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New thermoresponsive polyester-graft-polyoxazolines based on sulfonyl chloride macroinitiators

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§1. Materials and methods:

Materials and reagents

Monomers including 2-ethyl-, 2-isopropyl-2-oxazoline (Aldrich) and triethylamine, were distilled over calcium hydride. Decane-1,10-diol and propane-1,3-diol (Acros Organics) were purified by vacuum distillation. Poly(ethylene glycol) (PEG, M_n=200, Merck), poly(propylene glycol) (PPG, M_n=250, Merck) were dried by azeotropic distillation with benzene and stored over molecular sieves (4Å). 5-(Chlorosulfonyl)isophthaloyl dichloride was synthesized from 5-Sulfoisophthalic acid (monosodium salt, J&K) as reported [R. Navarro, M. P. Perrino, M. Gomez and H. Reinecke, *Macromol*., 2010, **43**, 2377]. Solvents were dried using standard methods.

Characterization of chemicals

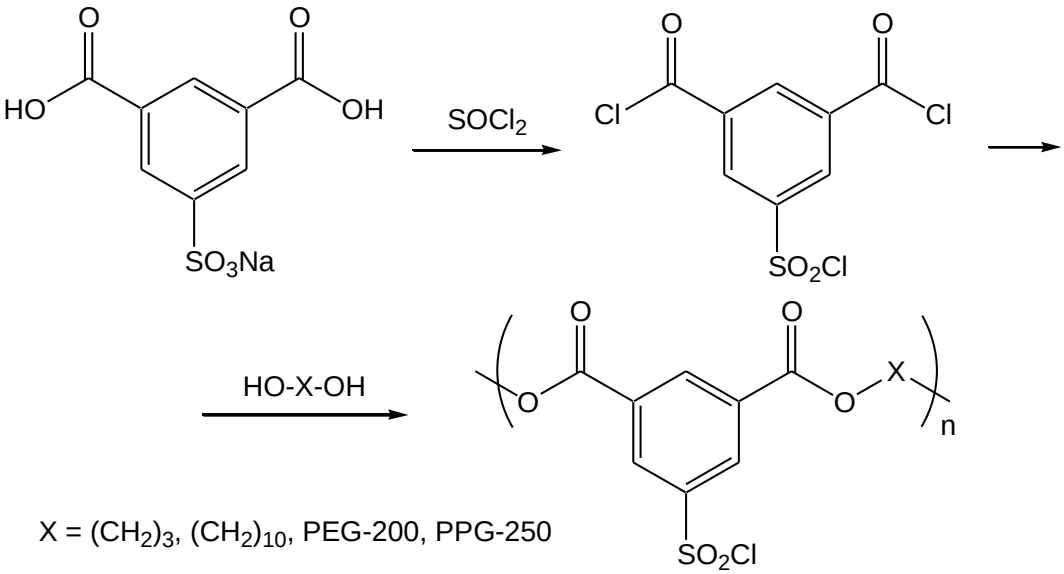
The ^{1}H NMR spectra were obtained on the Bruker AC400 instrument (400 MHz) in $CDCl_3$. Dialysis of polymers was performed using CellaSep dialysis tubes with MWCO 3500 D. Chromatographic analysis of polyester macroinitiators was performed on the Shimadzu LC-20AD chromatograph with TSKgel G5000HHR column (5 μm, 7.8×300 mm, TosohBioscience), using refractometric and scattering detectors. LiBr solution (0.1 mol dm^{-3}) in DMF at 60 °C was used as an eluent with the flow rate of 1 ml min^{-1}. On the other hand, after the alkaline hydrolysis of graft-copolymers, the linear polyoxazoline chains obtained were studied using the Shimadzu Prominence LC-20 instrument equipped with refractometric RID-10A detector and the Shim-pack GPC-80M column. THF was used as the eluent at 40°C with 1.0 ml min^{-1} flow rate. The calibration curve was calculated using polyethylene glycol standards.

Preparation of poly{1,10-decamethylene-[5-(chlorosulfonyl)isophthalate]} macroinitiator. A solution of 5-(chlorosulfonyl)isophthaloyl dichloride (3.01 g, 0.01 mol) and decane-1,10-diol (1.71 g, 0.01 mol) in dichloromethane (20 ml) was cooled to 0 °C, then triethylamine (2 ml) was added with the dropping funnel on stirring. After 12 hours, the polyester was precipitated with methanol, then re-precipitated from the chloroform to methanol and dried. Macroinitiators based on propane-1,3-diol, PEG-200 and PPG-250 were prepared using the same procedure [A. B. Razina and A. V. Tenkovtsev, *J. Polym. Sci. Ser. B.*, 2019, **61**, 589]. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 9.01 (m, 1H), 8.83 (s, 2H), 4.43 (t, 4H), 1.83 (qu, 4H), 1.46-1.36 (m, 12H).

