

Supporting Online Information Materials for

A new crosslinkable system based on thermal Huisgen reaction to enhance the stability of electro-optic polymers

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Material and Methods:

2-(N,N-ethyl-anilino)ethyl-methacrylate **2**,[1] 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methyl-morpholinium chloride DMTMM,[2] 2-Methacrylic acid 3-trimethylsilyl-prop-2-ynyl ester TMSMA[3] were prepared according to the methods described in the literature. Azobisisobutyronitrile (AIBN) initiator was purified by recrystallisation in methanol before use. MMA was distilled under reduced pressure before use to remove the inhibitor. 4-azidoaniline was purchased from Aldrich. All other chemicals were purchased from Acros and used as received. ^1H and ^{13}C NMR spectra were recorded on a ARX 300 MHz Bruker spectrometer. Chemical shifts for ^1H NMR spectra are referenced relative to residual protium in the deuterated solvent (CDCl_3 , $\delta = 7.26$ ppm). High resolution electro-spray mass spectra (HR-ESI) were recorded on a HP 5989A spectrometer. Elemental analyses were carried out by the ICSN laboratory (Gif sur Yvette, France) by combustion using a CHN 2400 analyzer for carbon, hydrogen and nitrogen and by pyrolysis using a O Vario EL III analyzer for oxygen. UV-Visible absorption spectra were recorded on a UV-2401PC Shimadzu spectrophotometer. IRTF spectra were obtained on a transient IR absorption spectrometer based on an amplified femtosecond Ti:sapphire laser system. Molecular weights and molecular weight distributions were measured using size exclusion chromatography (SEC) on a system equipped with a Spectra SYSTEM AS 1000 autosampler, with a guard column (Polymer Laboratories, PL gel 5 μm guard column) followed by two columns (Polymer

Laboratories (PL), 2 PL gel 5 μm MIXED-D columns), with a SpectraSYSTEM RI-150 detector. THF was used as the eluent at a flow rate of 1 $\text{mL}\cdot\text{min}^{-1}$ at 35 $^{\circ}\text{C}$. Polystyrene standards ($580 - 483.10^3 \text{ g}\cdot\text{mol}^{-1}$) were used to calibrate the SEC. Differential Scanning Calorimetry (DSC) measurements and thermogravimetric analyses (TGA) were conducted using a TA instruments Q500 apparatus under nitrogen atmosphere at a heating rate of 10 $^{\circ}\text{C}\cdot\text{min}^{-1}$ from room temperature up to a maximum of 600 $^{\circ}\text{C}$ and allowing us to determine T_g (glass transition temperature), T_c (crosslinking temperature) and T_d (decomposition temperature).

Film thicknesses were measured using a profilometer (DEKTAK 8, VECO).

SHG measurements were performed using the optical setup described in a previous study.[4] Polarized SHG Maker fringe patterns were recorded before and, from time to time, after the poling process, using a 1064 nm Nd:YAG laser operating at very low irradiance (pulse energy $< 50 \mu\text{J}$; repetition rate 200 Hz; pulse width 15 ns). A general SHG matrix method applicable to multilayered anisotropic linear/nonlinear media has been applied, allowing experimental determination of the resonance-enhanced NLO coefficients d_{ij} , as well as the linear absorption coefficients of the harmonic wave (532 nm) in the parallel (α_{\parallel}) and orthogonal (α_{\perp}) directions with respect to the poling field. To evaluate the anisotropic optical constants of any film, we have used a calculation procedure that allows a direct determination of the refractive indices and extinction coefficients from UV-Visible spectra.[5]

4-[4'-(N,N-methacryloyloxy-2-ethyl-ethylamino)phenyl]-3-nitro-benzoic acid (3):

