

Supporting Information

Nonfreezable water and polymer swelling control the marine antifouling performance of polymers with limited hydrophilic content

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1. PREPARATION OF POLYMERS

Polymer H-0 (pBMA): The n-butyl methacrylate homopolymer was prepared in a following manner. To the main polymerization vessel equipped with mechanical stirrer 22.5 g of methylated spirit was added and heated to 75 °C. Next two polymerization feeds were prepared. The first feed consisted only of methylated spirit (120 g), whereas the second feed consisted of first lot of AMBN initiator (4.87 g, 25 mmol) dissolved in n-BMA (143.96 g, 1012 mmol). Both feeds were gradually added to the main reactor during 4 h feeding period using two Watson Marlow 101 U/R peristaltic pumps. One hour after feeding completion the remaining amount of AMBN (1.17 g, 6 mmol) was dissolved in methylated spirit (7.5 g) and added directly to the reaction mixture to convert residual monomer. The main vessel was then stirred for another hour, cooled down and left overnight for subsequent post-processing. The next day the polymerization flask was fitted with a condenser, heated to 85 °C and methylated spirit (100 g) was distilled with simultaneous feed of xylene (131 g). After the distillation, polymer solution was allowed to cool down to room temperature.

Polymer E-L (pBMA-co-IBoMA-co-mPEG350MA): Due to high softness of pBMA-co-mPEG350MA copolymer (glass transition temperature $T_g = -36.5$ °C), the polymer composition was modified by adding a third comonomer isobornyl methacrylate (IBoMA) which increased polymer's T_g . The new copolymer pBMA-co-IBoMA-co-mPEG350MA was polymerized as follows. The mPEG350MA monomer (31.71 g, 74 mmol) was added to methylated spirit (120 g) and this made up the first feed. The first lot of AMBN (3.55 g, 18 mmol) was dissolved in n-BMA (59.78 g, 421 mmol) and IBoMA (54.11 g, 243 mmol) and this mixture made-up the second feed. Both feeds were simultaneously added to the reactor containing 22.5 g of methylated spirit and the polymerization was conducted at 75 °C. After feeding completion and mixing for another hour, the remaining AMBN (0.85 g, 4.4 mmol) in 7.5 g of methylated spirit was added to the vessel and

the mixing continued for another hour before stopping the reaction. The next day the post processing step included distillation of methylated spirit (100 g) at 85 °C with simultaneous addition of xylene (131 g).

Polymer H-L (pBMA-co-HEMA): To the main polymerization vessel 22.5 g of methylated spirit was added and heated to 75 °C. Next two polymerization feeds were prepared with first feed consisting of HEMA (13.28 g, 102 mmol) and methylated spirit (120 g) and second feed made-up from first lot of AMBN (4.91 g, 26 mmol) and n-BMA (130.63 g, 919 mmol). Both feeds were simultaneously added to the main vessel for four hours. One hour after feeding completion remaining AMBN (1.18 g, 6 mmol) was dissolved in small amount of methylated spirit (7.5 g) and added to the vessel. The contents of the vessel was mixed for another hour and then the reaction was stopped. The next day methylated spirit (100 g) was distilled at 85 °C and xylene (131 g) was simultaneously added to the reactor.

Polymer G-L (pBMA-co-DHPMA): The polymerization vessel containing small amount of methylated spirit (22.5 g) was heated to 75 °C, while two monomer feeds were prepared. The first feed contained DHPMA (16.03 g, 100 mmol) and methylated spirit (120 g), and the second feed comprised of AMBN (4.81 g, 25 mmol) dissolved in n-BMA (128.01 g, 900 mmol). Both feeds were simultaneously added to the reactor during four hour feeding process. One hour after feeding completion remaining AMBN (1.15 g, 6 mmol) was dissolved in 7.5 g of methylated spirit and added to the vessel. After additional hour of mixing the reaction was stopped and left overnight. The next day methylated spirit (100 g) was distilled at 85 °C and xylene (131 g) was simultaneously added to the polymer solution.

Polymer M-L (pBMA-co-MAA): To the main polymerization reactor small amount of methylated spirit was added (22.5 g) and the reactor was heated to 75 °C. Next, MAA (9.06 g, 105

mmol) was added to methylated spirit (120 g) and this made-up the first feed. The second feed was made of AMBN (5.06 g, 26 mmol) and n-BMA (134.67 g, 947 mmol). Both feeds were simultaneously added to the main reactor during four hour long feeding period. One hour after feeding completion remaining AMBN (1.21 g, 6 mmol) was dissolved in 7.5 g of methylated spirit and added to the reactor and the mixing proceeded for another hour before being stopped. The next day 100 g of methylated spirit was distilled at 85 °C with simultaneous feed of 131 g of xylene.

Polymer Z-L (pBMA-co-SBMA): The main polymerization vessel containing methylated spirit (22.5 g) was heated to 75 °C. Two monomer feeds were prepared prior to running reaction. The first feed consisted of zwitterionic SBMA (25.89 g, 93 mmol) and methylated spirit (120 g), and the second feed comprised of first lot of AMBN initiator (4.46 g, 23 mmol) dissolved in n-BMA (118.59 g, 834 mmol). To improve the solubility of SBMA the flask was preheated to 70 °C under magnetic stirrer. When necessary the first feed line was gently heated with a heat gun to remove blocking deriving from SBMA crystallization. One hour after feeding completion second lot of AMBN (1.06 g, 6 mmol) was dissolved in methylated spirit (7.5 g), added to the main vessel and the mixing continued for another hour before being stopped. The next day methylated spirit (100 g) was distilled at 85 °C with simultaneous feed of xylene (131 g). Due to high polymer viscosity and difficulty in application 60 g of xylene was additionally added to the ready polymer solution.

Polymer A-L (pBMA-co-SPMA): The polymerization vessel containing small amount of methylated spirit (22.5 g) was heated to 75 °C. Next, two monomer feeds were prepared. The first feed contained the anionic SPMA salt (23.3 g, 95 mmol) and methylated spirit (120 g) and was preheated to 70 °C under magnetic stirrer. The second feed consisted of first lot of AMBN (4.55 g, 24 mmol) and n-BMA (121.06 g, 851 mmol). Both feeds were added to the main reactor for

four hours. As in case of SBMA, the SPMA salt also was prone to crystallization and heat gun was used when necessary to remove feed line blocking. One hour after feeding completion remaining AMBN (1.09 g, 6 mmol) was dissolved in methylated spirit (7.5 g) and added to the vessel and the mixing continued for another hour. After this time the reaction was stopped and left overnight. The next day methylated spirit (100 g) was distilled at 85 °C with simultaneous feed of xylene (131 g). The obtained polymer was viscous and difficult to apply and in order to ease its application additional 60 g of xylene was added to the ready polymer.

Polymer C-L (pBMA-*co*-METAC): Before preparing the actual polymer residual water was removed from METAC (25.18 g) by precipitating the monomer in THF and discarding the supernatant. Next, to the polymerization reactor 22.5 g of methylated spirit was added and heated to 75 °C. Two polymerization feeds were prepared as follows. First feed consisted of earlier dried METAC salt (20.14 g, 97 mmol) and was added to methylated spirit (120 g) and this made up first feed, whereas feed two consisted of AMBN (4.66 g, 24 mmol) dissolved in n-BMA (124.08 g, 872 mmol). When needed the first feed line was heated with heat gun to remove line blocking deriving from crystallizing METAC. The feeds were added simultaneously to the reactor for four hours and one hour after feeding completion the remaining AMBN (1.12 g, 6 mmol) was dissolved in methylated spirit (7.5 g) and added to the reactor. After additional hour the stirring and heating was turned off. The next day 100 g of methylated spirit was distilled at 85 °C with simultaneous feed of 131 g of xylene. Due to high polymer viscosity and difficulty in application 60 g of xylene was additionally added to the ready polymer solution.

Polymer P-L10 (pBMA-*co*-SPMA_{5mol%}-*co*-METAC_{5mol%}): Prior to running polymerization specific amount of METAC (12.45 g) was precipitated in THF and the resulting supernatant discarded. Dried METAC (9.96 g, 48 mmol) together with SPMA (11.81 g, 48 mmol) were

dissolved in methylated spirit (120 g) and this solution constituted as feed one. The second feed consisted of first lot of AMBN (4.61 g, 24 mmol) and n-BMA (122.7 g, 863 mmol). The main reaction vessel containing 22.5 g of methylated spirit was heated to 75 °C and two monomer feeds were simultaneously added for four hours. When necessary the first feed line was heated with heat gun to remove blocking from salt crystallisation. One hour after feed completion second lot of AMBN (0.92 g, 5 mmol) in methylated spirit (7.5 g) was added to the vessel and the mixing continued for another hour, before turning it off and leaving overnight. The next day 100 g of methylated spirit was distilled at 85 °C with simultaneous feed of 131 g of xylene.

P-L20 (pBMA-*co*-SPMA_{10mol%}-*co*-METAC_{10mol%}): First METAC (23.61 g) was precipitated in THF and the supernatant was removed. Dried METAC (18.89 g, 91 mmol) and SPMA (22.4 g, 91 mmol) were dissolved in methylated spirit (120 g) and this solution constituted as feed one. The second feed consisted of first lot of AMBN (4.37 g, 23 mmol) dissolved in n-BMA (103.46 g, 728 mmol). The main reaction vessel containing 22.5 g of methylated spirit was heated to 75 °C and two monomer feeds were simultaneously added for four hours. When necessary the feed line one was heated with heat gun to remove blocking from salt crystallisation. One hour after feed completion second lot of AMBN (0.88 g, 5 mmol) was dissolved in methylated spirit (7.5 g) and added to the vessel. After additional hour of mixing the reaction was turned off and left overnight. The next day 100 g of methylated spirit was distilled at 85 °C with simultaneous feed of 131 g of xylene. Due to high polymer viscosity and difficulty in application 90 g of xylene was additionally added to the ready polymer solution.

