 6.92 (s, 2H, Ar), 4.27 (1H, -O-CH_2-CH-), 4.17 (1H, N-CH_2-CH-,), 4.02 (1H, -O-CH_2-CH-), 3.67 (2H, N-CH_2-), 3.60 (OMe of PMMA), 3.25 (3H, N-Me), 1.82 (3H, Me-C-). IR (NaCl, ν/cm^{-1}): 3437 (OH), 2996, 2950, 2864 (CH_2), 1731 (C=O), 1602, 1588, 1520, 1381 (–N=N–), 1339 (NO_2), 1245, 1147 (COC), 827 (Ph). Found (%): C 57.59, H 7.51, N 1.69. Calc. (%): C 60.03, H 7.62, N 2.46.

2b: **1b** (0.175 g, 1.625 mmol), 4-nitrobenzenediazonium tetrafluoroborate (0.043 g), sodium acetate (0.025 g), THF (5.58 ml). Yield 0.189 g (95.09%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.30 (s, 2H, Ar), 7.90 (s, 4H, Ar), 6.89 (s, 2H, Ar), 4.27 (1H, -O-CH_2-CH-), 4.14 (1H, N-CH_2-CH-), 4.02 (1H, -O-CH_2-CH-), 3.73 (2H, N-CH_2-), 3.58 (OMe of PMMA), 3.25 (3H, N-Me), 1.79 (3H, Me-C-). IR (KBr, ν/cm^{-1}): 3433 (OH), 2996, 2949, 2863 (CH_2), 1731 (C=O), 1601, 1589, 1519, 1383 (–N=N), 1339 (NO_2), 1247, 1149 (COC), 828 (Ph). Found (%): C 55.80, H 6.91, N 4.16. Calc. (%): C 60.07, H 7.29, N 4.29.

2c: **1c** (0.223 g, 2.066 mmol), 4-nitrobenzenediazonium tetrafluoroborate (0.084 g), sodium acetate (0.048 g), THF (7.08 ml). Yield 0.22 g (96.25%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.28 (s, 2H, Ar), 7.87 (s, 4H, Ar), 6.79 (s, 2H, Ar), 4.22 (1H, -O-CH_2-CH-), 4.13 (1H, N-CH_2-CH-), 3.97 (1H, -O-CH_2-CH-), 3.72 (2H, N-CH_2-), 3.57 (OMe of PMMA), 3.16 (3H, N-Me), 1.84 (3H, Me-C-). IR (KBr, ν/cm^{-1}): 3436 (OH), 2949 (CH_2), 2866 (CH_2), 1732 (C=O), 1602 (Ph), 1588 (Ph), 1519 (NO_2),1377 (–N=N–), 1339 (NO_2), 1243 (COC), 1137 (COC), 826 (Ph), 299 (CH_2). Found (%): C 57.66, H 6.75, N 6.28. Calc. (%): C 60.12, H 6.93, N 6.33.

2d: **1d** (0.237 g, 2.201 mmol), 4-nitrobenzenediazonium tetrafluoroborate (0.126 g), sodium acetate (0.073 g), THF (7.55 ml). Yield 0.259 g (95.16%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.24 (s, 2H, Ar), 7.84 (s, 4H, Ar), 6.76 (s, 2H, Ar), 4.22 (1H, -O-CH_2-CH-), 4.11 (1H, N-CH_2-CH-,), 3.67 (1H, -O-CH_2-CH-), 3.74 (2H, N-CH_2-), 3.58 (OMe of PMMA), 3.12 (3H, N-Me), 1.81 (3H, Me-C-). IR (NaCl, ν/cm^{-1}): 3499 (OH), 2993, 2948, 2865 (CH_2), 1731 (C=O), 1602, 1588, 1519, 1376 (–N=N–), 1339 (NO_2), 1244, 1139 (COC), 826 (Ph). Found (%): C 57.83, H 6.42, N 7.70. Calc. (%): C 60.16, H 6.61, N 8.15.

2e: **1e** (0.282 g, 2.617 mmol), 4-nitrobenzenediazonium tetrafluoroborate (0.207 g), sodium acetate (0.121 g), THF (8.97 ml). Yield 0.307 g (88.69%). ^{1}H NMR (400 MHz, C_4D_8O) δ: 8.31 (s, 2H, Ar), 7.91 (s, 4H, Ar), 6.89 (s, 2H, Ar), 4. 63 (1H, -O-CH_2-CH-), 4.15 (1H, N-CH_2-CH-), 3.73 (1H, -O-CH_2-CH-), 3,98 (2H, N-CH_2-), 3.52 (OMe of PMMA), 3.19 (3H, N-Me), 1.85 (3H, Me-C-). IR (KBr, ν/cm^{-1}): 3432 (OH), 2991, 2947, 2866 (CH_2), 1731 (C=O), 1601, 1588, 1518, 1376 (–N=N–), 1338 (NO_2), 1250, 1138 (COC), 825 (Ph). Found (%): C 57.10, H 6.00, N 9.82. Calc. (%): C 60.21, H 6.21, N 10.40.

