

Electronic Supplementary Information

Amino modified 2-oxazoline copolymers for complexation with DNA

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Optimization of the addition reaction of aminothiols onto vinyl double bonds present in the substituents of P(iPrOx₇₀-co-MetOx₁₅-co-ButEnOx₁₅):

The addition of cysteamine or 2-(butylamino)ethanethiol onto vinyl double bonds present in the copolymers was possible only after the photosensitizer was added to the system. In the case of cysteamine, it was necessary to add the photosensitizer DMPA (0.05 equiv) and then the highest substitution efficiency achieved was ~70%. 2-(Butylamino)ethanethiol was adduced to the double bond of the copolymer substituent after a tenfold increase in the amount of the photosensitizer DMPA (0.5 equiv.) and after the addition of an additional photosensitizer benzophenone (0.5 equiv) and a simultaneous increase in the amount of thiol with respect to C=C (10 equiv). 2-(Butylamino)ethanethiol was added to the double bond of the copolymer substituent after a tenfold increase in the amount of photosensitizer DMPA (0.5 equiv) and after the addition of an additional photosensitizer benzophenone (0.5 equiv) and a simultaneous increase in the amount of thiol with respect to C=C (10 equiv). The highest substitution yield achieved by this reaction was ~80%. An additional reaction was also carried out using thioacetic acid, a thiol that does not contain an amino group. Thioacetic acid was added to the double bond of the copolymer substituent under standard conditions described in the literature (without the addition of a photosensitizer) with an efficiency of ~20%. This means that the presence of an amino group in the thiol affects the efficiency of the thio-click reaction, and the addition of a photosensitizer seems to be necessary for an efficient addition reaction to the double bond.

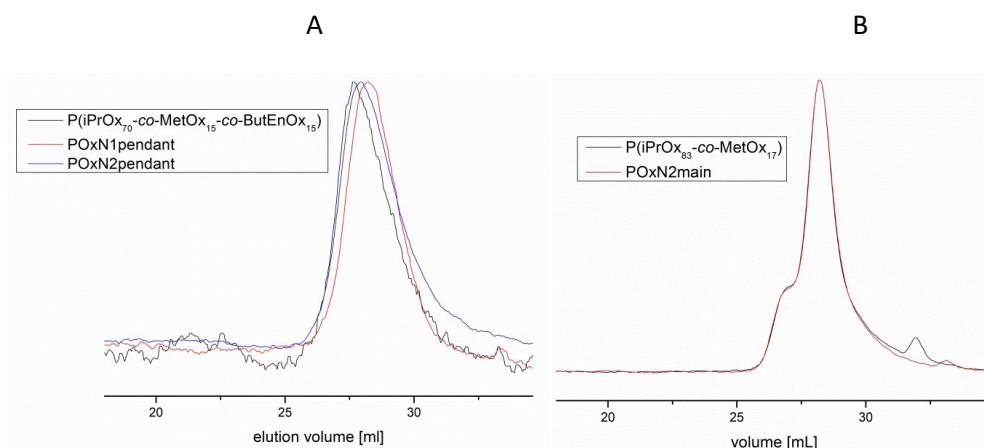


Fig. S1. SEC traces (RI signal) of P(iPrOx₇₀-co-MetOx₁₅-co-ButEnOx₁₅), POxN1pendant and POxN2pendant (A), and P(iPrOx₈₃-co-MetOx₁₇) and POxN2main (B). DMF with 5 mmol LiBr as eluent, 1 mL/min.