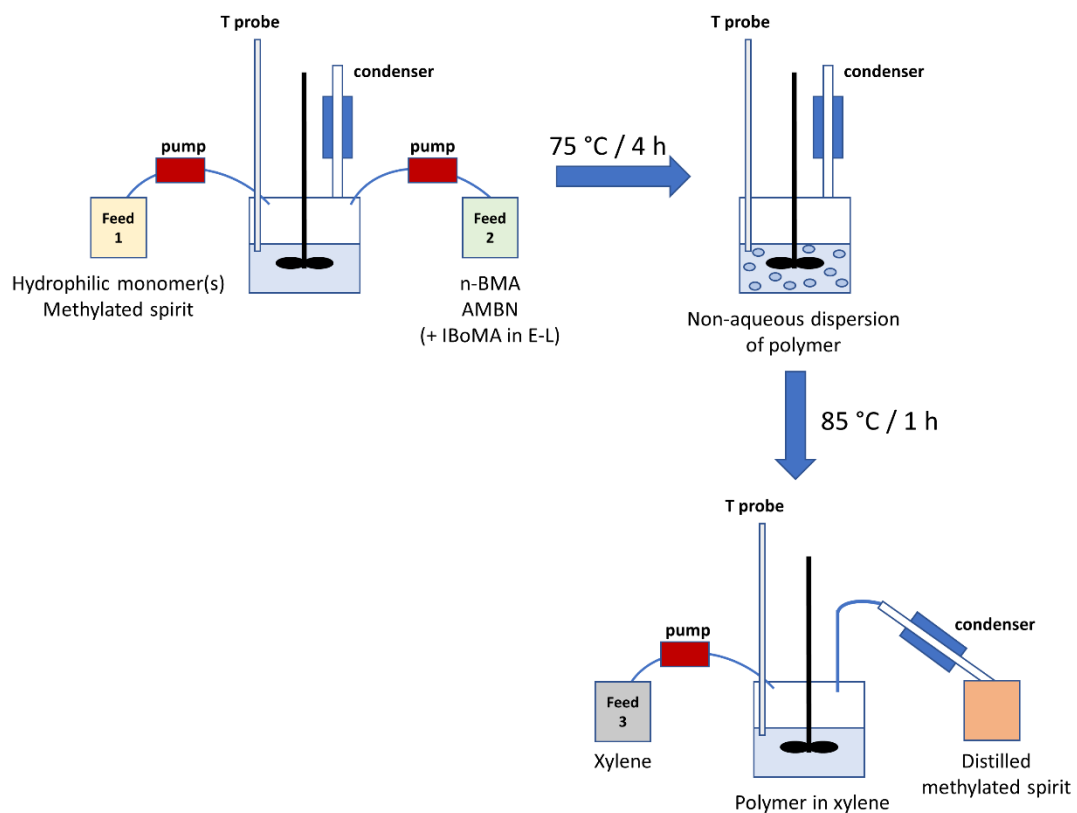


Figure S1. Schematic preparation of hydrophilic copolymers using the dual-feed technique.

2. POLYMER COMPOSITION DETERMINATION BY ^1H NMR

Polymer E-L (pBMA-*co*-IBoMA-*co*-mPEG350MA): In case of the IBoMA monomer the single proton at around 4.5 ppm (-OCH) was assigned based on the published data for the pBMA-*co*-IBoMA copolymer.¹ The peaks deriving from mPEG350MA were assigned according to Harrell and Bergbreiter.² The copolymer composition was established by integrating and comparing the areas of the -CH₂ group of the n-BMA (**d**; $\delta = 3.99 - 3.83$ ppm), -OCH proton of the IBoMA (**g**; $\delta = 4.5 - 4.25$ ppm) and -CH₃ terminal group of the mPEG350MA (**r**; $\delta = 3.44 - 3.31$ ppm). Based on the integral data, the mole basis of n-BMA = $2.00 / 2\text{H} = 1$ mole, IBoMA = $0.63 / 1\text{H} = 0.63$ mole and mPEG350MA = $0.66 / 3\text{H} = 0.22$ mole. Final molar composition: n-BMA = $1 / 1.85 = 54$ mol %, IBoMA = $0.63 / 1.85 = 34$ mol %, mPEG350MA = $0.22 / 1.85 = 12$ mol %.

Polymer H-L (pBMA-*co*-HEMA): In order to estimate the copolymer composition a following procedure was undertaken. Knowing that the signal at $\delta = 1.69 - 1.5$ ppm belongs to -CH₂ group of n-BMA (**c**) and the signal at $\delta = 4.28 - 3.51$ ppm could be assigned to -CH₂ groups of n-BMA and HEMA (**d + g + h**), thus the integral value $I = 2.39$ can be assigned to 2 protons of n-BMA and 0.39 protons of HEMA. Ultimately, the mole basis of n-BMA = $2.00 / 2\text{H} = 1$ mole and mole basis of HEMA = $0.39 / 4\text{H} = 0.098$ mole. Final molar composition: n-BMA = $1 / 1.098 = 91$ mol % and HEMA = $0.098 / 1.098 = 9$ mol %.

Polymer G-L (pBMA-*co*-DHPMA): Copolymer composition was determined in a following manner. Knowing that the signal at $\delta = 1.69 - 1.52$ ppm belongs only to -CH₂ group of the n-BMA (**c**) and the signal at $\delta = 4.25 - 3.50$ ppm belongs to both n-BMA and DHPMA (**d + g + h + i**), thus the integral value $I = 2.53$ can be assigned to 2 protons from n-BMA and 0.53 protons of DHPMA. Based on the above information the mole basis of n-BMA = $2.00 / 2\text{H} = 1$ mole and

mole basis of DHPMA = $0.53 / 5H = 0.106$ mole. Final molar composition: n-BMA = $1 / 1.106 = 90$ mol % and DHPMA = $0.106 / 1.106 = 10$ mol %.

Polymer M-L (pBMA-co-MAA): The composition of this copolymer was established in a following manner. Knowing that the signal at $\delta = 1.71 - 1.5$ ppm belongs only to $-\text{CH}_2$ group of n-BMA (**c**), the large $-\text{CH}_3$ signal at $\delta = 1.28 - 0.31$ ppm can be assigned to $-\text{CH}_3$ groups (**a + e + g**) of both n-BMA and MAA. Consequently, the integral value $I = 6.29$ can be attributed to 6 protons from $-\text{CH}_3$ of n-BMA (**a + e**) and 0.29 protons from $-\text{CH}_3$ of MAA (**g**). If we just consider the $-\text{CH}_3$ groups in polymer backbone (**e + g**) then we can calculate the copolymer composition: n-BMA = $3 / 3.29 = 91$ mol % and MAA = $0.29 / 3.29 = 9$ mol %.

Polymer Z-L (pBMA-co-SBMA): The composition of zwitterionic copolymer was determined by comparing integrated areas of the $-\text{CH}_2$ group of n-BMA (**c**; $\delta = 1.69 - 1.5$ ppm) with $-\text{CH}_3$ groups of the SBMA (**j**; $\delta = 3.56 - 3.15$ ppm). Based on the integral data the mole basis of n-BMA = $2.00 / 2H = 1$ mole and SBMA = $0.45 / 6H = 0.075$ mole. Final molar composition: n-BMA = $1 / 1.075 = 93$ mol % and SBMA = $0.075 / 1.075 = 7$ mol %.

Polymer A-L (pBMA-co-SPMA): Copolymer composition was established by comparing integrated area of the $-\text{CH}_2$ group of n-BMA (**c**; $\delta = 1.67 - 1.52$ ppm) with $-\text{CH}_2$ group of SPMA (**g**; $\delta = 3.45 - 3.04$ ppm). Based on the integral data, the mole basis of n-BMA = $2.00 / 2H = 1$ mole and SPMA = $0.17 / 2H = 0.085$ mole. Final molar composition: n-BMA = $1 / 1.085 = 92$ mol % and SPMA = $0.085 / 1.085 = 8$ mol %.

Polymer C-L (pBMA-co-METAC): The chemical composition of the copolymer was determined by comparing integrated area of the $-\text{CH}_2$ group of n-BMA (**c**; $\delta = 1.68 - 1.47$ ppm) with $-\text{CH}_3$ groups of METAC (**g**; $\delta = 3.7 - 3.32$ ppm). Based on the integral data the mole basis of

n-BMA = $2.00 / 2H = 1$ mole, METAC = $0.96 / 9H = 0.107$ mole. Final molar composition: n-BMA = $1 / 1.107 = 90$ mol % and METAC = $0.107 / 1.107 = 10$ mol %.

Polymer P-L10 (pBMA-co-SPMA_{5mol%}-co-METAC_{5mol%}): The composition of this mixed-charged copolymer was determined by comparing integrated areas of the -CH₂ group of n-BMA (**c**; $\delta = 1.66 - 1.51$ ppm) with -CH₂ group of SPMA (**g**; $\delta = 3.09 - 2.83$ ppm) and -CH₃ groups of METAC (**l**; $\delta = 3.62 - 3.34$ ppm). Based on the integral data the mole basis of n-BMA = $2.00 / 2H = 1$ mole, SPMA = $0.09 / 2H = 0.045$ mole, METAC = $0.5 / 9H = 0.056$ mole. Final molar composition: n-BMA = $1 / 1.101 = 91$ mol %, SPMA = $0.045 / 1.101 = 4$ mol %, METAC = $0.056 / 1.101 = 5$ mol %.

Polymer P-L20 (pBMA-co-SPMA_{10mol%}-co-METAC_{10mol%}): The composition of this copolymer was determined by comparing integrated areas of the -CH₂ group of n-BMA (**c**; $\delta = 1.67 - 1.5$ ppm) with -CH₂ group of SPMA (**g**; $\delta = 2.99 - 2.77$ ppm) and -CH₃ groups of METAC (**l**; $\delta = 3.58 - 3.3$ ppm). Based on the integral data the mole basis of n-BMA = $2.00 / 2H = 1$ mole, SPMA = $0.21 / 2H = 0.105$ mole, METAC = $1.00 / 9H = 0.111$ mole. Final molar composition: n-BMA = $1 / 1.216 = 82$ mol %, SPMA = $0.105 / 1.216 = 9$ mol %, METAC = $0.111 / 1.216 = 9$ mol %.