3. ^{1}H NMR, IR and UV-VIS spectra

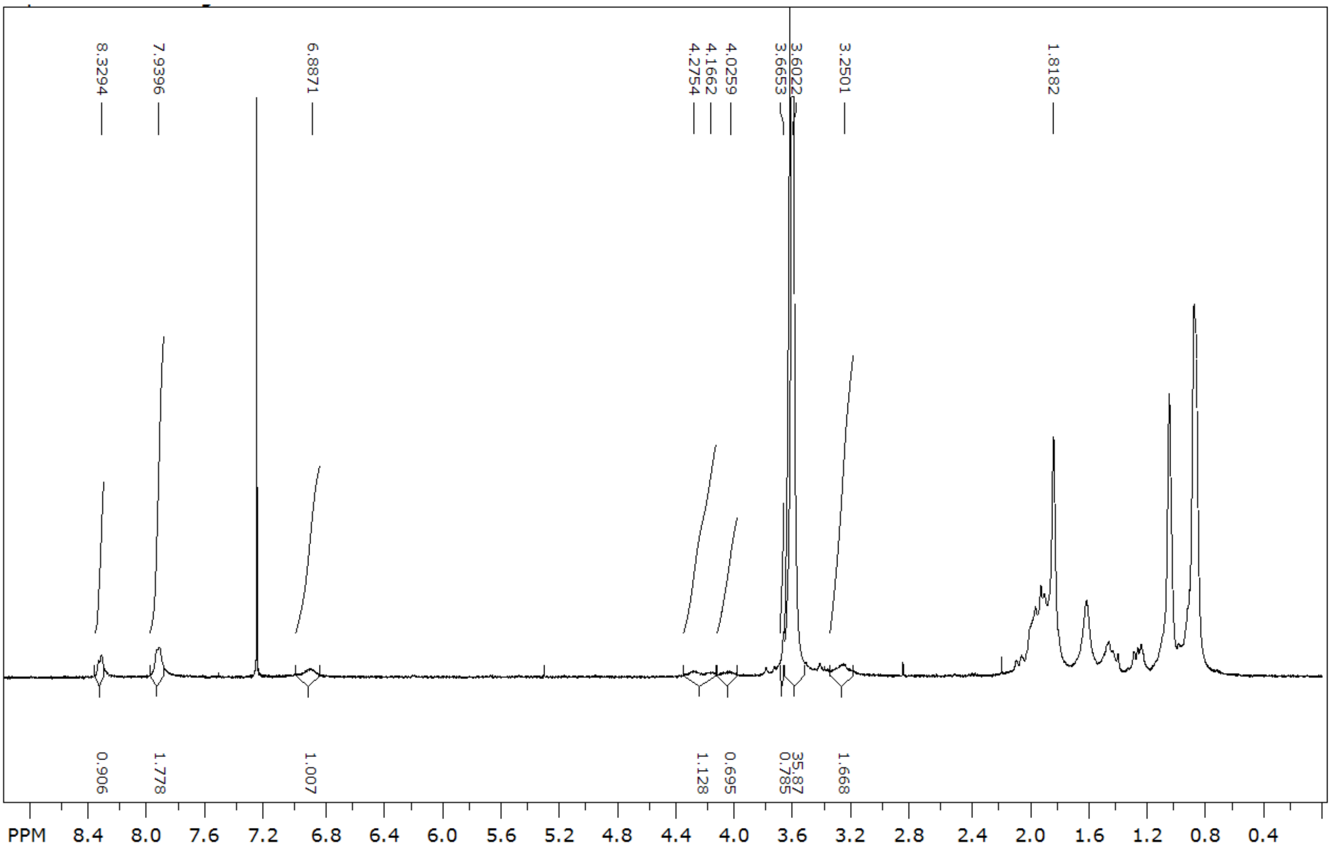

Figure S1 ^{1}H NMR of copolymer **2a.**

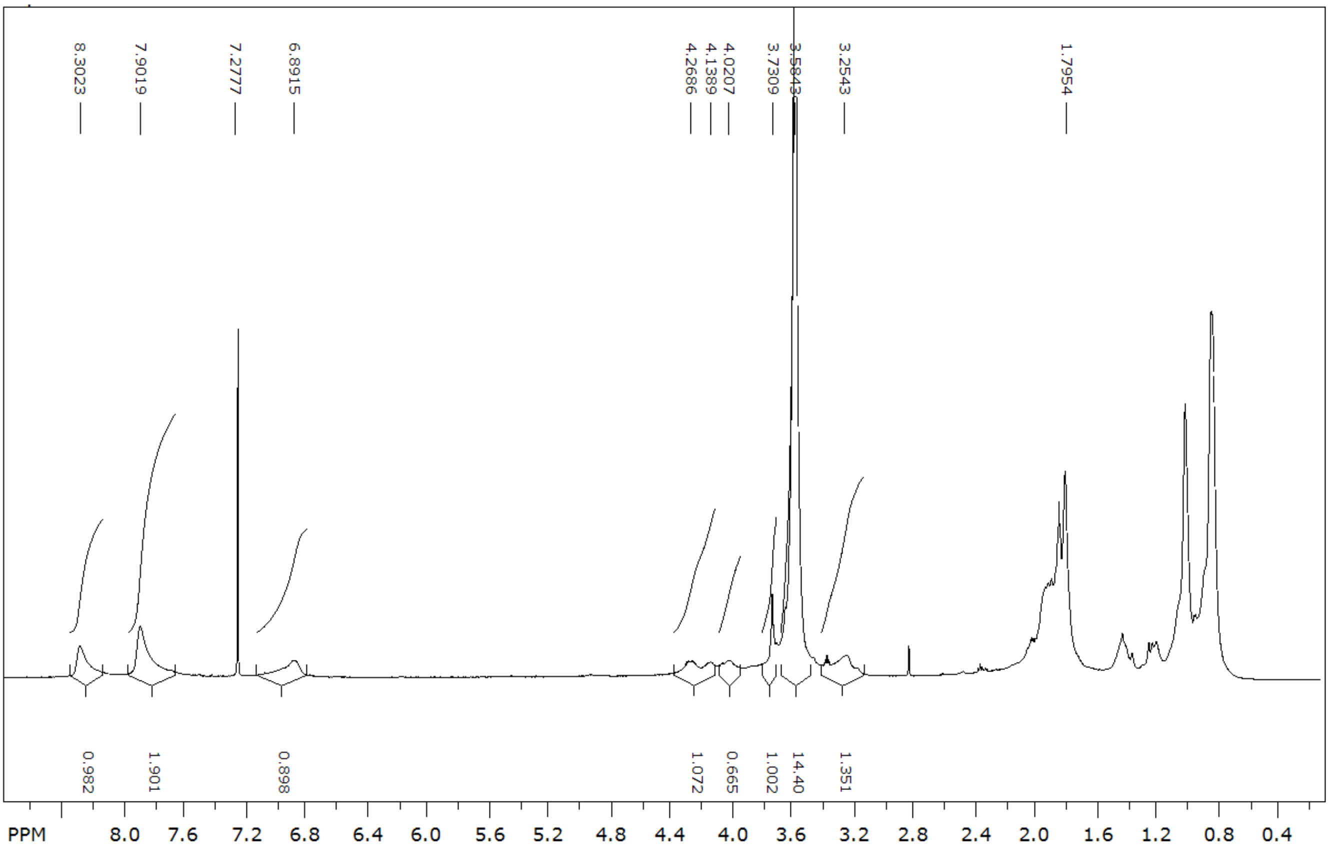

Figure S2 ^{1}H NMR of copolymer **2b.**