To an aqueous solution of 5 N HCl (10.2 mL) was added an aqueous solution of NaNO_2 (97 mg, 1.406 mmol, 0.2 equiv. in 1.27 mL of water) at 0 $^{\circ}\text{C}$. After complete dissolution of 4-amino-3-nitrobenzoic acid **1** (1.28g, 7.03 mmol, 1 equiv.) in an aqueous solution of NaOH (281 mg, 7.03 mmol, 1 equiv. in 10.6 mL of water), an aqueous solution of NaNO_2 (511 mg, 7.38 mmol, 1.05 equiv. in 3.3 mL of water) was added. The solution of 4-amino-3-

nitrobenzoic acid was then slowly added to the acidic solution at 5-10°C and stirred for 30 min to give a yellow precipitate. A spatula of urea (210 mg, 3.51 mmol, 0.5 equiv.) was added to quench any potential excess of NaNO₂ and the solution was then slowly added to a solution of compound **2** in ethanol (12.8 mL) at 5-10°C. The mixture was then stirred for 40 min at this temperature leading to the formation of a red precipitate. After neutralization of the solution with an aqueous solution of AcONa (548 mg) and NaCl (1.09g) in 18.3 mL of water, the mixture was filtered. The reddish solid was dissolved in dichloromethane and was filtered through silica gel eluted with dichloromethane/methanol : 9/1 to give 1.99 g of compound **3** (67 %). ¹H NMR (300 MHz, CDCl₃, δ): 8.55 (s, 1H, Ar H) ; 8.29 (dd, 1H, *J* = 8.4 Hz, *J* = 2.4 Hz, Ar H) ; 7.87 (d, 2H, *J* = 8.7 Hz, Ar H) ; 7.78 (dd, 1H, *J* = 8.4 Hz, *J* = 2.4 Hz, Ar H) ; 6.80 (d, 2H, *J* = 8.7 Hz, Ar H) ; 6.10 (s, 1H, C=CH) ; 5.60 (s, 1H, C=CH) ; 4.36 (t, 2H, *J* = 5.7 Hz, CH₂) ; 3.73 (t, 2H, *J* = 6 Hz, CH₂) ; 3.53 (m, 2H, CH₂) ; 1.94 (s, 3H, CH₃) ; 1.25 (t, 3H, *J* = 6.9 Hz, CH₃); ¹³C NMR (75 MHz, CDCl₃, δ): 185.73, 184.44, 174.08, 173.64, 150.05, 146.54, 146.10, 142.13, 134.47, 131.05, 124.50, 122.93, 115.88, 109.60, 59.76, 46.58, 43.35, 15.59, 9.59; IR (KBr): ν = 3428 (vs; ν (OH)), 2976 (s; ν (CH₂)), 2928 (s; ν (CH₂)), 1718 (vs; ν (C=O)), 1694 (s; ν (C=C)), 1596 cm⁻¹ (s; ν (C=C)); UV-vis. (DMF): λ_{max} (ε) = 490 nm (30 600); HRMS (ESI, m/z): [MH]⁺ calcd for C₂₁H₂₃N₄O₆ : 427.1618; found, 427.1613. Anal. calcd. for C₂₁H₂₂N₄O₆·0.5(CH₃OH): C, 58.3; H, 5.47; N, 12.6. Found: C, 58.3; H, 5.56; N, 12.3.

4''-azido-phenyl-4-[4'-(N,N-methacryloyloxy-2-ethyl-ethylamino)phenyl]-3-nitro-benzoate
(**5**):

To a solution of carboxylic acid compound **3** (1 g, 2.346 mmol, 1 equiv.) and 4-azidoaniline hydrochloride **4** (440 mg, 2.58 mmol, 1.1 equiv.) in THF (5 mL) was added *N*-methylmorpholine (0.77 mL, 7.04 mmol, 3 equiv.) and then DMTMM (779 mg, 2.81 mmol, 1.2 equiv.). The solution was stirred one night at room temperature. Solvents were then