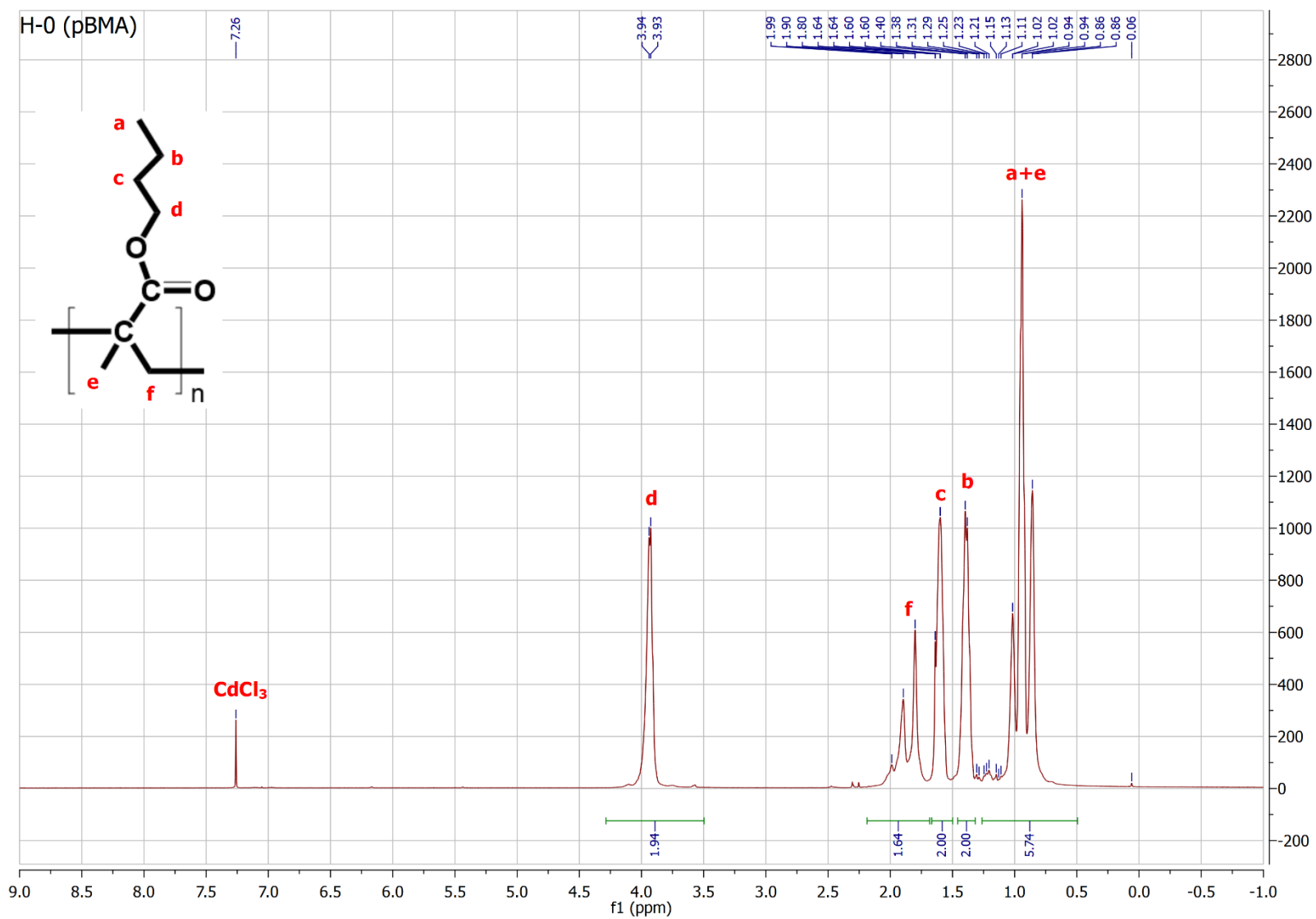


Figure S2. ^1H NMR spectrum of H-0 homopolymer (pBMA) in CdCl_3 .

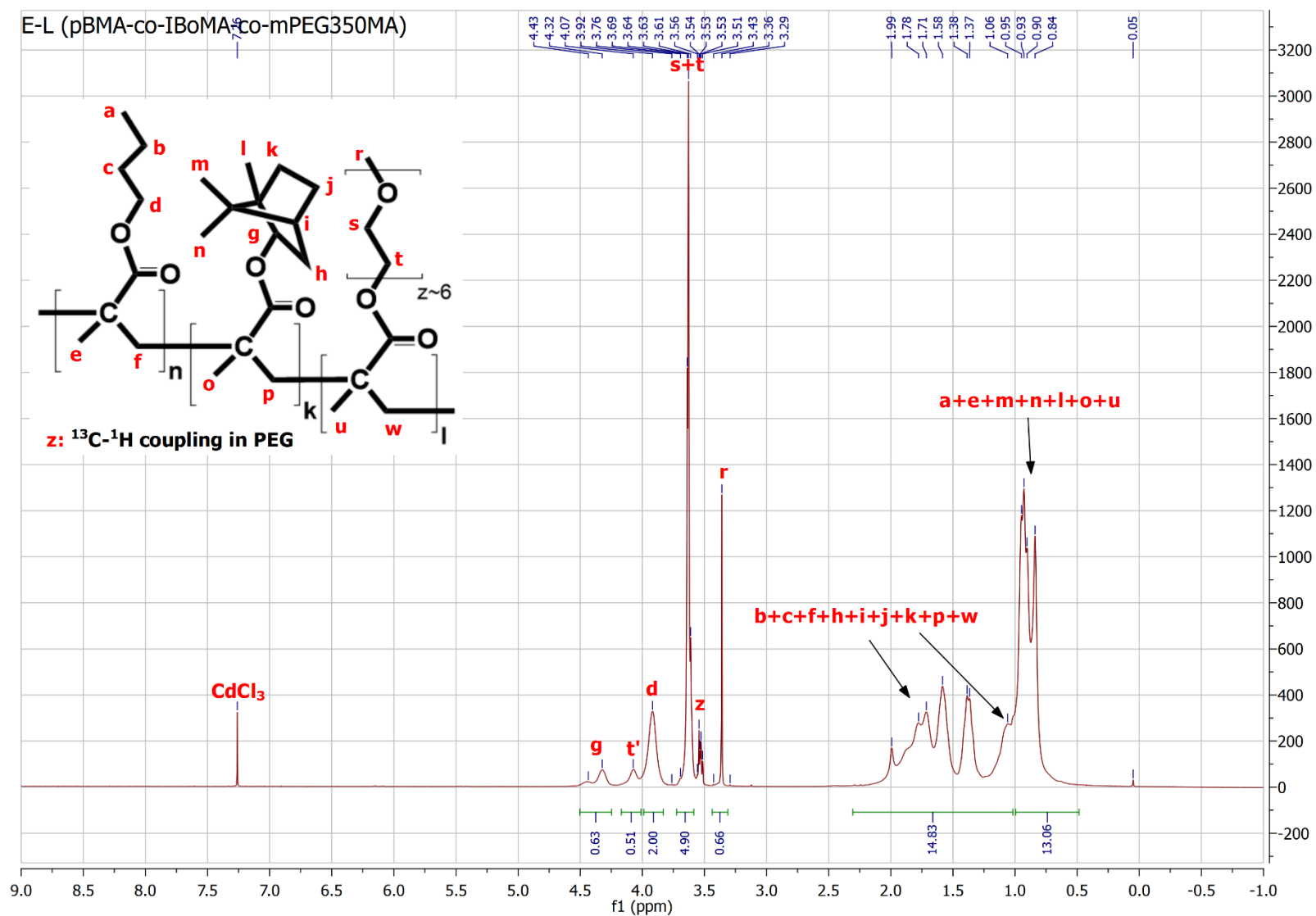


Figure S3. ^1H NMR spectrum of E-L copolymer (pBMA-co-IBoMA-co-mPEG350MA) in CdCl_3 .

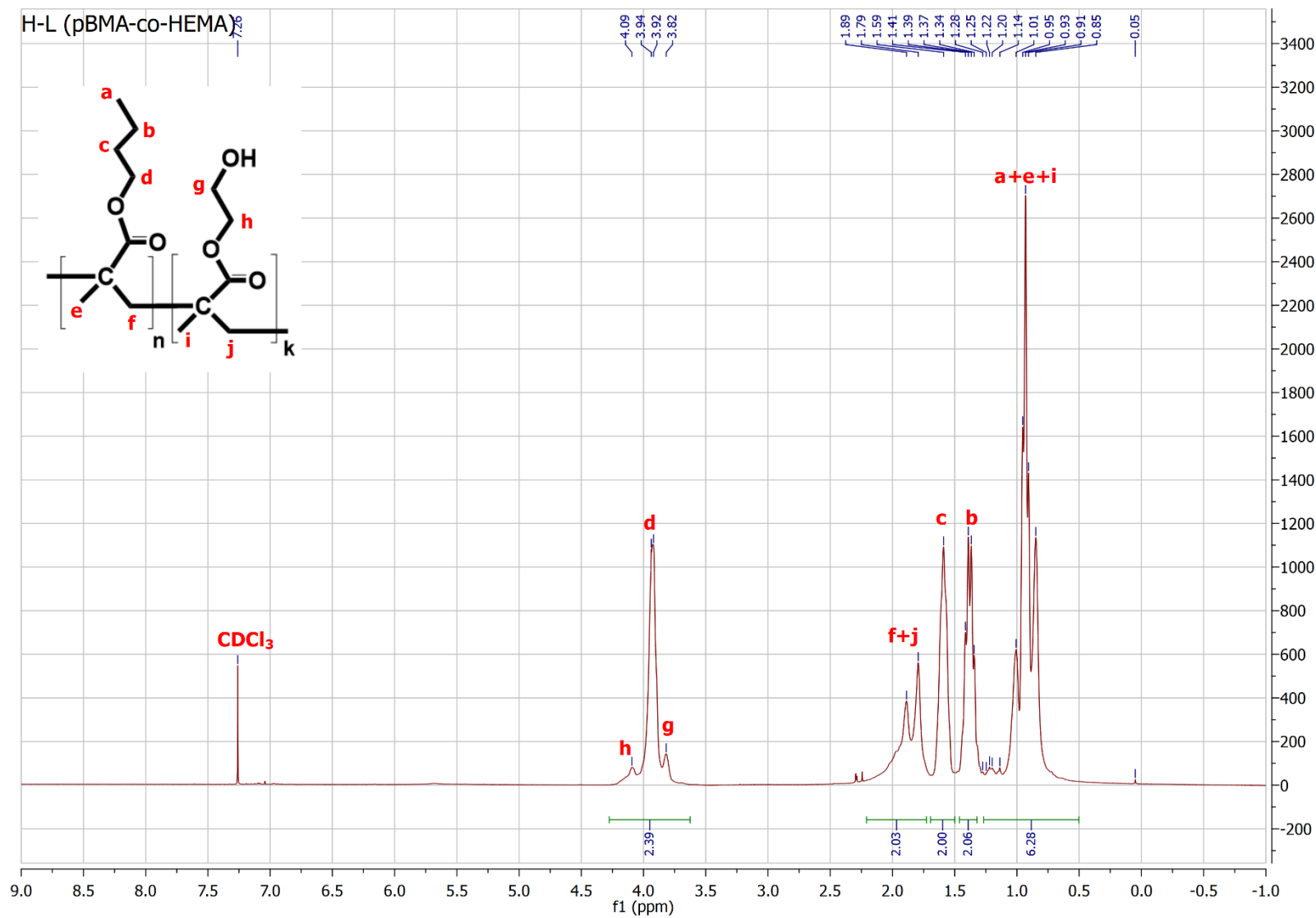


Figure S4. ^1H NMR spectrum of H-L copolymer (pBMA-co-HEMA) in CDCl_3 .