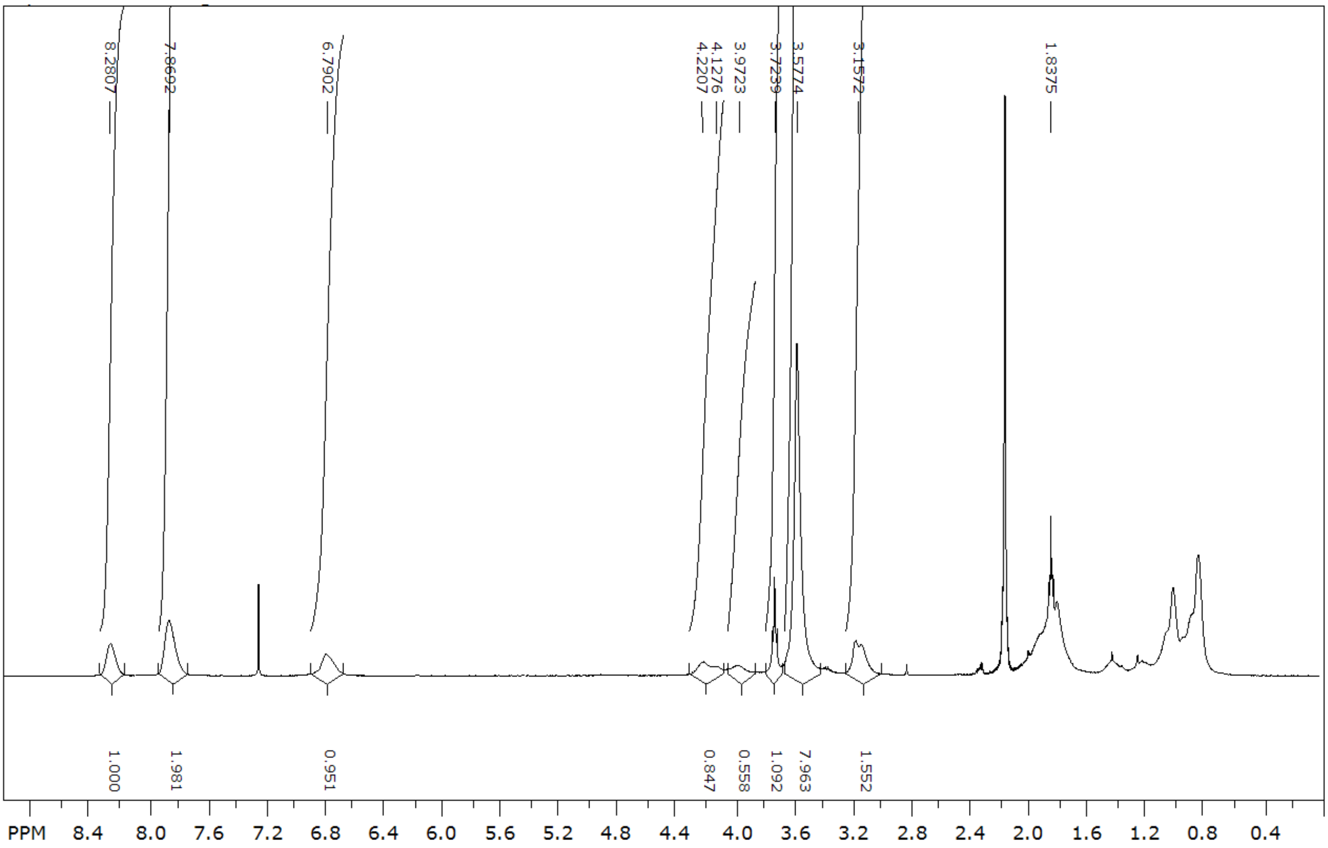

Figure S3 ^{1}H NMR of copolymer **2c**.

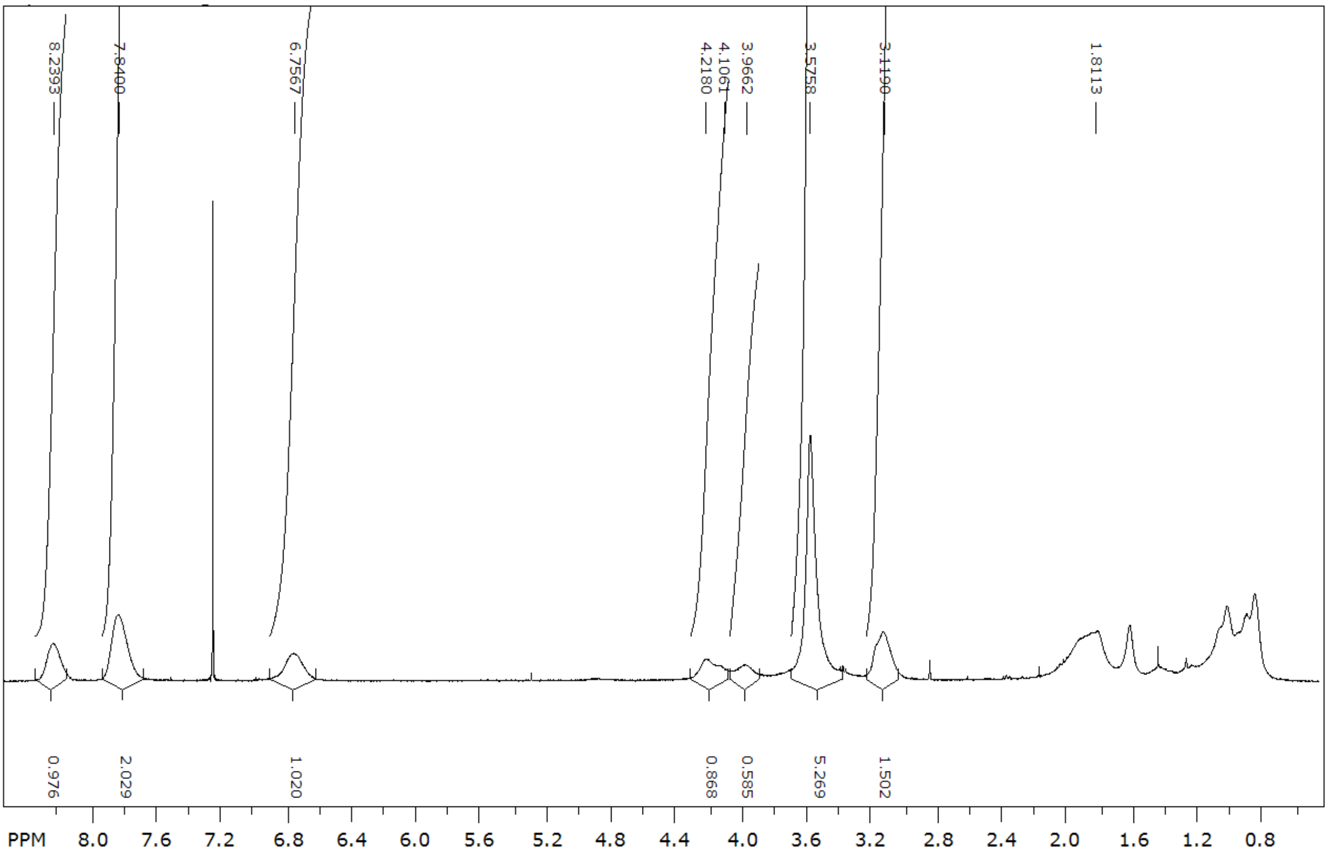

Figure S4 ^{1}H NMR of copolymer **2d**.