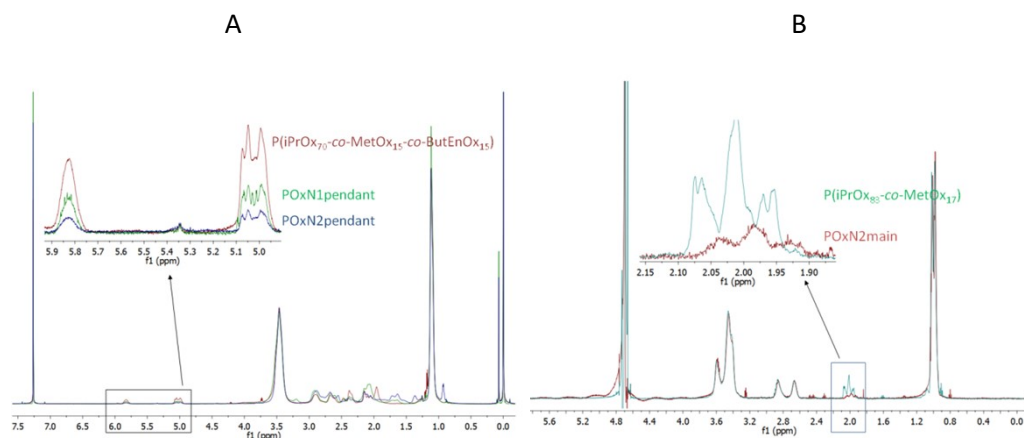


Fig. S2. ¹H NMR of P(iPrOx₇₀-co-MetOx₁₅-co-ButEnOx₁₅), POxN1pendant and POxN2pendant (CDCl₃) (A), and P(iPrOx₈₃-co-MetOx₁₇) and POxN2main (D₂O) (B). The signal intensities of the spectra were normalized to the peak of the polymer backbone signal at around 3.5 ppm.

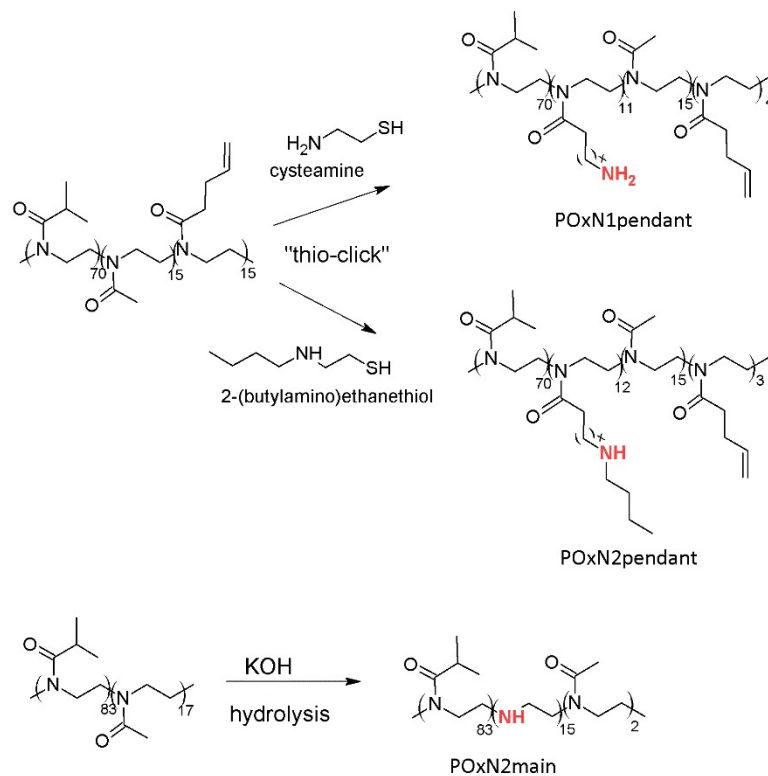


Fig. S3. A synthetic scheme showing the post-polymerization modifications of copolymers.