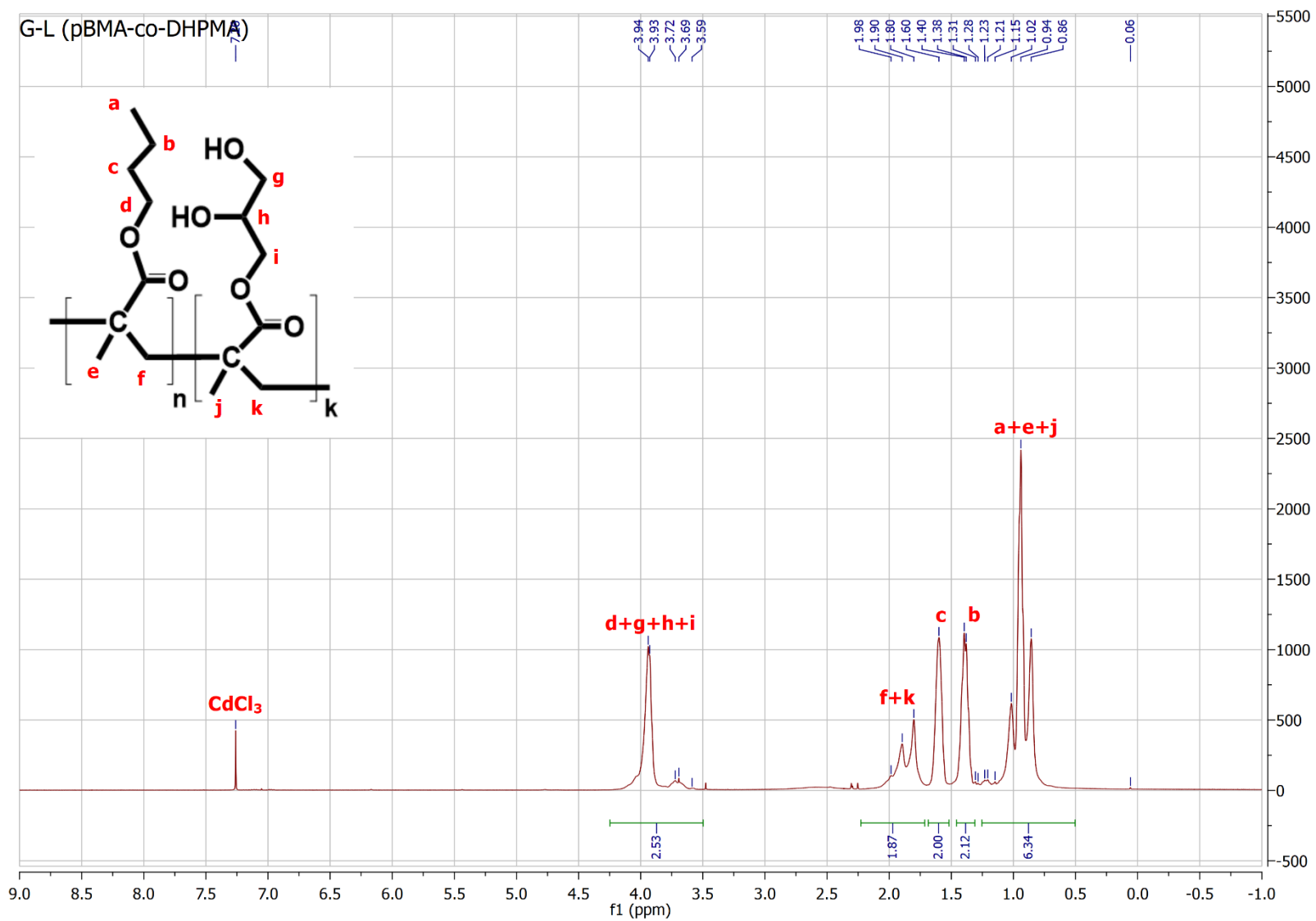


Figure S5. ^1H NMR spectrum of G-L copolymer (pBMA-co-DHPMA) in CdCl_3 .

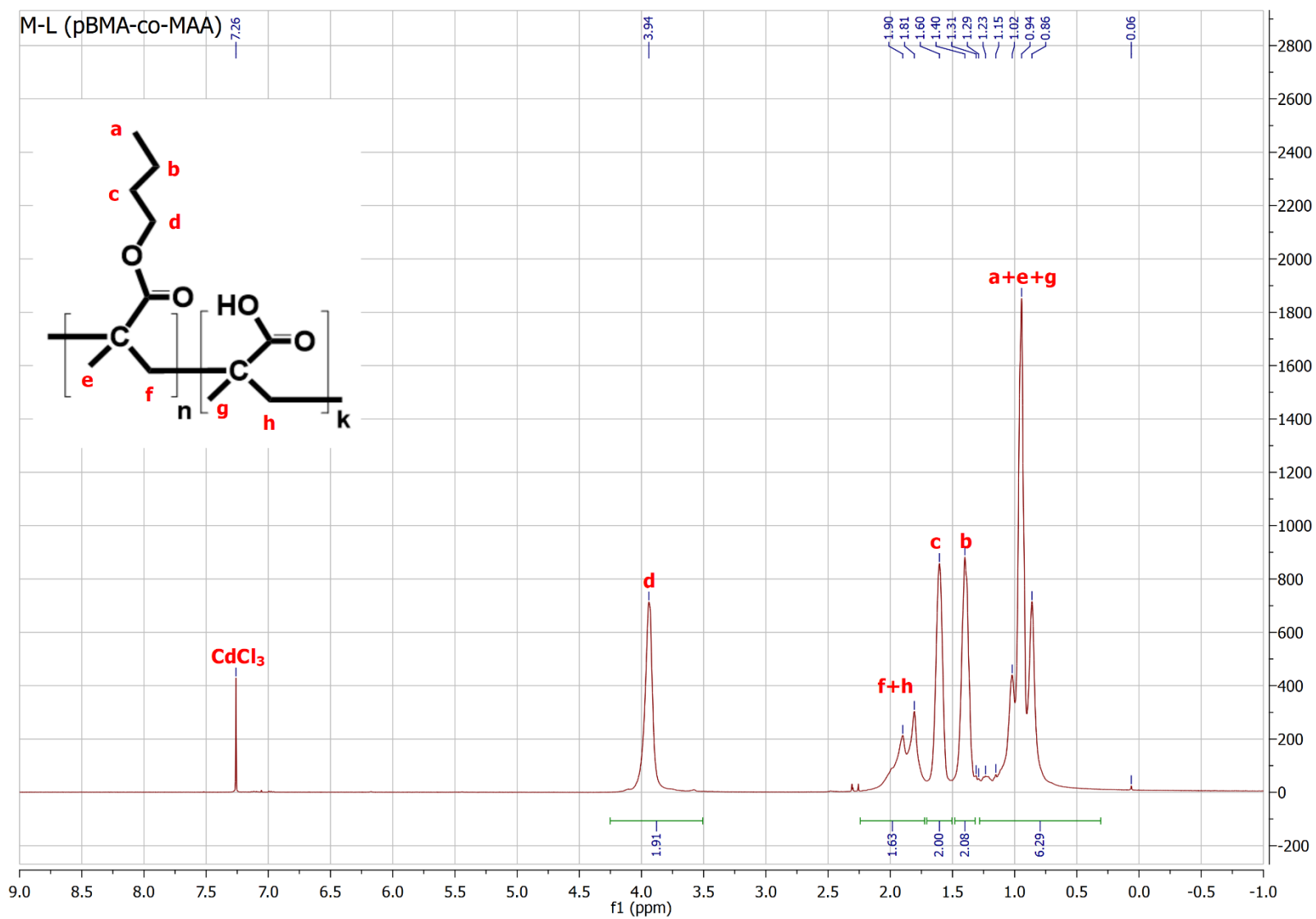


Figure S6. ^1H NMR spectrum of M-L copolymer (pBMA-co-MAA) in CdCl_3 .

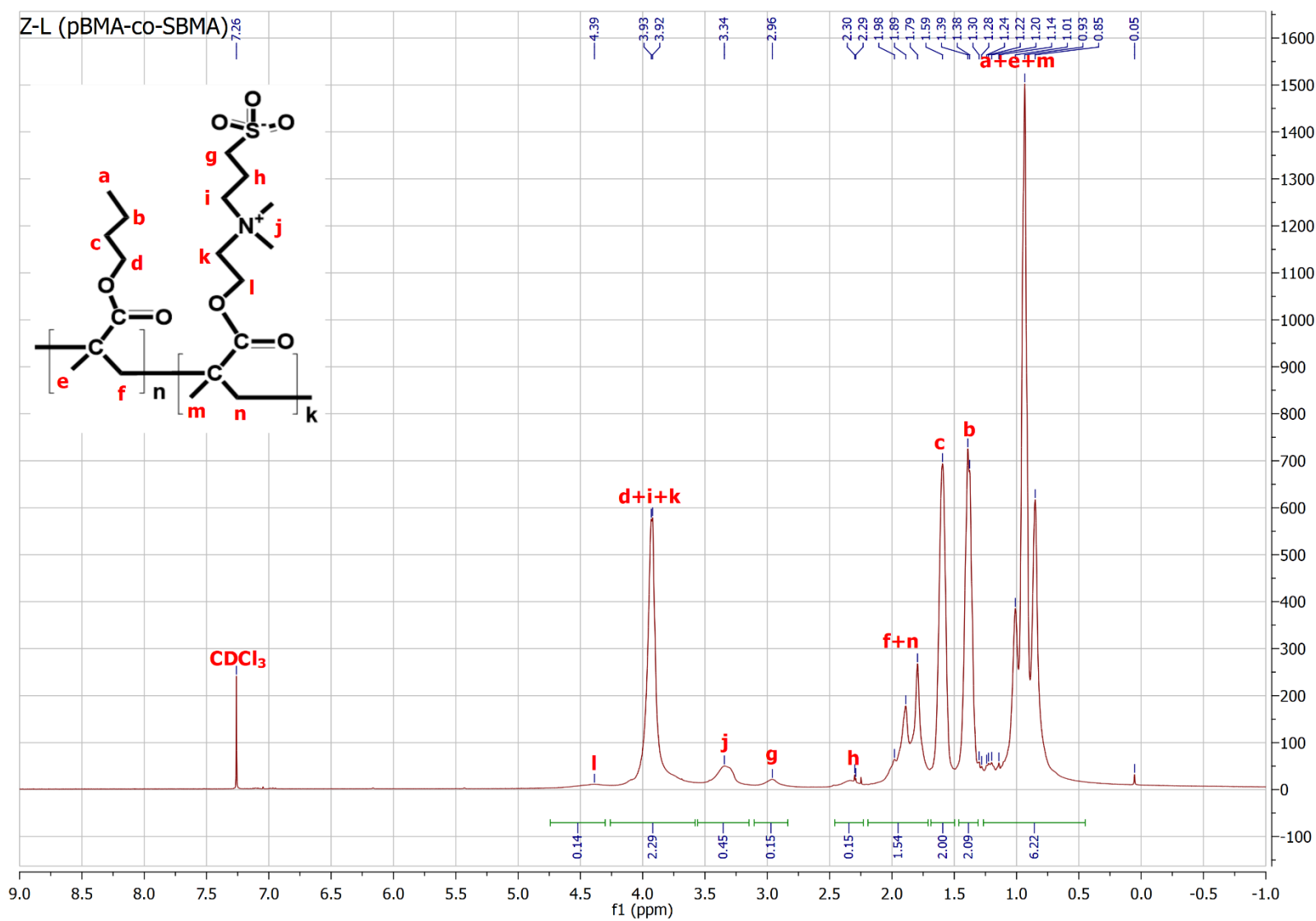


Figure S7. ^1H NMR spectrum of Z-L copolymer (pBMA-co-SBMA) in CDCl_3 .