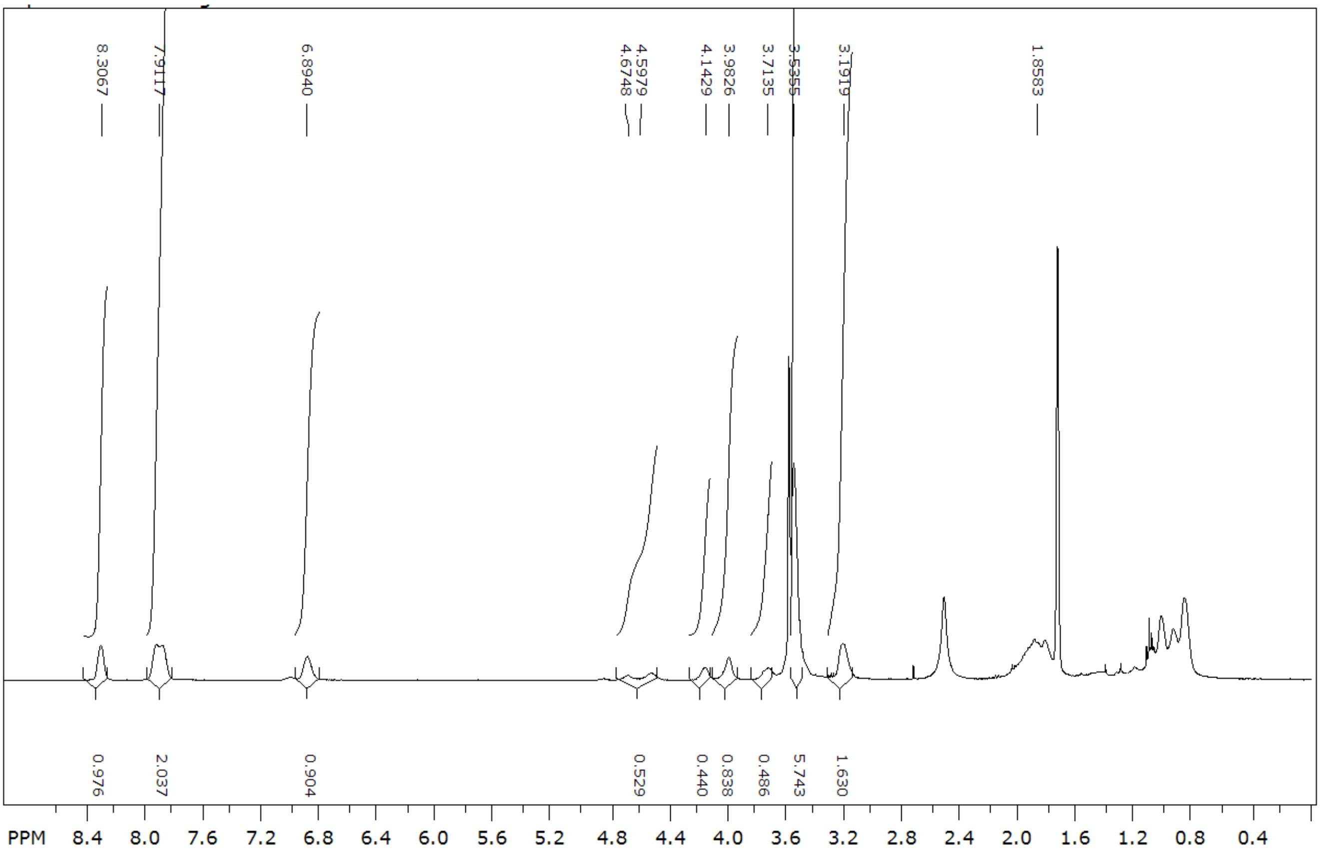

Figure S5 ^{1}H NMR of copolymer **2e**.