evaporated under reduced pressure to give a crude product, which was purified by silica gel column chromatography using dichloromethane as eluting system leading to 1.27 mg of compound **5** (100%). ^1H NMR (300 MHz, CDCl_3 , δ): 8.32 (d, 1H, $J = 1.8$ Hz, Ar H) ; 8.10 (dd, 1H, $J = 8.4$ Hz, $J = 2.1$ Hz, Ar H) ; 7.87 (d, 2H, $J = 9.3$ Hz, Ar H) ; 7.85 (bs, 1H, NH) ; 7.82 (d, 1H, $J = 8.4$ Hz, Ar H) ; 7.66 (d, 2H, $J = 9$ Hz, Ar H) ; 7.06 (d, 2H, $J = 9$ Hz, Ar H) ; 6.80 (d, 2H, $J = 9.3$ Hz, Ar H) ; 6.10 (s, 1H, C=CH) ; 5.59 (s, 1H, C=CH) ; 4.37 (t, 2H, $J = 6.6$ Hz, CH_2) ; 3.73 (t, 2H, $J = 6$ Hz, CH_2) ; 3.53 (q, 2H, $J = 6.9$ Hz, CH_2) ; 1.94 (s, 3H, CH_3) ; 1.26 (t, 3H, $J = 7.2$ Hz, CH_3). ^{13}C NMR (75 MHz, CDCl_3 , δ): 164.68, 157.24, 151.80, 146.88, 143.39, 136.62, 135.81, 134.39, 134.27, 131.28, 126.33, 122.70, 121.94, 119.69, 119.27, 111.55, 96.36, 61.65, 55.90, 48.80, 21.76, 18.33, 12.28; IR (KBr): $\nu = 2967$ (s; ν (CH_2)), 2114 (vs; ν (N_3)), 1717 (vs; ν ($\text{C}=\text{O}$)), 1676 (s; ν ($\text{C}=\text{C}$)), 1598 cm^{-1} (s; ν ($\text{C}=\text{C}$)). UV-vis. (CH_2Cl_2): λ_{max} (ϵ) = 480 nm (28 200); HRMS (ESI, m/z): $[\text{MH}]^+$ calcd for $\text{C}_{27}\text{H}_{27}\text{N}_8\text{O}_5$: 543.2104 (MH^+); found, 543.2105. Anal. calcd. for $\text{C}_{27}\text{H}_{26}\text{N}_8\text{O}_5 \cdot 0.5(\text{H}_2\text{O})$: C, 58.8; H, 4.93; N, 20.3. Found: C, 58.9; H, 4.89; N, 20.0.

General procedure for the preparation of the polymers:

Compound **5** (3 equiv., generally 600 mg), compound TMSMA (4 or 7 equiv), in some cases freshly distilled methylmethacrylate (3 equiv.) and AIBN (5%w equiv.) were dissolved in distilled tetrahydrofuran (8 mL) in a dry schlenk tube. The mixture was degassed by three freeze-pump-thaw cycles, and heated for 18 hours at 70°C in the dark. After cooling back to room temperature, the mixture was precipitated by dropping the crude reaction mixture in methanol (80 mL). The solid was washed twice and isolated by centrifugation. The solid was dried for 12 hours by heating at 35°C under reduced pressure. A red powder was obtained.

PAS1 (Yield : 75%) ^1H NMR (300 MHz, CDCl_3 , δ): 8.81 (m, 7H, Ar H) ; 8.86 (m, 4H, Ar H) ; 4.58 (s, 3.9H, CH_2) ; 4.11 (s, 1.2H, CH_2) ; 3.51 (m, 4.4H, CH_2) ; 1.94 (m, 2.4H, CH_3) ;

1.10 (m, 16H, CH₃) ; 0.16 (s, 28.9H, Si-CH₃); IR (KBr): $\nu = 2956$ (s; ν (CH₂)), 2184 (s; ν (C≡C)), 2098 (vs; ν (N₃)), 1732 (vs; ν (C=O)), 1598 cm⁻¹ (s; ν (C=C)). UV-vis. (CH₂Cl₂): λ_{max} (ϵ) = 476 nm; SEC(polystyrene): Mn (g/mol): 7 500, PDI = 1.8. TGA-DSC (10°C/min): Tg = 75°C, Tr = 166°C, Td = 274°C. Anal. calcd. for x = 2; y = 4; z = 4: C, 60.3; H, 6.78; N, 9.79. Found: C, 59.9; H, 6.66; N, 9.85.