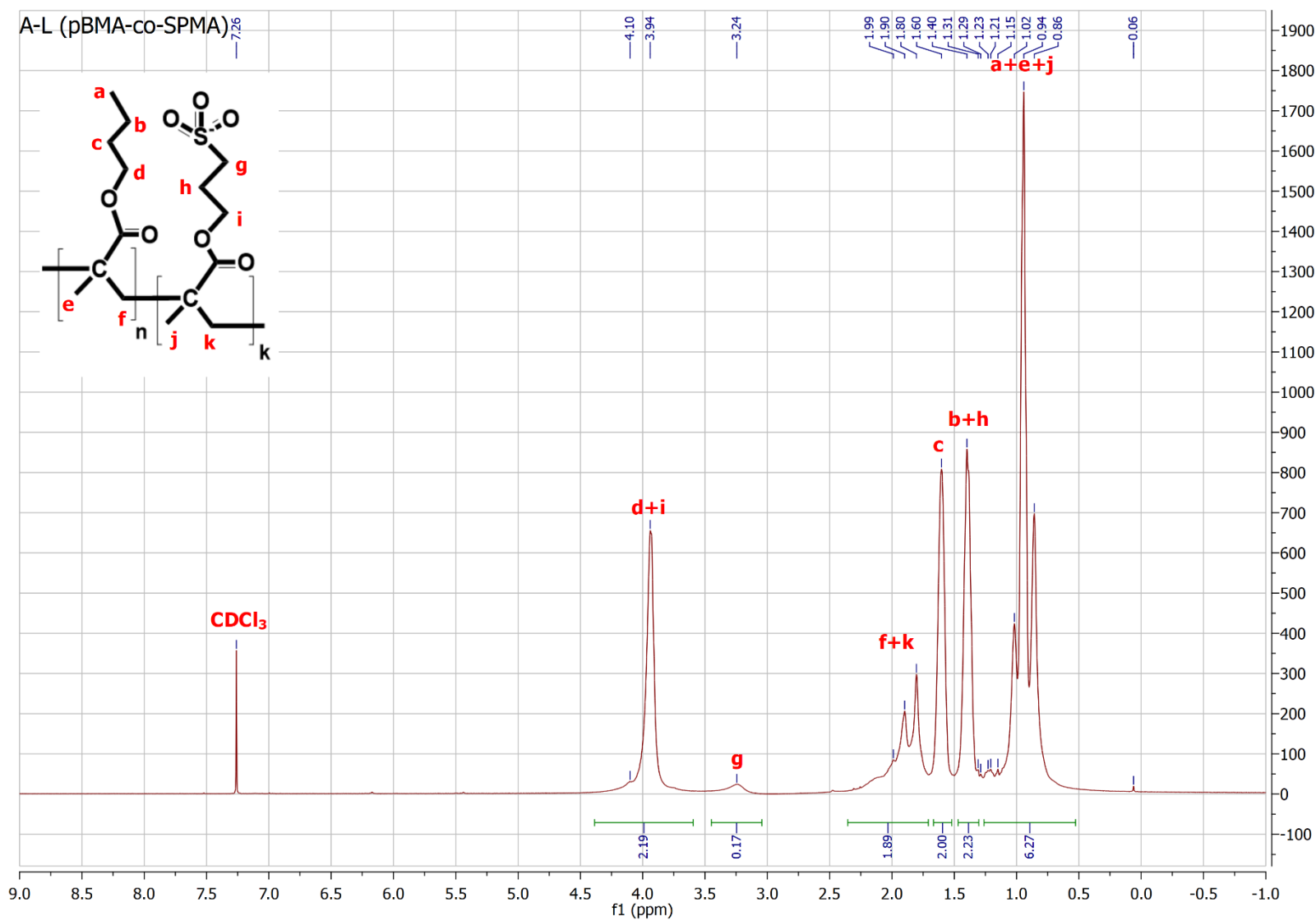


Figure S8. ^1H NMR spectrum of A-L copolymer (pBMA-co-SPMA) in CDCl_3 .

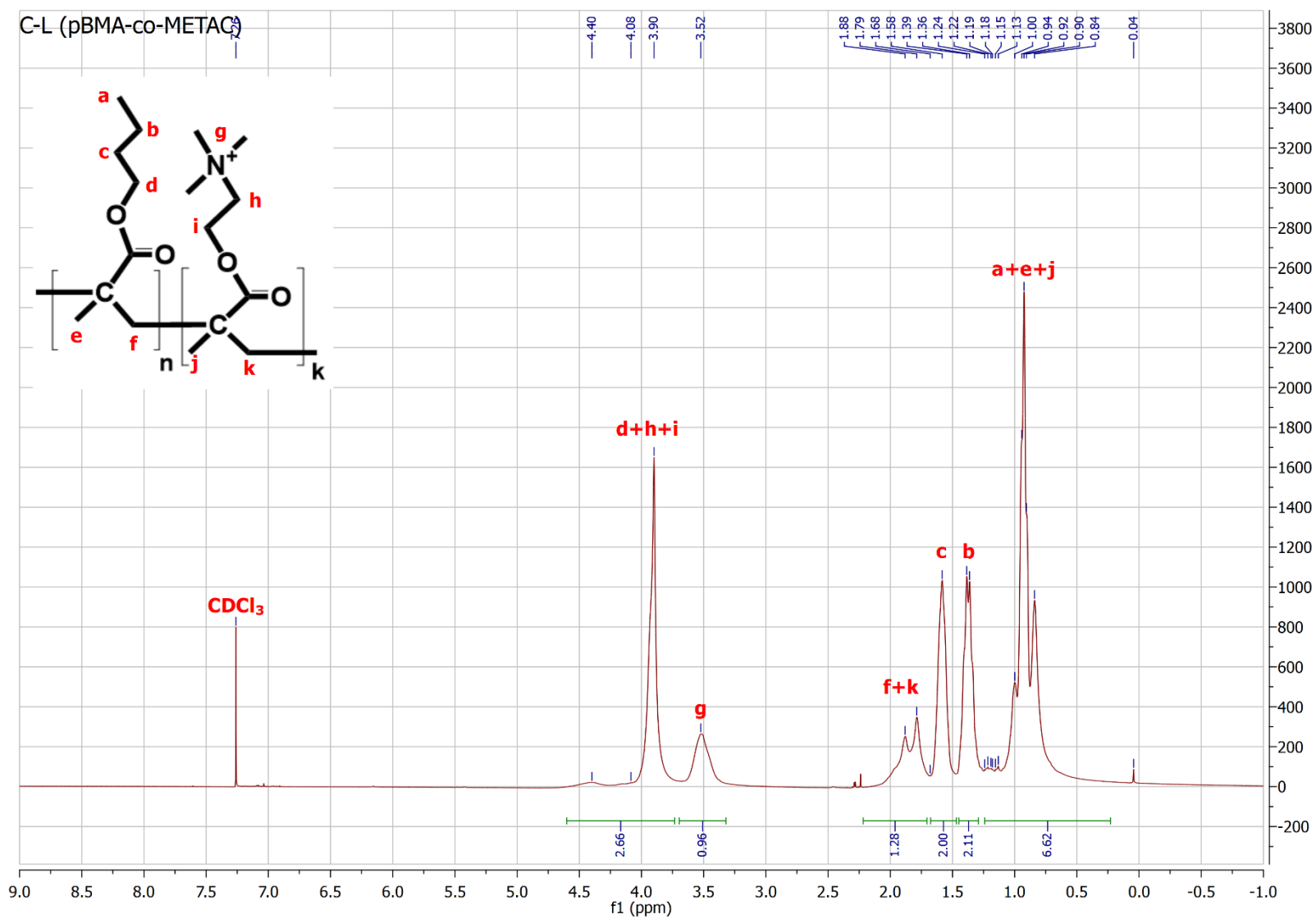


Figure S9. ^1H NMR spectrum of C-L copolymer (pBMA-co-METAC) in CDCl_3 .

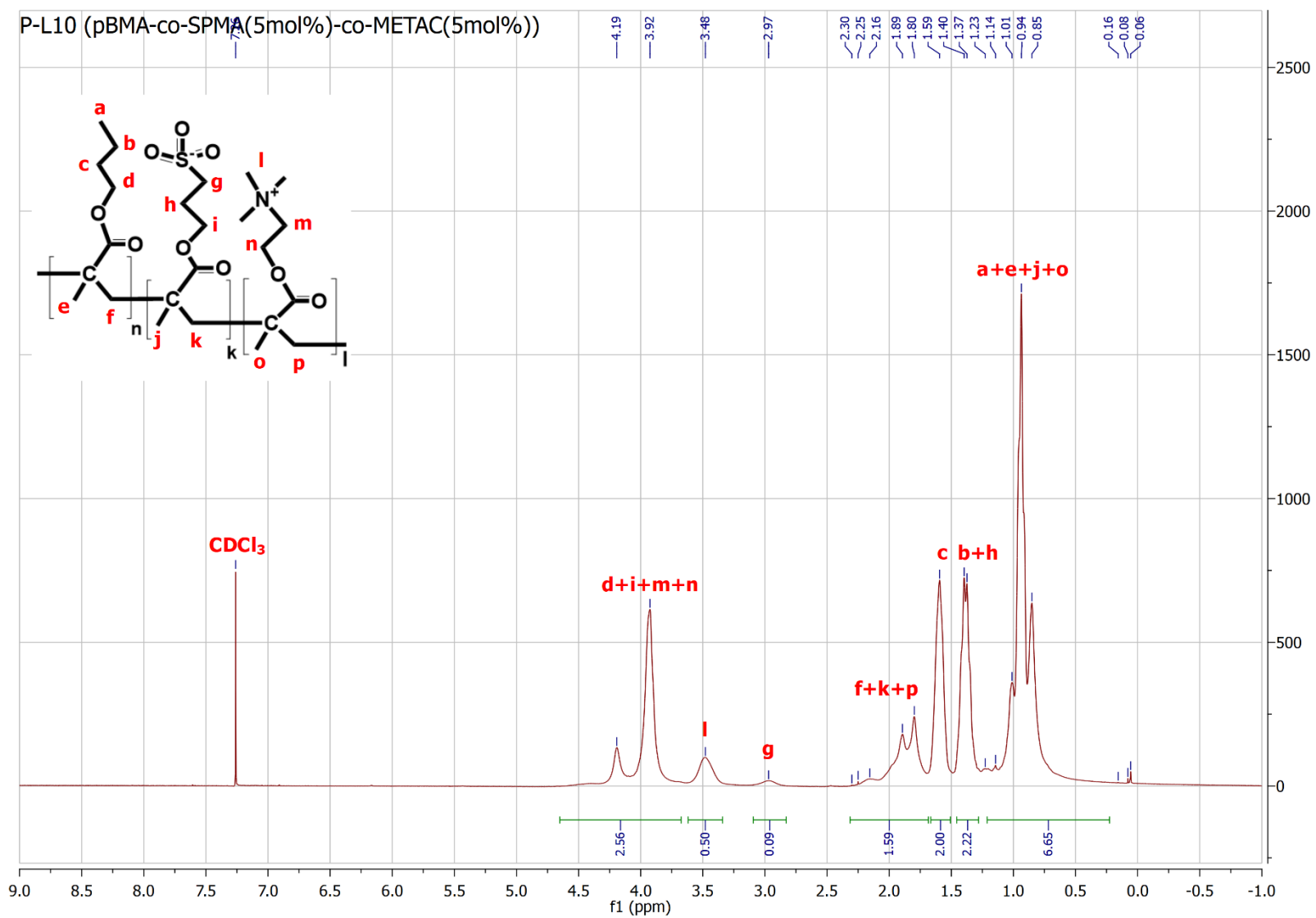


Figure S10. ¹H NMR spectrum of P-L10 copolymer (pBMA-co-SPMA_{5mol%}-co-METAC_{5mol%}) in CdCl₃.