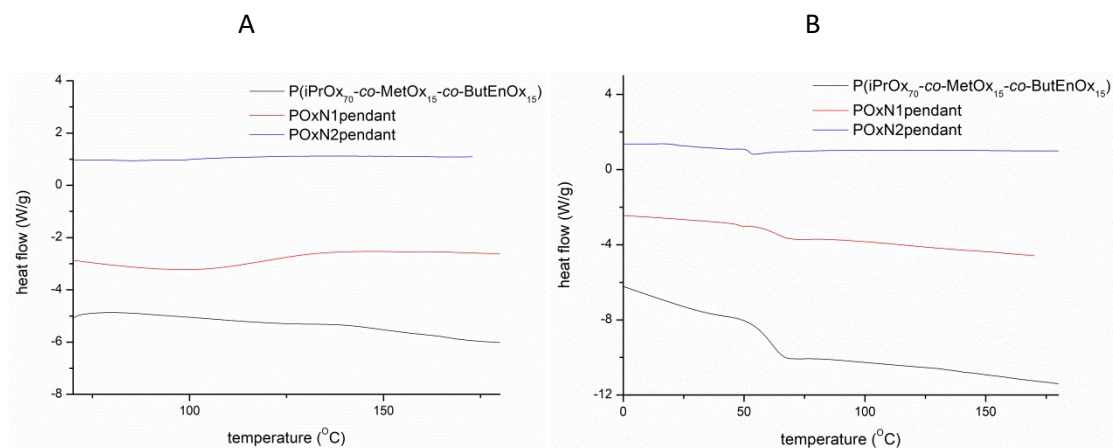


Fig. S4. DSC curves of copolymers incubated at 180°C for 12h (A) and copolymers after rapid quenching (B).

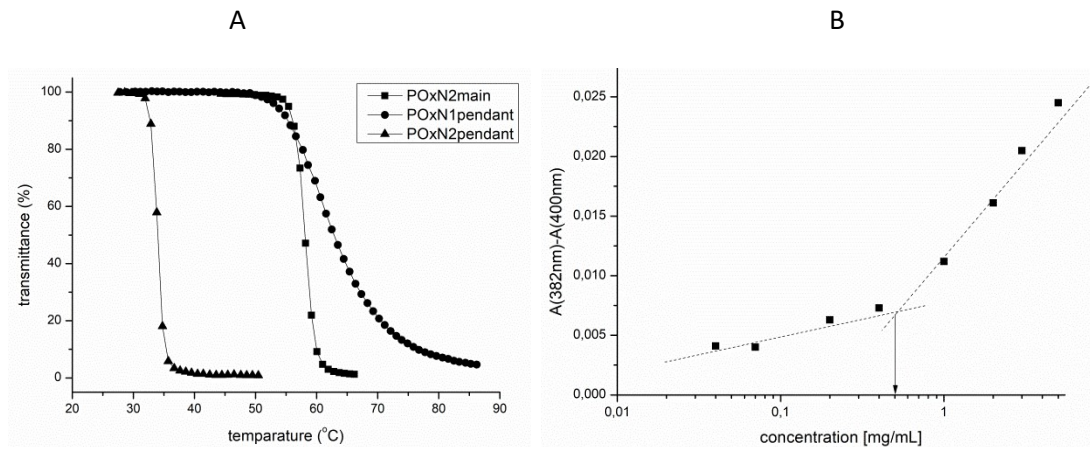


Fig. S5. Uv vis studies: T_{CP} (A), C_{ac} of POxN2pendant (probe with DPH, UV Vis measurement) (B).

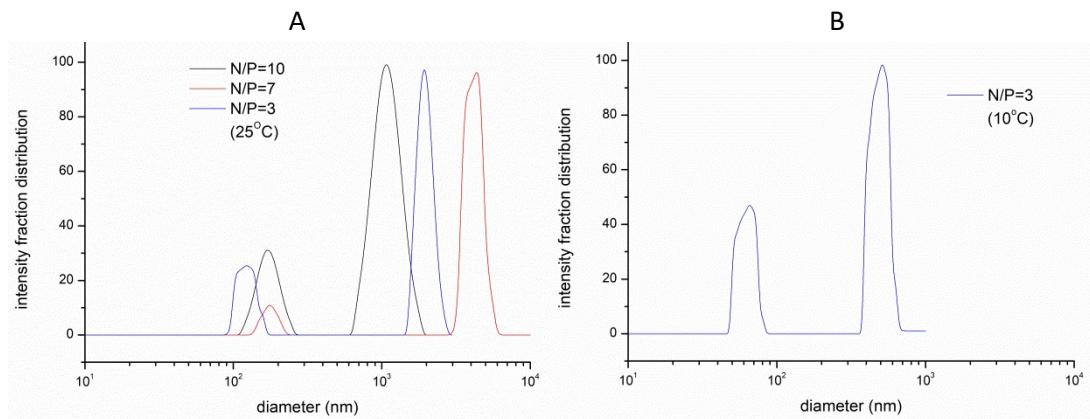


Fig. S6. Intensity fraction distribution of the hydrodynamic diameter for aqueous solutions (7.5 g/L) of DNA-POxN1pendant polyplexes, at different N/P, at 25°C (A) and 10°C (B).