Poly{1,3-trimethylene-[5-(chlorosulfonyl)isophthalate]} macroinitiator. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 9.00-8.62 (m, 3H), 4.64 (m, 4H), 2.40 (m, 2H).

Poly{polyethylene glycol-200-[5-(chlorosulfonyl)isophthalate]} macroinitiator. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.48 (m, 1H), 8.40 (s, 2H), 4.55 (t, 2H), 3.83 (t, 2H), 3.66-3.36 (m, 8H).

Poly{polypropylene glycol-250-[5-(chlorosulfonyl)isophthalate]} macroinitiator ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 9.03-8.55 (m, 3H), 4.92-4.22 (m, 3H), 3.16-4.03 (m, 12H), 1.48-1.02 (m, 15H).



Scheme S1 Synthesis of polyester macroinitiators.

Preparation of polyester-graft-polyoxazolines A solution of the corresponding macroinitiator (0.2 g) in 1,2-dichloroethane (2 ml) was placed in a vial, and the appropriate amount of 2-alkyl-2-oxazoline (with the initiator-to-monomer ratio equalling 1:50 by functional groups) was added. The vial was sealed in argon atmosphere and heated at 100 °C for 120 hours. After that, the vial was opened, 50% pyrrolidine solution in dichloroethane (2 ml) was added, and the mixture was kept at room temperature for 24 hours. The solvent was removed in vacuum (0.1 Torr) at room temperature. Finally, the product was dissolved in ethanol, dialyzed against water for 24 hours and lyophilized.

Poly{1,10-decamethylene-[5-(chlorosulfonyl)isophthalate]}-graft-poly(2-ethyl-2-oxazoline) **1**. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.81 (s) 8,66 (s), 3,5 (m), 2,2-2,6 (m), 1.89-1.35 (m),1,12 (m).

Poly{1,10-decamethylene-[5-(chlorosulfonyl)isophthalate]}-graft-poly(2-isopropyl-2-oxazoline) **2**. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 3.62-3.32 (m, 4H), 3.01-2.57 (m, 1H), 1.13 (d, 6H).

Poly{1,3-trimethylene-[5-(chlorosulfonyl)isophthalate]}-graft-poly(2-ethyl-2-oxazoline) **3**. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 3.57-3.30 (m, 4H), 2.48-2.19 (dq, 2H), 1.10 (t, 3H).

Poly{1,3-trimethylene-[5-(chlorosulfonyl)isophthalate]}-graft-poly(2-isopropyl-2-oxazoline) **4**. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 3.62-3.34 (m, 4H), 3.02-2.56 (m, 1H), 1.14 (s, 6H).

Poly{polyethylene glycol-200-[5-(chlorosulfonyl)isophthalate]}-graft-poly(2-ethyl-2-oxazoline) **5**. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8,45 (s) 8,38 (s), 4,51 (t), 3,83 (t), 3.66-3,36 (m).

Poly{polyethylene glycol-200-[5-(chlorosulfonyl)isophthalate]}-graft-poly(2-isopropyl-2-oxazoline) **6**. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 3.60-3.33 (m, 4H), 3.01-2.55 (m, 1H), 1.11 (s, 6H).

Poly{polypropylene glycol-250-[5-(chlorosulfonyl)isophthalate]}-graft-poly(2-ethyl-2-oxazoline) **7**. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 3.57-3.37 (s, 4H), 2.50-2.24 (dq, 2H), 1.13 (s, 3H).

Poly{polypropylene glycol-250-[5-(chlorosulfonyl)isophthalate]}-graft-poly(2-isopropyl-2-oxazoline) **8**. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 3.61-3.36 (m, 4H), 2.99-2.58 (m, 1H), 1.13 (s, 6H).

Alkaline hydrolysis of graft-copolymers

Polymer sample (0.2 g) was dissolved in 2-ethoxyethanol (25 ml), then KOH (1 g, 0.025 mol) was added. The reaction mixture was stirred at 120 °C for 10 minutes. After cooling, aqueous 1M HCl was added in order to bring pH value to 7. Finally, the solution was purified by dialysis against water for 24 hours and lyophilized.