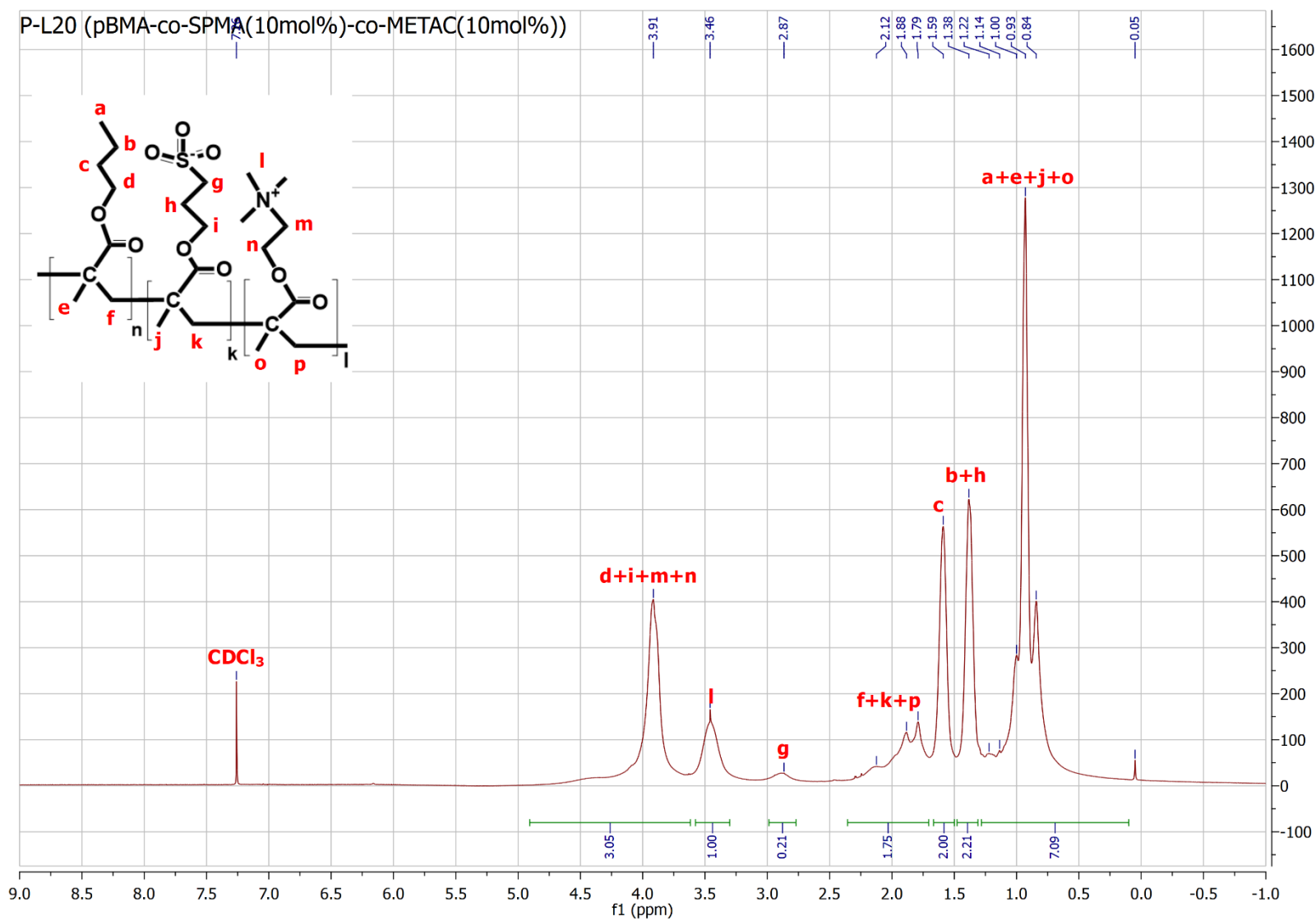


Figure S11. ^1H NMR spectrum of P-L20 copolymer (pBMA-co-SPMA_{10mol%}-co-METAC_{10mol%}) in CDCl₃.

3. SEC TRACES OF POLYMERS

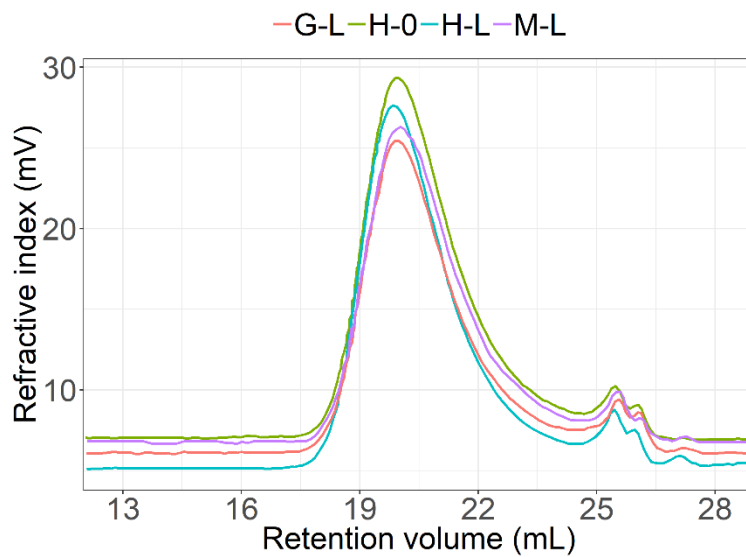


Figure S12. SEC traces of polymers G-L, H-0, H-L, M-L. Refractive index (mV) vs Retention Volume (mL).

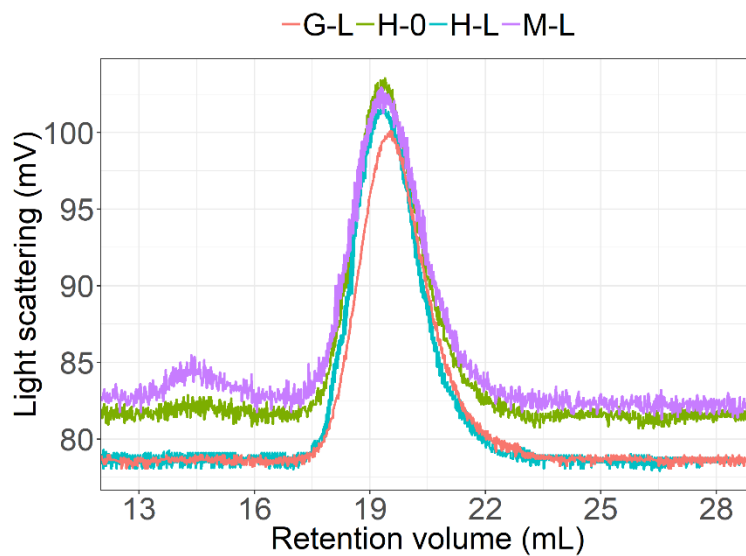


Figure S13. SEC traces of polymers G-L, H-0, H-L, M-L. Light scattering (mV) vs Retention Volume (mL).

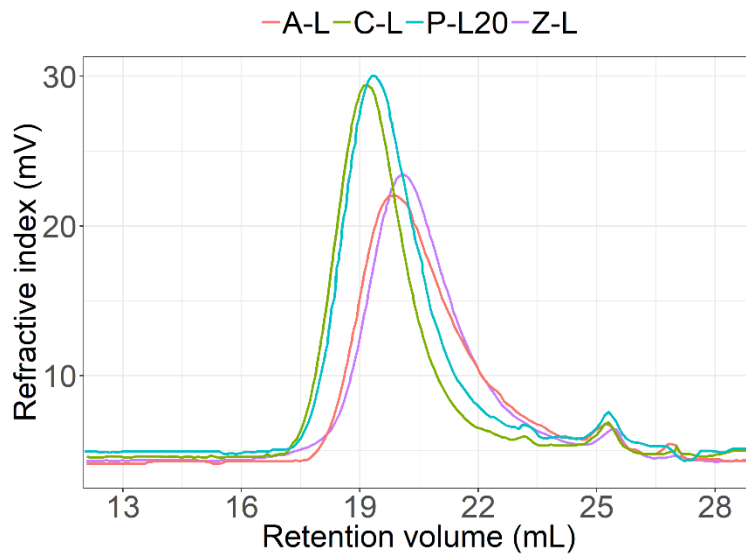


Figure S14. SEC traces of polymers A-L, C-L, P-L20, Z-L. Refractive index (mV) vs Retention volume (mL).

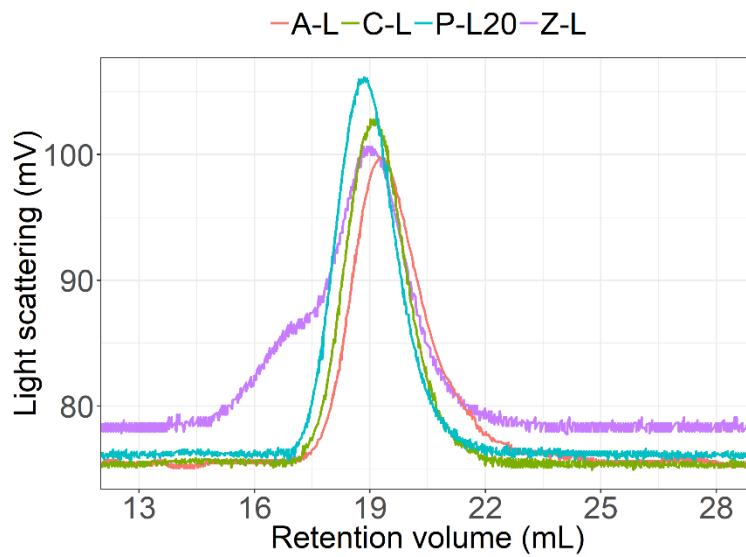


Figure S15. SEC traces of polymers A-L, C-L, P-L20, Z-L. Light scattering (mV) vs Retention volume (mL).