PAS2 (Yield : 50%) ¹H NMR (300 MHz, CDCl₃, δ): 8.81 (m, 7H, Ar H) ; 8.86 (m, 4H, Ar H) ; 4.58 (s, 3.9H, CH₂) ; 4.11 (s, 1.2H, CH₂) ; 3.51 (m, 4.4H, CH₂) ; 1.94 (m, 2.4H, CH₃) ; 1.10 (m, 16H, CH₃) ; 0.16 (s, 28.9H, Si-CH₃); IR (KBr): $\nu = 2956$ (s; ν (CH₂)), 2184 (s; ν (C≡C)), 2098 (vs; ν (N₃)), 1732 (vs; ν (C=O)), 1598 cm⁻¹ (s; ν (C=C)). UV-vis. (CH₂Cl₂): λ_{max} (ϵ) = 476 nm; SEC(polystyrene): Mn (g/mol): 7 100, PDI = 1.9; TGA-DSC (10°C/min): Tg = 77°C, Tr = 168°C, Td = 263°C; Anal. calcd. for x = 4; y = 0; z = 8: C, 60.4; H, 6.46; N, 11.9. Found: C, 60.0; H, 6.27; N, 11.7.

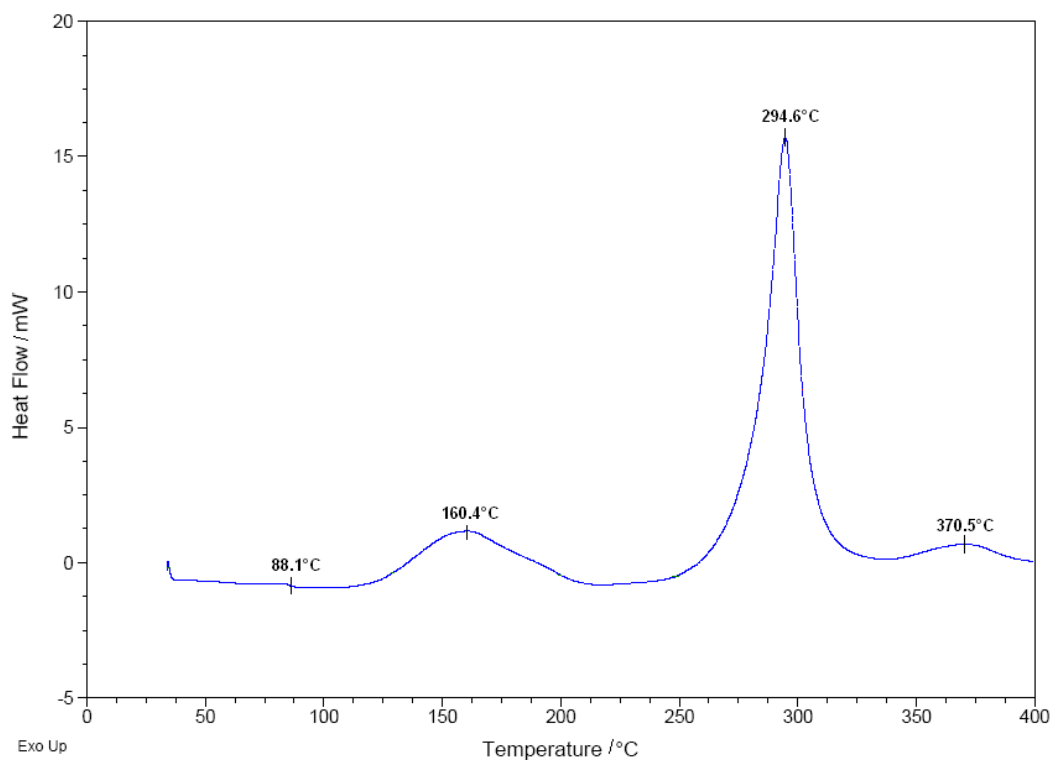


Figure 1. DSC analysis of the polymer PAS1

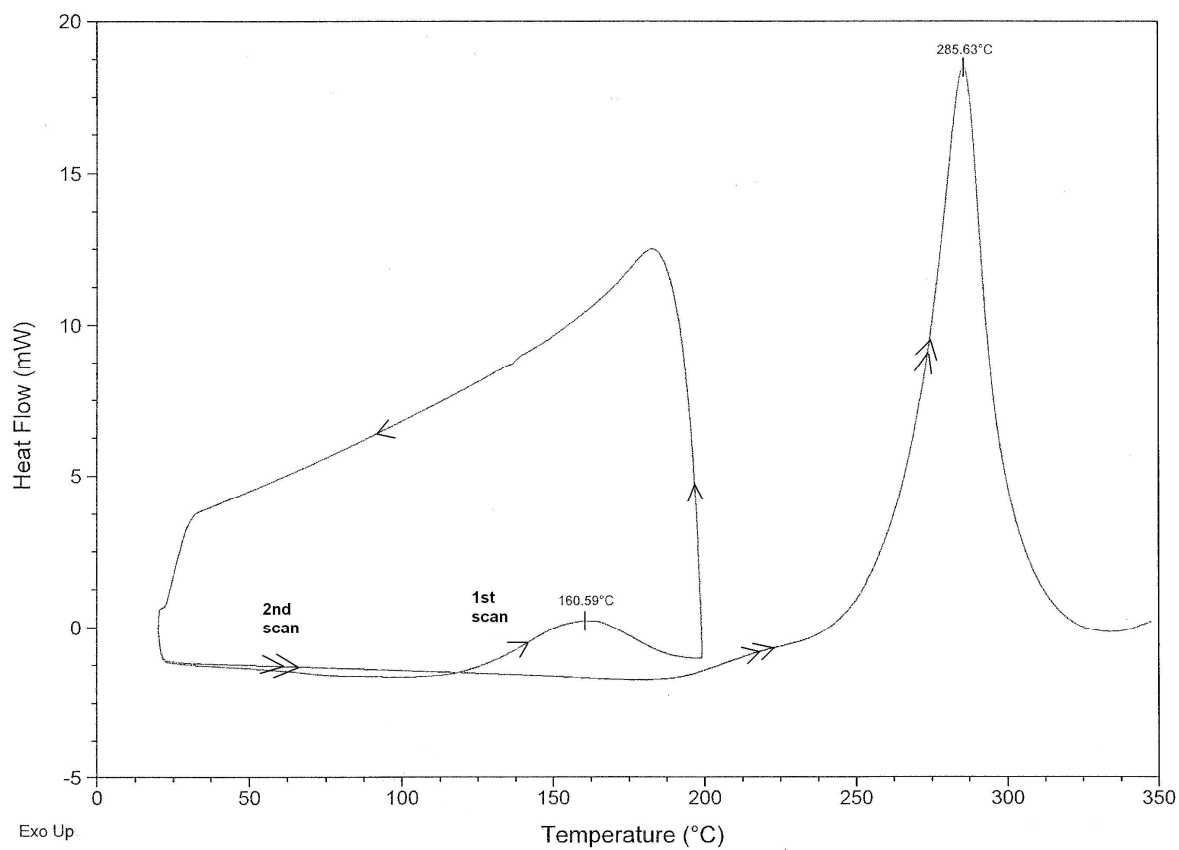


Figure 2. DSC analysis of the polymer PAS2

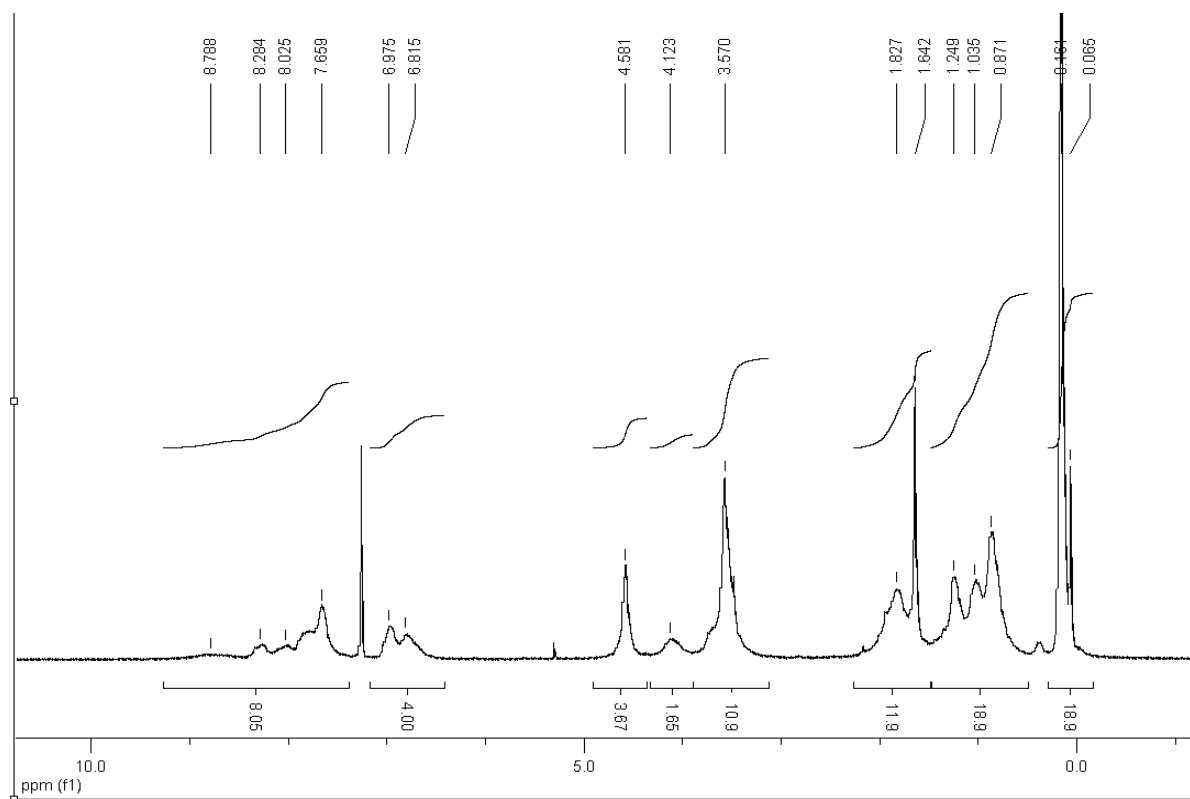


Figure 3. ^1H NMR spectrum of the polymer PAS1 recorded in CDCl_3 .