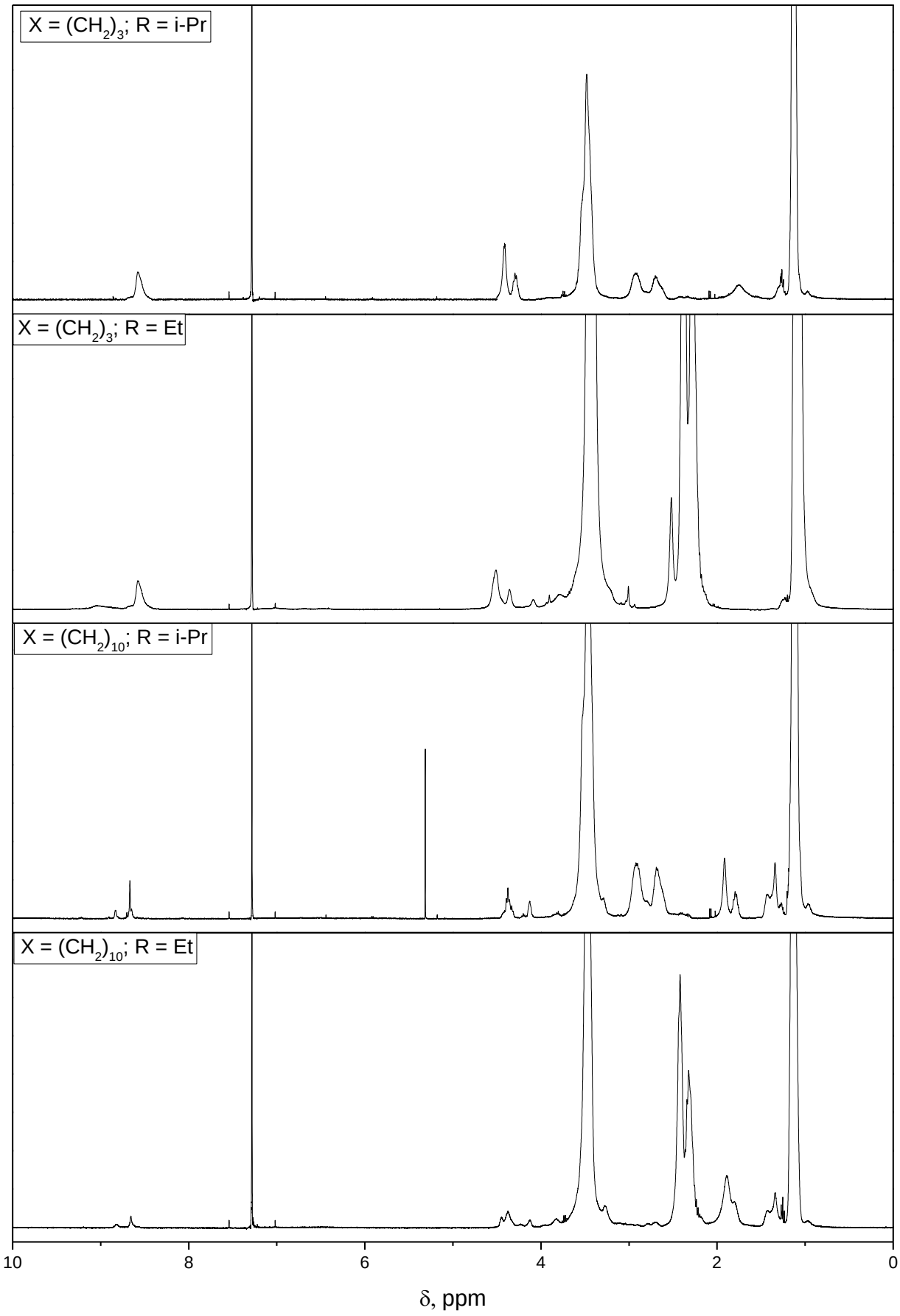
Determination of grafting density

Grafting density of synthesized graft-copolymers was determined using ^{1}H NMR spectral data analysis. At first, average degree of polymerization of grafted chains separated from polyester backbone by the alkaline hydrolysis was calculated using their ^{1}H NMR spectra based on the integral intensities of signals of side chain alkyl substutients and signals of pyrrolidyl end-groups. After that, the grafting density was calculated using ^{1}H NMR spectra of whole graft copolymers based on the ratio of polyester backbone and poly(2-oxazoline) chain signals.