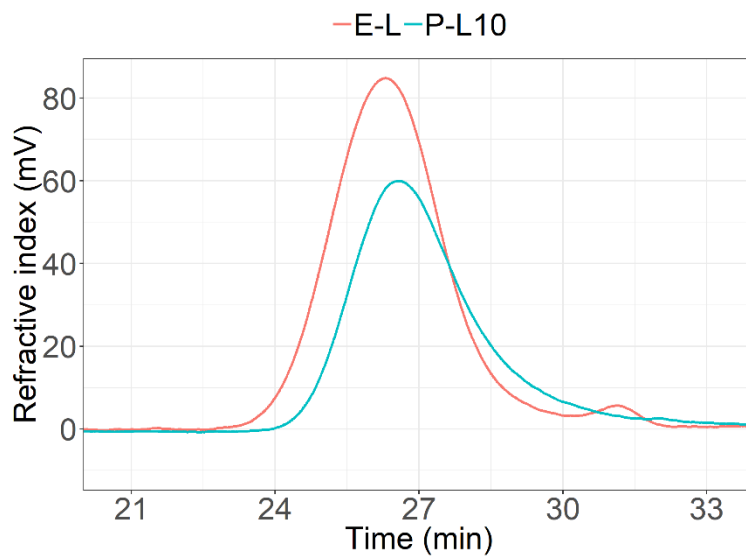


Figure S16. SEC traces of polymers E-L, P-L10. Refractive index (mV) vs Time (min).

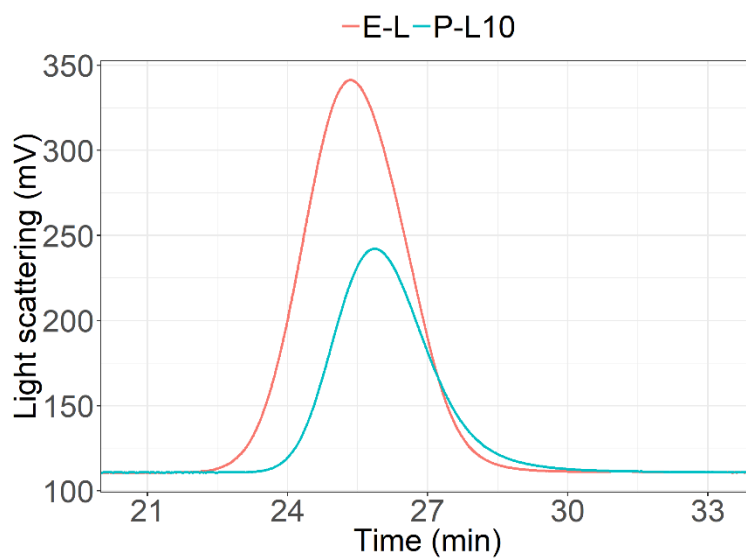


Figure S17. SEC traces of polymers E-L, P-L10. Light scattering (mV) vs Time (min).

4. SURFACE ENERGY DERIVATIONS FOR UNDERWATER CONTACT ANGLE MEASUREMENTS

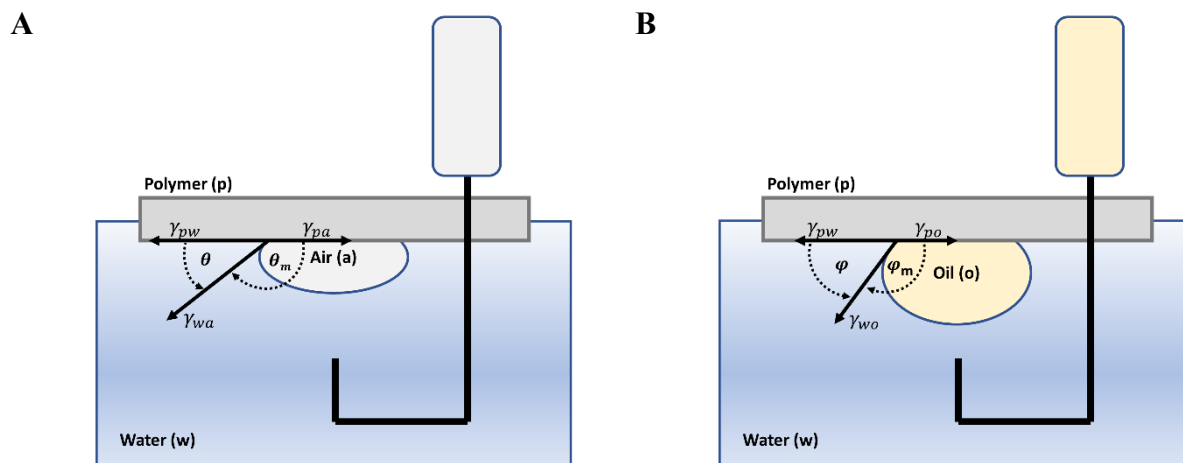


Figure S18. Schematic representation of underwater contact angles measurements using air bubble (A) and silicone oil droplet (B). θ_m , ϕ_m in degrees is the measured angle between the polymer surface and the air bubble/oil droplet inside the probing liquid. Larger measured angle inside the bubble/droplet corresponds to higher surface wettability. The actual contact angles used in surface energy calculations are expressed as $\theta = 180^\circ - \theta_m$ for air bubble and $\phi = 180^\circ - \phi_m$ for oil droplet.

ESTIMATION OF DISPERSIVE COMPONENT OF SFE OF HYDRATED POLYMER γ_{pa}^d :

Young's equation of air bubble:	Young's equation of oil droplet:
$\theta = 180^\circ - \theta_m$ $\gamma_{pa} - \gamma_{pw} - \gamma_{wa} \cos \theta = 0$ $\gamma_{pa} - \gamma_{pw} = \gamma_{wa} \cos \theta$ $\gamma_{pa} - \gamma_{po} + \gamma_{wo} \cos \varphi = \gamma_{wa} \cos \theta$ $-\gamma_{oa} + 4 \frac{\gamma_{pa}^d \gamma_{oa}^d}{\gamma_{pa}^d + \gamma_{oa}^d} + \gamma_{wo} \cos \varphi = \gamma_{wa} \cos \theta$	$\varphi = 180^\circ - \varphi_m$ $\gamma_{po} - \gamma_{pw} - \gamma_{wo} \cos \varphi = 0$ $\gamma_{pw} = \gamma_{po} - \gamma_{wo} \cos \varphi$
$4 \frac{\gamma_{pa}^d \gamma_{oa}^d}{\gamma_{pa}^d + \gamma_{oa}^d} = \gamma_{wa} \cos \theta - \gamma_{wo} \cos \varphi + \gamma_{oa}$	<p>Wu's harmonic mean estimation of interfacial energy at polymer-oil interface:</p>
<p>(...)</p> $\gamma_{pa}^d = \frac{\gamma_{oa}(\gamma_{wa} \cos \theta - \gamma_{wo} \cos \varphi) + \gamma_{oa}^2}{\gamma_{wo} \cos \varphi - \gamma_{wa} \cos \theta + 3\gamma_{oa}}$ <p><u>Where:</u></p> $\gamma_{oa} = \gamma_{oa}^d = 19.7 \frac{mN}{m}$ $\gamma_{wa} = 72.8 \frac{mN}{m}$ $\gamma_{wo} = 37.8 \frac{mN}{m}$	$\gamma_{po} = \gamma_{pa} + \gamma_{oa} - 4 \frac{\gamma_{pa}^d \gamma_{oa}^d}{\gamma_{pa}^d + \gamma_{oa}^d}$ $- 4 \frac{\gamma_{pa}^p \gamma_{oa}^p}{\gamma_{pa}^p + \gamma_{oa}^p} (\sim 0)^*$ $\gamma_{po} = \gamma_{pa} + \gamma_{oa} - 4 \frac{\gamma_{pa}^d \gamma_{oa}^d}{\gamma_{pa}^d + \gamma_{oa}^d}$ <p>(*) Silicone oil does not have polar contributions of energy, thus $\gamma_{oa}^p = 0$.</p>

ESTIMATION OF POLAR COMPONENT OF SFE OF HYDRATED POLYMER γ_{pa}^p :

Young's equation of air bubble:	Wu's harmonic mean estimation of interfacial energy at polymer-water interface:
$\theta = 180^\circ - \theta_m$ $\gamma_{pa} - \gamma_{pw} - \gamma_{wa} \cos \theta = 0$ $\gamma_{pa} - \gamma_{pw} = \gamma_{wa} \cos \theta$ $-\gamma_{wa} + 4 \frac{\gamma_{pa}^d \gamma_{wa}^d}{\gamma_{pa}^d + \gamma_{wa}^d} + 4 \frac{\gamma_{pa}^p \gamma_{wa}^p}{\gamma_{pa}^p + \gamma_{wa}^p} = \gamma_{wa} \cos \theta$ <p>(...)</p> $\gamma_{pa}^p = \frac{\gamma_{wa}^p (\gamma_{wa} (1 + \cos \theta) - 4 \frac{\gamma_{pa}^d \gamma_{wa}^d}{\gamma_{pa}^d + \gamma_{wa}^d})}{4 \gamma_{wa}^p + 4 \frac{\gamma_{pa}^d \gamma_{wa}^d}{\gamma_{pa}^d + \gamma_{wa}^d} - \gamma_{wa} (1 + \cos \theta)}$ <p><u>Where:</u></p> $\gamma_{wa}^p = 46.4 \frac{mN}{m}$ $\gamma_{wa}^d = 26.4 \frac{mN}{m}$ $\gamma_{wa} = 72.8 \frac{mN}{m}$ $\gamma_{pa}^d = \frac{\gamma_{oa} (\gamma_{wa} \cos \theta - \gamma_{wo} \cos \varphi) + \gamma_{oa}^2}{\gamma_{wo} \cos \varphi - \gamma_{wa} \cos \theta + 3 \gamma_{oa}}$	$\gamma_{pw} = \gamma_{pa} + \gamma_{wa} - 4 \frac{\gamma_{pa}^d \gamma_{wa}^d}{\gamma_{pa}^d + \gamma_{wa}^d}$ $- 4 \frac{\gamma_{pa}^p \gamma_{wa}^p}{\gamma_{pa}^p + \gamma_{wa}^p}$

ESTIMATION OF TOTAL SFE OF HYDRATED POLYMER γ_{pa}^{TOT} :

$$\gamma_{pa}^{TOT} = \gamma_{pa}^d + \gamma_{pa}^p$$

ESTIMATION OF IFE POLYMER / WATER γ_{pw} :

$$\gamma_{pw} = \gamma_{pa}^{TOT} + \gamma_{wa} - 4 \frac{\gamma_{pa}^d \gamma_{wa}^d}{\gamma_{pa}^d + \gamma_{wa}^d} - 4 \frac{\gamma_{pa}^p \gamma_{wa}^p}{\gamma_{pa}^p + \gamma_{wa}^p}$$

5. BARNACLE CULTURING

Adult barnacles of *B. improvisus* were allowed to release stage one nauplii which were attracted to a light source and collected with a plastic pipette to a solution of *Tetraselmis suecica*. After collecting sufficient nauplii they were transferred to a 10 L plastic bucket containing 22 ppt seawater with 35.6 mg*L⁻¹ of streptomycin sulphate and 21.9 mg*L⁻¹ of penicillin G and kept in the incubator at 28 °C. Larvae was fed every 2-3 days using *Tetraselmis suecica* and *Thalassiosira pseudonana* until metamorphosis to the cyprid stage and subsequently filtered using a 250 µm mesh. Filtered cyprids were transferred to a petri dish containing 22 ppt artificial seawater (ASW) and used immediately for leaching and settlement experiments.