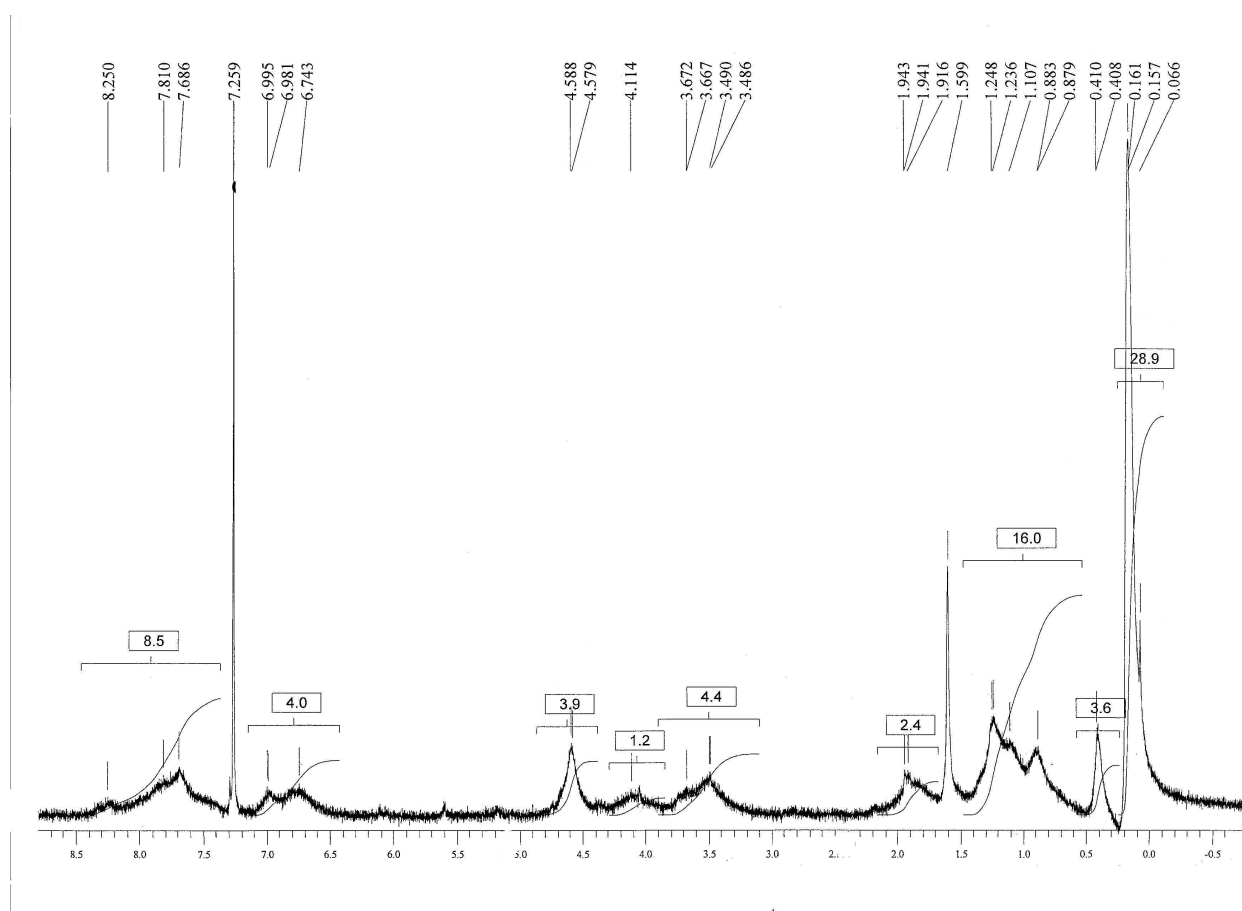


Figure 4. ^1H NMR spectrum of the polymer PAS2 recorded in CDCl_3 .