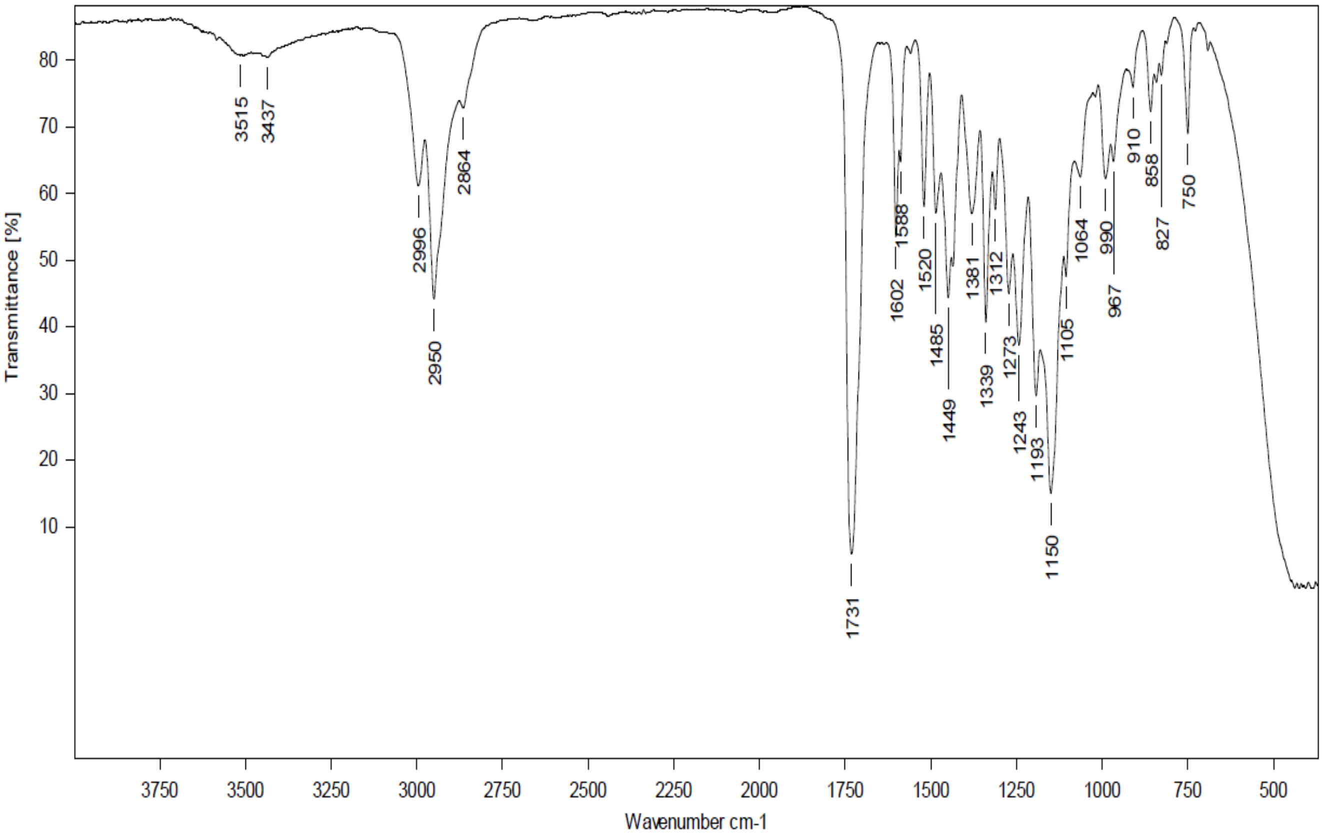

Figure S6 IR spectra of copolymer **2a**.

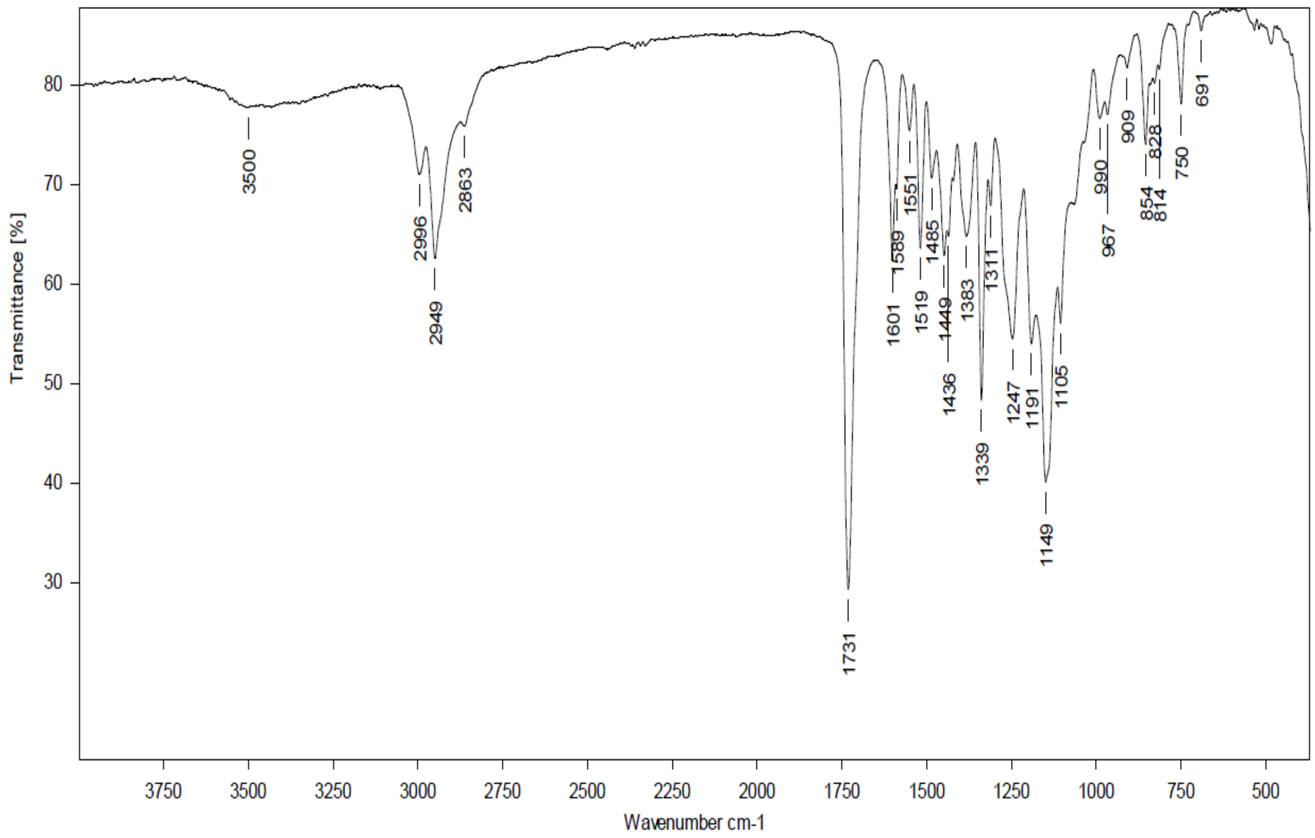

Figure S7 IR spectra of copolymer **2b**.