6. SINGLE SETTLEMENT EXPERIMENT USING BARNACLE CYPRIS LARVAE AND COMPARISON WITH META-ANALYSIS APPROACH

In a single settlement experiment eight slides per polymer set were used. Leached slides were transferred to quadriPERM dishes and on each slide 0.5 mL of ASW (22 ppt) was added, followed by addition of 20 ± 2 freshly filtered larvae (0-day) in a minimal volume of ASW. The dishes were then wrapped with paper towel, covered with aluminium foil and placed in the incubator at 28°C

in the dark. After 72 h dishes were carefully removed from incubator and number of settled cyprids was enumerated using a dissection microscope.

Figure S19 presents settlement data as percent of settled cyprids of *B. improvisus*. Settlement differed across all surfaces (Welch ANOVA $F_{9,70} = 40.93$, $p \leq 0.001$) and in general surfaces could be divided based on their antifouling performance into two distinct groups following their ionic/non-ionic character (Games-Howell tests, $p \leq 0.001$). Smallest settlement was observed on ionic polymers i.e. Z-L ($9.98 \pm 6.07\%$), A-L ($8.27 \pm 6.39\%$), C-L ($1.32\% \pm 2.58\%$), P-L20 ($0.63 \pm 1.23\%$) and the non-ionic polymer E-L with PEG functionality ($3.19 \pm 3.25\%$).

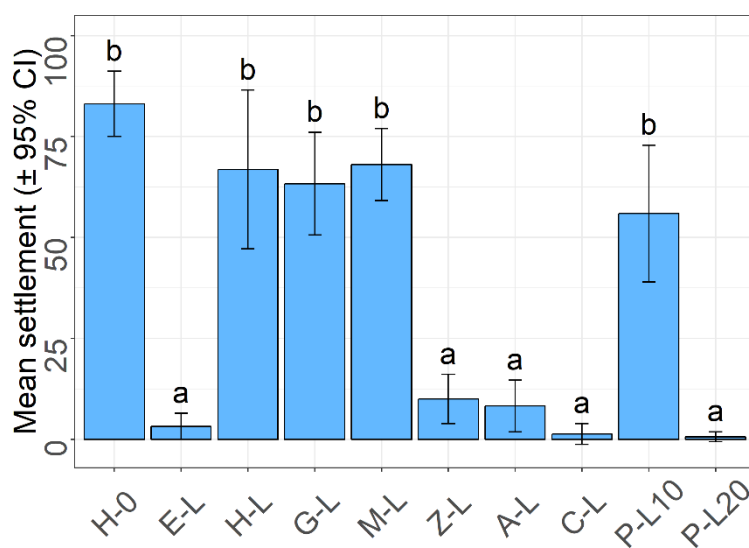
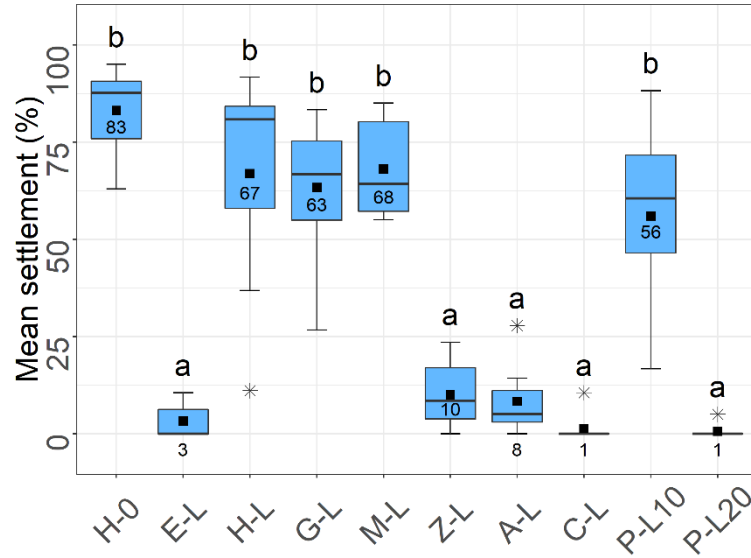


Figure S19. Mean percent settlement with 95% CIs of *B. improvisus*. Letters represent pairwise comparisons and bars that do not share a letter are significantly different.

In order to compare settlement results obtained with both statistical approaches and graphically visualize any potential trends, the mean settlement from single experiment and summary effect sizes derived from meta-analysis were plotted on box plots (Figure S20).

(A)



(B)

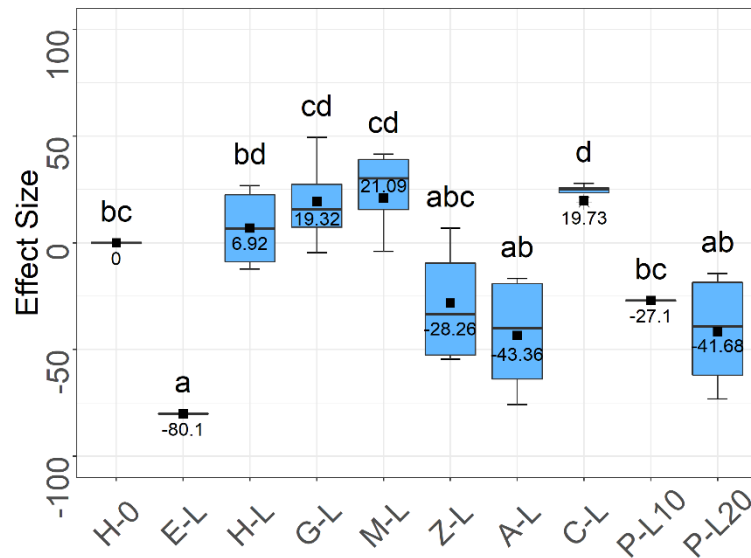


Figure S20. (A) Box plot presenting single settlement experiment results of cyprids larvae of *B. improvisus*. (B) Box plot presenting settlement results from four independent studies combined using meta-analysis. Black squares inside the boxes together with attached labels represent the mean settlement or summary effect sizes. Outliers are presented with asterisks. Letters indicate pairwise comparisons and boxes that do not share a letter are significantly different.

7. BIOFILM GROWTH AND REMOVAL

Figure S21 presents the results of biofilm (biomass) growth after 14 days of immersion in slime farm as determined by fluorescence plate reader and expressed using relative fluorescence units (RFUs). The amount of biomass varied significantly among surfaces (one-way ANOVA using square-root transformed data $F_{9,20} = 10.12$, $p \leq 0.001$). The smallest amount of biomass was recorded on polymers A-L, Z-L and P-L20, whilst the highest biomass growth was on PDMS (Dow Corning 3-0213).

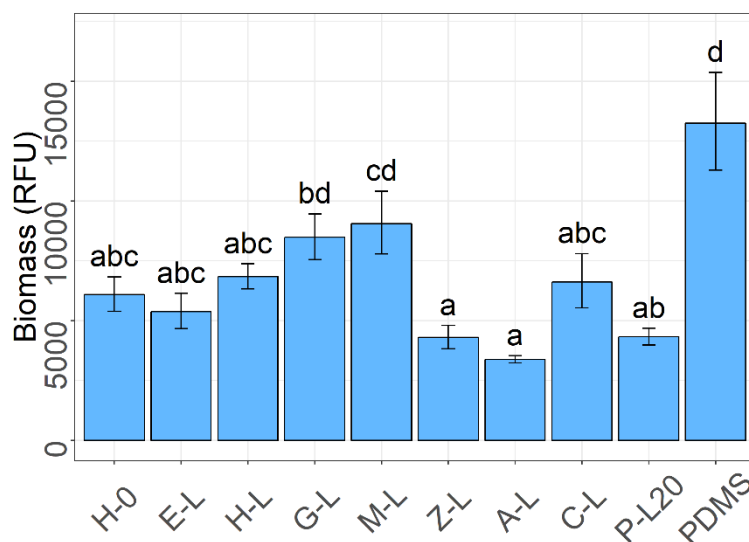


Figure S21. Biomass generated by multispecies biofilm after 14 days of immersion in the slime farm quantified as relative fluorescence units (RFUs) using fluorescence plate reader. Mean RFUs were calculated from three slides using square root transformed data. Error bars represent SEs of the mean. Letters indicate Tukey's pairwise comparisons and points that do not share a letter are significantly different.

Coatings with attached biofilm were exposed to 8.2 Pa wall shear stress and the amount of retained biomass was measured directly after testing (Figure S22). There was a significant variation in the amount of biomass retained among the polymers after exposure to flow (one-way ANOVA using square-root transformed data $F_{9,20} = 18.9$, $p \leq 0.001$). Furthermore, all polymers except polymer M-L retained significantly lower biomass after flow than the PDMS (Tukey tests, $p > 0.05$).

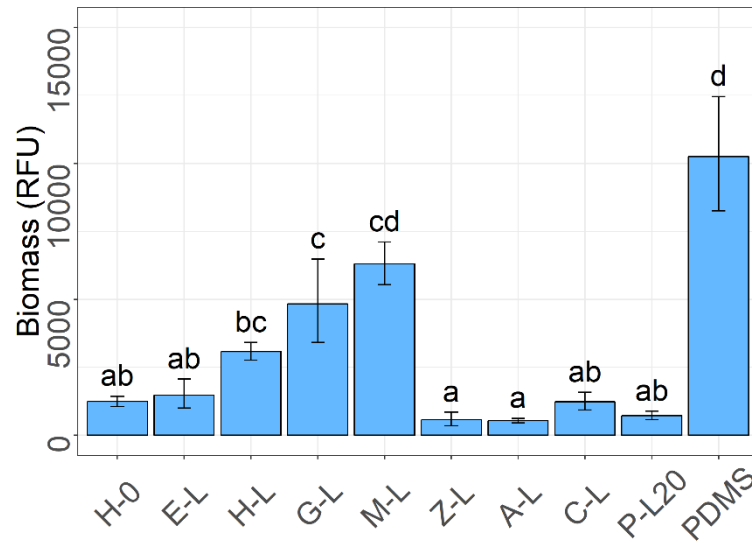


Figure S22. Amount of remaining biomass after removal in the water channel quantified as relative fluorescence units (RFUs) using fluorescence plate reader. Mean RFUs were determined from three replicates after exposure to flow (8.2 Pa) and were calculated using square root transformed data. Letters indicate Tukey's pairwise comparisons and points that do not share a letter are significantly different.

REFERENCES

- (1) Khandelwal, D.; Hooda, S.; Brar, A. S.; Shankar, R. 1D and 2D NMR Studies of Isobornyl Acrylate – Methyl Methacrylate Copolymers. *Journal of Molecular Structure* **2011**, *1004*, 121-130.
- (2) Harrell, M. L.; Bergbreiter, D. E. Using ^1H NMR Spectra of Polymers and Polymer Products to Illustrate Concepts in Organic Chemistry. *Journal of Chemical Education* **2017**, *94*, 1668-1673.