Thermoresponsive effect studies

Thermoresponsive properties of graft-copolymers **1-8** were studied using SF-256 LOMO-Fotonika spectrophotometer equipped with the thermostatically controlled cell. The temperature of phase transition was set as the point where the optical transmission (λ=635 nm) of the solution is reduced by 50% of the maximum. The heating rate was equal to 0.5 K min^{-1}. Cloud points were determined for 1% aqueous solutions of polymers.

§2. NMR spectra



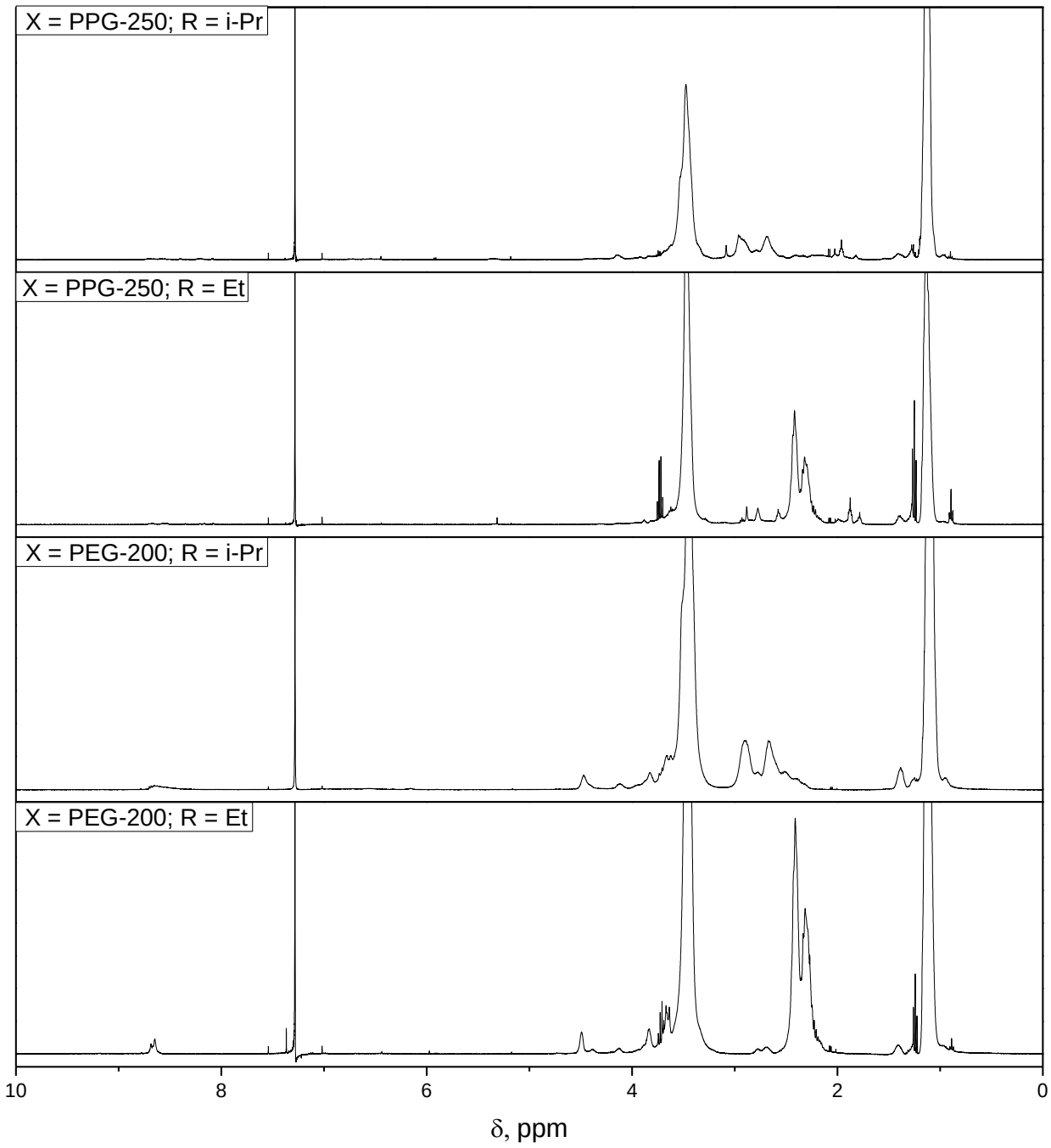


Figure S1. NMR spectra of graft-copolymers.