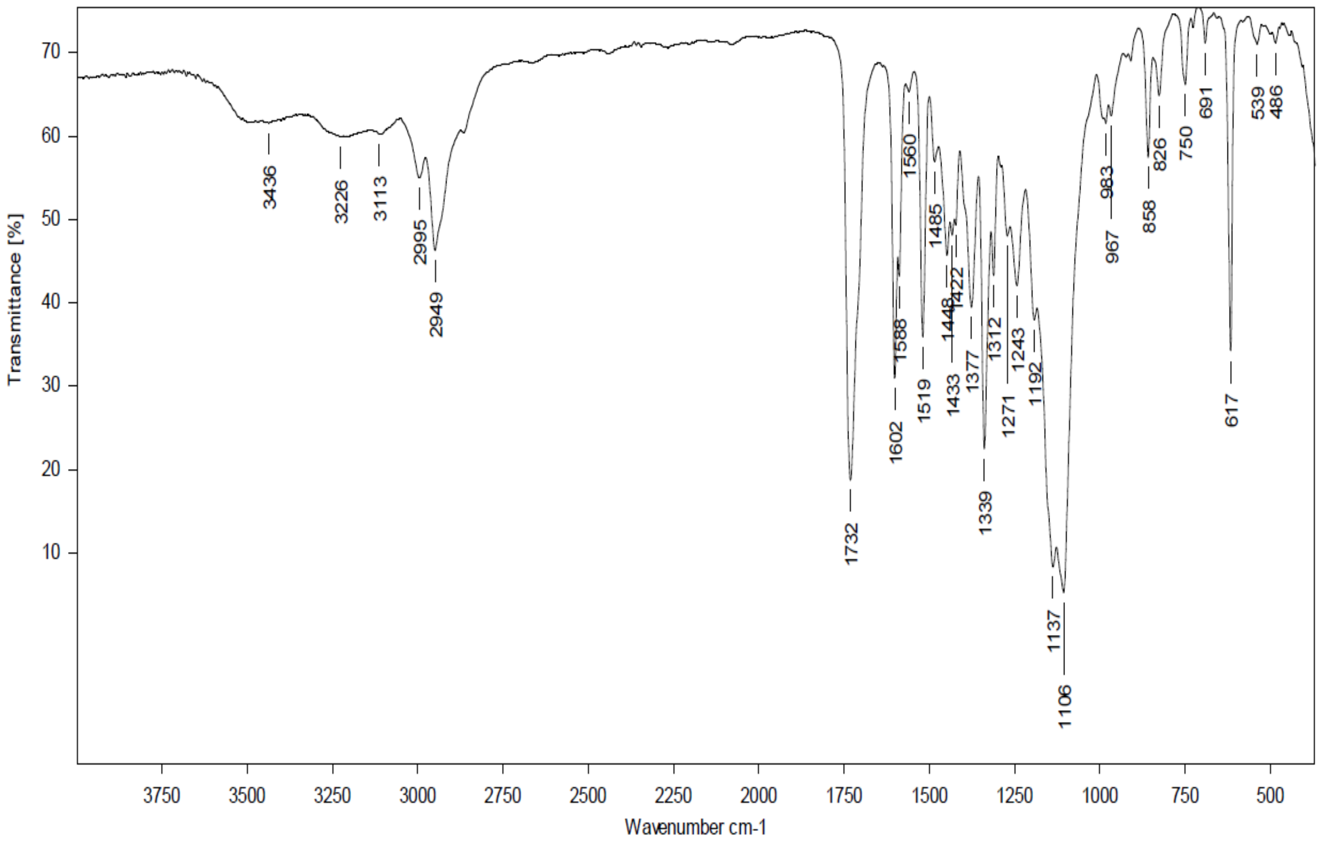

Figure S8 IR spectra of copolymer **2c**.

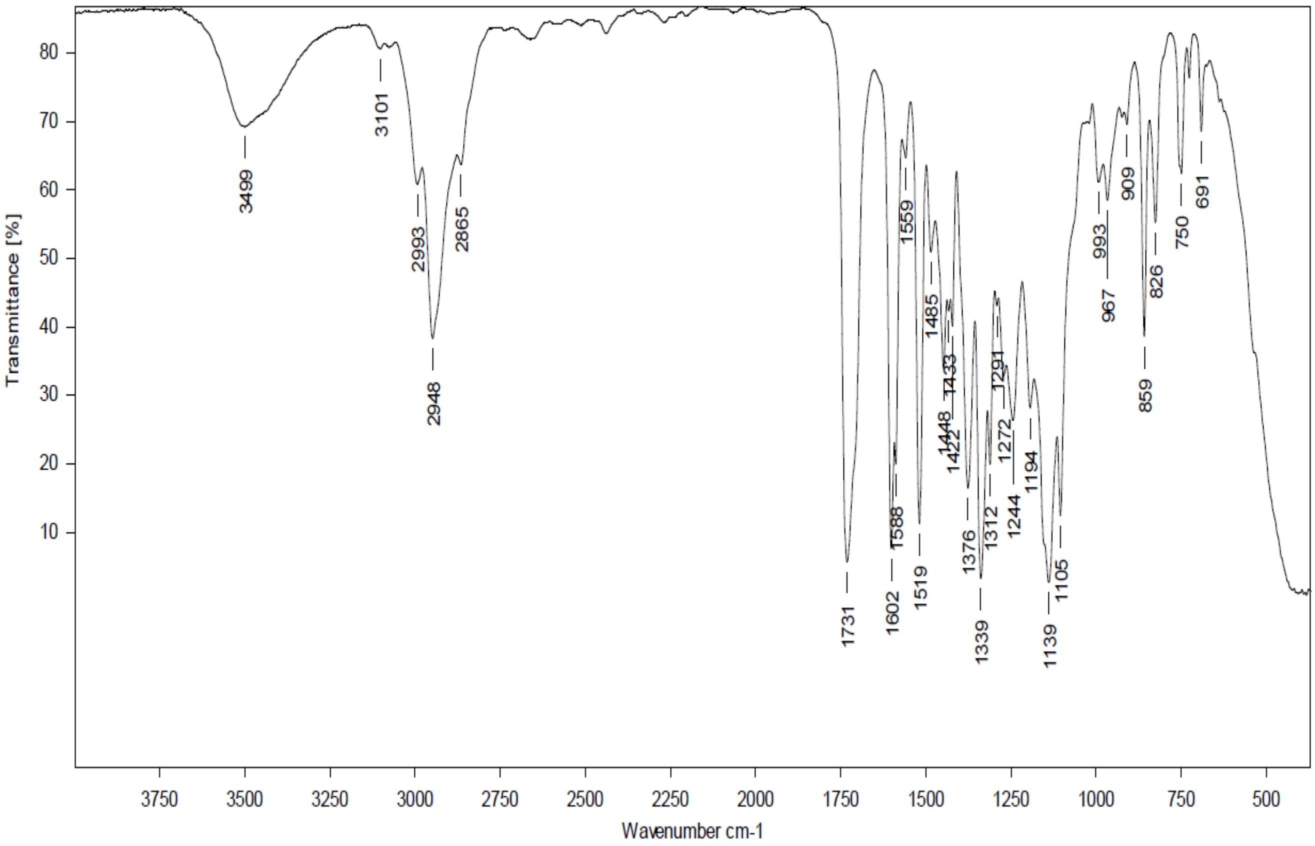

Figure S9 IR spectra of copolymer **2d**.