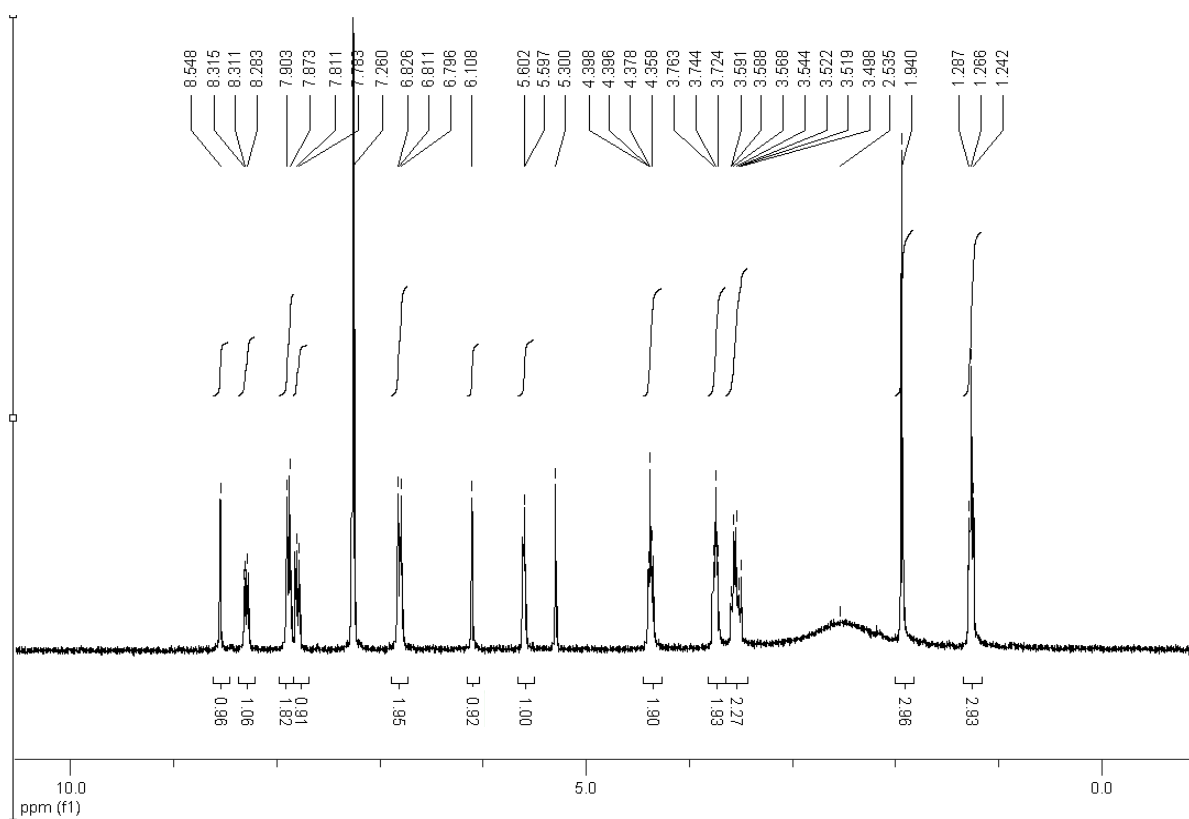


Figure 5. ^1H NMR spectrum of the chromophore **3** recorded in CDCl_3 .