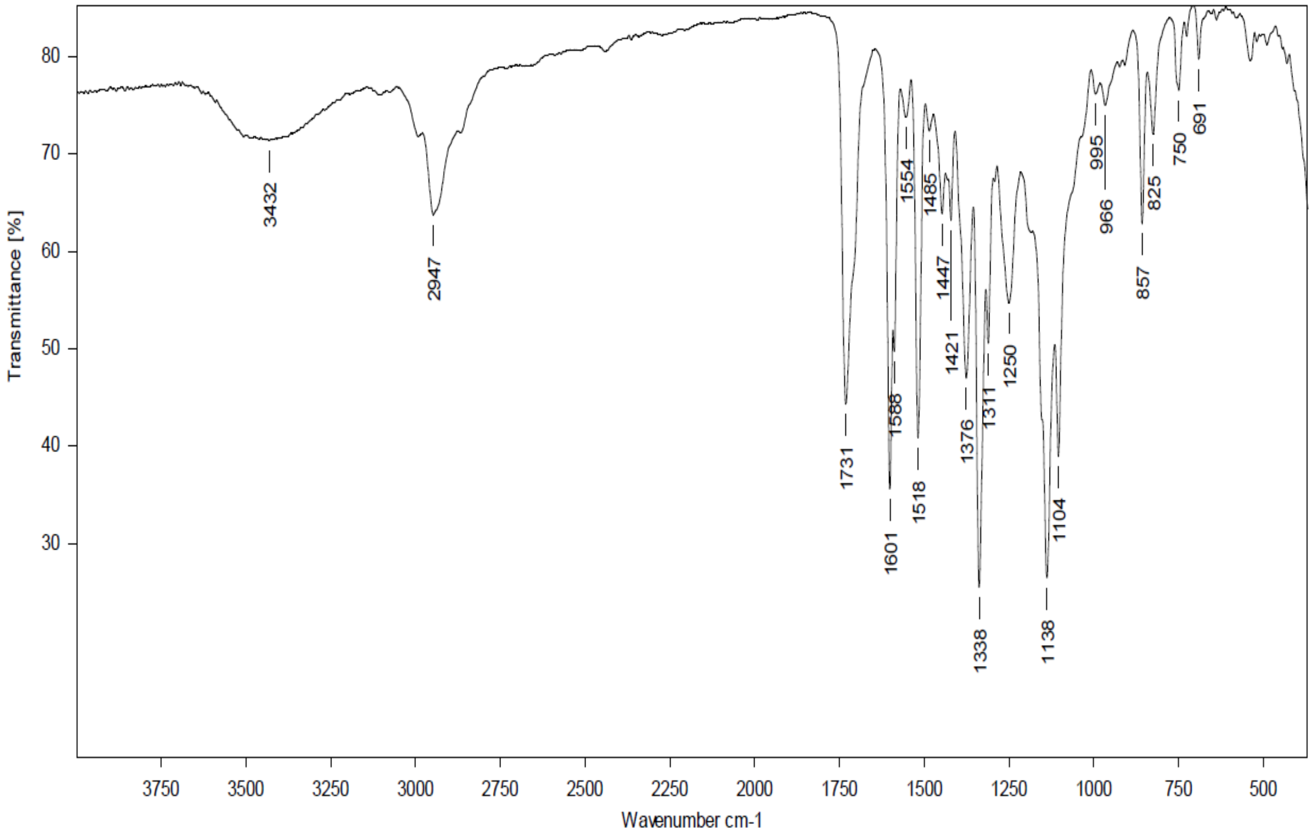

Figure S10 IR spectra of copolymer **2e**.

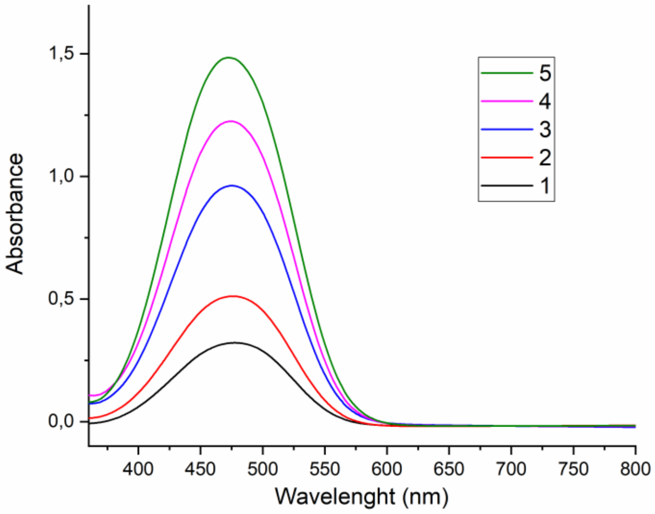

Figure S11 UV-VIS spectra of copolymers **2** with chromophore content of (1) 4.4, (2) 9.3, (3) 18, (4) 23 and (5) 39 mol%.

4. Production and poling of films

To study the quadratic nonlinear optical properties of the obtained polymers, films were made by centrifuging from a 7% polymer solution in cyclohexanone on 24×24 mm glass substrates at a centrifuge speed of 5000 rpm for 60 s. To remove residual solvent, the samples were kept in a vacuum cabinet at room temperature for 24 h, then at 60 °C for 16 h.

The thickness of the films was measured on a Bruker Dimension FastScan high-resolution scanning probe microscope (Germany). Ultra-sharp silicon probes Bruker ScanAssyst-air with a tip curvature radius of ~2 nm were used.

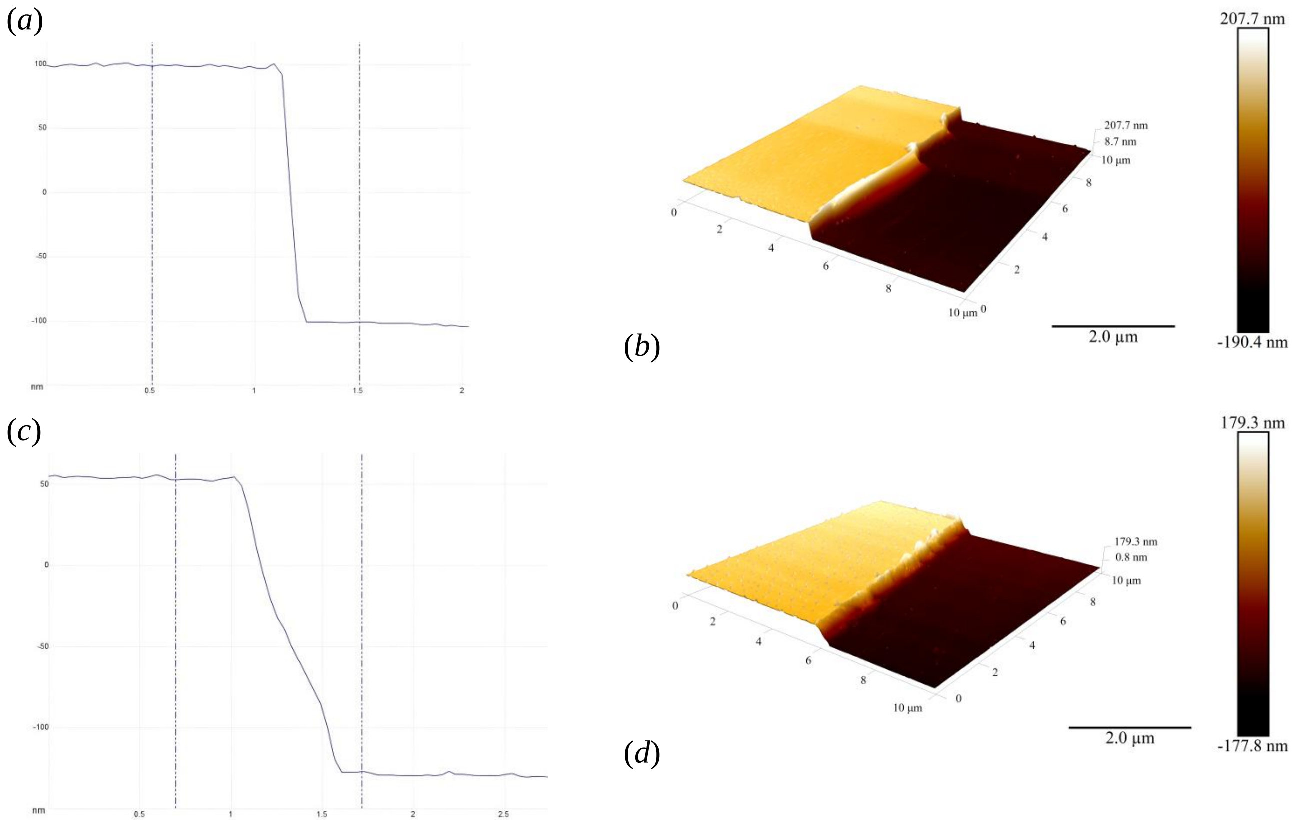

Figure S12 Profile and surface in 3D format of films of (*a*),(*b*) polymer **2a** and (*c*),(*d*) polymer **2c**.

The films were poled using a corona triode setup (positive corona) created in the Functional materials laboratory of the A.E. Arbuzov Institute of Organic Physical Chemistry. The voltage on the tungsten needle was 5.5 kV, and the voltage on the grid – the control electrode – varied within the range from 0.8 to 0.9 kV, the distance from the needle to the film surface was 1 cm. The film was heated above T_g, then the electric field was turned on, the sample was kept under these conditions for 20 min, then the film was cooled to room temperature to fix the obtained orientation of the chromophores, after cooling the film the field was turned off. Poling was carried out at a temperature of 125–135 °C. The quality of orientation was characterized by the order parameter η estimated according to the formula $\eta = 1 - A/A_0$, where A_0 and A are absorption intensities of the film before and after poling, respectively (the UV-VIS spectra for film **2c** are presented in Figure S13, as an example).

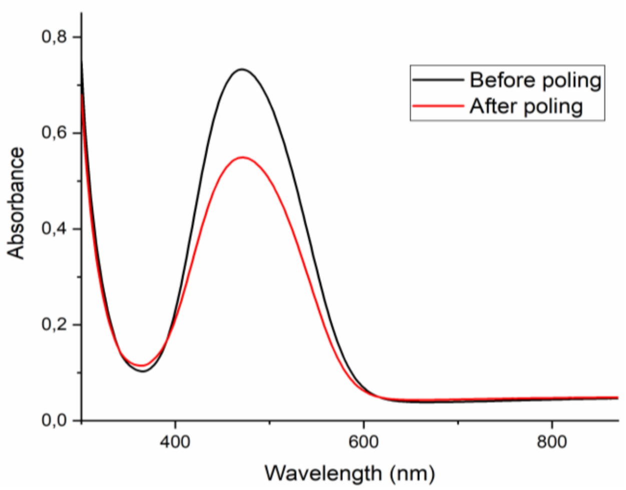

Figure S13 UV-VIS spectra of film **2c**.

5. Measurements of NLO coefficients

The measurements of NLO coefficients d_{33} were performed within two approaches.

In the framework of the first approach SHG technique was used: pulsed Nd^{3+}:YAG laser, radiation wavelength 1028 nm, pulse duration 200 fs, power density on the sample 10 kW cm^{-2}. This approach does not require the information about absorption and exact values of the complex refractive index of the samples. The NLO coefficient of the sample $d_{33,s}$ was estimated as follows:[S4] $\frac{d_{33,s}}{d_{11,q}} = \sqrt{I_s/I_q}\frac{l_{c,q}}{l_s}F$, where $d_{11,q}$ is known quartz nonlinear coefficient (0.45 pm V^{-1}), I_s and I_q are SHG intensities produced by the sample and quartz, respectively, and measured in the same configuration, $l_{c,q}$ is quartz coherence length related to 1028 nm (calculated as 13 μm), l_s is sample thickness, F is correction factor (1.2 when $l_{c,q} \gg l_s$).

In the second approach, the d_{33} coefficients are measured with the Maker fringes technique, which takes into account the refraction and absorption of radiation. The refractive indices were directly measured at several wavelengths by Metricon prism coupler (model 2010/M) with error ± 0.001. Calculations of dispersion in the VIS-IR region of the refractive index were carried out in a model based on the classical theory of dispersion using the direct measurements of indexes at fixed wavelengths and the absorption spectra of the films, including IR spectra (Figures S6-S10). Error of the calculations is estimated as ± 0/01. Typical result is presented in Figure S14. The second harmonic measurements were carried out using pulsed Nd^{3+}:YAG laser, radiation wavelength 1064 nm, pulse energy 3 mJ, pulse duration 10 ns, 10 Hz repetition rate. The measurement error is 15% and is determined by the instability of the parameters of the exciting laser beam.

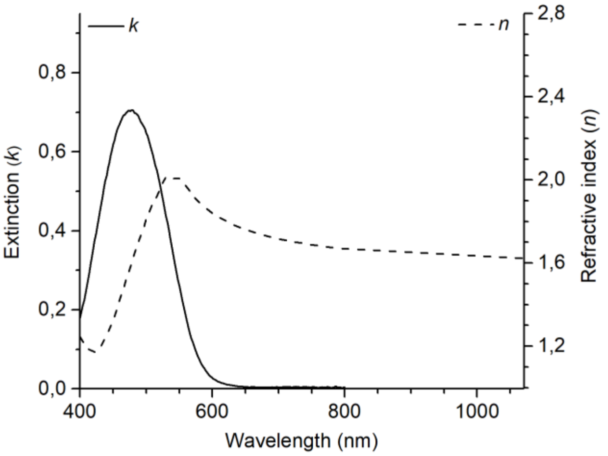

Figure 14 Typical extinction and refractive index of copolymer **2**.

References

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