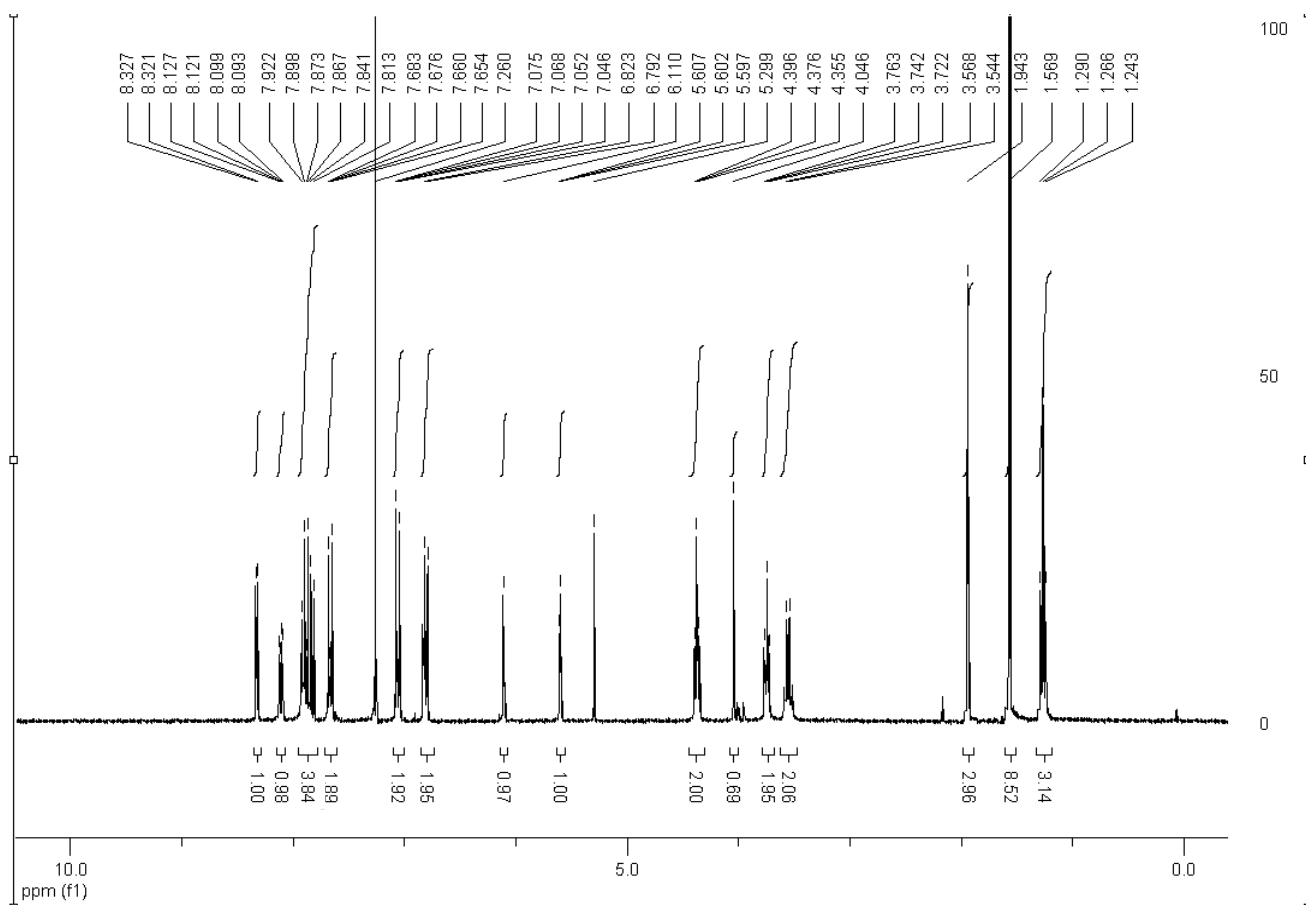


Figure 6. ^1H NMR spectrum of the chromophore **5** recorded in CDCl_3 .

References

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