



# Main-chain sulphur containing water soluble poly(*N*-isopropylacrylamide-*co*-*N,N'*-dimethylacrylamide sulphide) copolymers *via* interfacial polycondensation

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## ABSTRACT

Here, we report the first synthesis of water soluble poly(*N*-isopropylacrylamide-*co*-*N,N'*-dimethylacrylamide sulfide) copolymers *via* conventional interfacial polycondensation method using phase transfer catalyst (PTC). The effect of various kinds of PTC having different aliphatic chain length and counter ion were employed to examine the kinetics of polysulfide polymer formation. The reactivity ratios, determined employing extended Kelene–Tüdös method using feed composition obtained from <sup>1</sup>H NMR analysis, suggest that *N*-isopropylacrylamide (NIPAM) is more reactive than *N,N'*-dimethylacrylamide (DMA) in both mono- and di-sulfide polymers. Thermal transition behavior investigated by differential scanning calorimetry (DSC) demonstrated that as the sulphur rank of the sulfide main chain linkages increased, the flexibility of the polymers increased reflected by lower glass transition temperature (*T*<sub>g</sub>) values. The thermal degradation behavior and the major degradation products have been characterized by thermogravimetric analysis (TGA) and electron-impact mass spectroscopy (EI-MS), respectively. Both the studies reveal that the degradation takes place due to weak-link scission of the polymeric main chain. Solubility in water and in most of the common organic solvents even after the sulphur rank increased from 1 to 2 in the main chain, is expected to render potential applications in biological field as well as in industry for these interesting new class of polymers.

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## 1. Introduction

Polysulfide polymers, an interesting class of weak-link polymers [1], possess high thermal stability in comparison with other main-chain weak-link polymers such as polyperoxides and polyselenides [2]. Polysulfide polymers also show other excellent properties such as weatherability, solvent and oil resistance [3]. This class of polymers find extensive applications as sealants, adhesives, insulators, coatings, etc [4]. They are also industrially important materials as chain transfer agents in vinyl polymerization [5], vulcanizing agents for rubbers, and stabilizer for vinyl polymers such as poly(methyl methacrylate) [6]. Main chain disulfide and side chain peroxide linkage containing poly[3-(*t*-butylperoxy)propyl disulfide] is reported to function as a 'macroiniferter' to prepare

branched polymers with relatively narrow molecular weight distribution [7].

Commercial synthesis of polysulfide polymers involves conventional condensation polymerization of aliphatic or aromatic dihalides with sodium polysulfides [1]. Methylene and ethylene dichloride have been used to prepare polysulfide polymers by Thiokol [8], although the resultant polymers are insoluble in most of the organic solvents. Interfacial polycondensation in the presence of a phase transfer catalyst (PTC) resulted in high molecular weight poly(aryldisulfide) polymers at low conversions [9]. Polycondensation of bis(4-mercaptophenyl) sulfide with bis(4-chloro-3-nitrophenyl) sulfone with various organic or inorganic bases in mixed solvents of *N*-methyl-2-pyrrolidone and water or in water resulted in the synthesis of the corresponding polysulfide polymers [10]. Most of the reported polysulfide polymers, although long known, are insoluble in common organic solvents. To the best of our knowledge, hitherto there has been no report of synthesis of water soluble polysulfide polymers *via* interfacial polycondensation, notwithstanding the environmental significance of water soluble polymers [11].

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Several commercially available monomers including *N*-isopropylacrylamide (NIPAM) and *N,N*-dimethylacrylamide (DMA) yield water soluble polymers [12]. Among the polymers synthesized from NIPAM and DMA, poly(*N*-isopropylacrylamide) (PNIPAM) is the most widely studied polymer because of its thermo-responsive behavior, as it exhibits sharp phase transition (Lower Critical Solution Temperature; LCST) around 32 °C in aqueous solution [13]. Copolymerization of NIPAM with DMA also produced thermo-responsive polymers with modifiable properties [14,15]. LCST of copolymers are strongly dependent on parameters such as the polymer chain length, copolymer composition, and solution concentration [16]. Herein, we synthesized water soluble polysulfide polymers, poly(*N*-isopropylacrylamide sulphide) (PNIPAMS), poly(*N,N*-dimethylacrylamide sulphide) (PDMAS), and their copolymers poly(*N*-isopropylacrylamide sulphide-*co-N,N*-dimethylacrylamide sulphide) (P(NIPAMS-*co*-DMAS)). Also, main-chain disulphide polymers, poly(*N*-isopropylacrylamide disulphide) (PNIPAMDS), poly(*N,N*-dimethylacrylamide disulphide) (PDMADS), and their copolymers poly(*N*-isopropylacrylamide disulphide-*co-N,N*-dimethylacrylamide disulphide) (P(NIPAMDS-*co*-DMADS)) have been prepared *via* interfacial polycondensation techniques using various PTCs. For the copolymerization reactions, the reactivity ratios of NIPAM and DMA were calculated by the extended Kelen–Tüdös method at high conversions [17], using compositions obtained from <sup>1</sup>H NMR analysis. Thermal properties and solubility behavior of these copolymers were studied in detail as well.

## 2. Experimental section

### 2.1. Materials

DMA (Sigma, 99%) was passed through a basic alumina column and NIPAM (Sigma, 97%) was purified by re-crystallization from a mixture of benzene and hexane (1/3, v/v). Tetrabutylammonium bromide (TBAB, Sigma), tetrapropylammoniumbromide (TPAB, Spectrochem, India), cetyltrimethylammoniumbromide (CTAB, Spectrochem), trimethylammonium chloride (TMAC, Spectrochem), analytical grade sodium sulfide nonahydrate (Sigma), bromine (Merck), anhydrous Na<sub>2</sub>SO<sub>4</sub> (Merck), Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O (Merck) and CDCl<sub>3</sub> (Cambridge Isotope Laboratories, Inc., 99% D) were used as received. Solvents such as petroleum ether (boiling range, 60–80 °C), tetrahydrofuran (THF), methanol (CH<sub>3</sub>OH), chloroform (CHCl<sub>3</sub>), dichloromethane (DCM), diethyl ether (Et<sub>2</sub>O) were purified by standard procedures. De-ionized (DI) water, purified by passing through ion-exchange column, was used for all condensation polymerization.

### 2.2. Characterization methods

The <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic measurements were carried out on a Bruker Avance III 500 spectrometer in CDCl<sub>3</sub> with TMS as an internal standard. Positive mode electrospray ionization mass spectrometry (ESI-MS) was performed on a Q-ToF Micro YA263 high resolution mass spectrometer from Waters Corporation. Electron-impact mass spectrometry (EI-MS) spectra in the positive mode were obtained at 70 eV in a Shimadzu QP5050A gas chromatograph-mass spectrometer with a direct inlet. The FT-IR spectrum was recorded on KBr pellets using a Perkin–Elmer RXI spectrometer. Number average molecular weight (*M<sub>n</sub>*) and molecular weight distribution (polydispersity index, PDI) values for polymers were determined by gel permeation chromatography (GPC) using a Viscotek instrument with a Viscotek refractive index detector operating at λ = 660 nm, and one polargel-M column. The eluent was *N,N*-dimethylformamide (DMF) at 40 °C and the flow rate was 0.5 mL/min. Narrow molecular weight poly(methyl

methacrylate) standards were used to create the calibration curve. Thermogravimetric analysis (TGA) was carried out on a Mettler Toledo TGA/SDTA 851e instrument at a heating rate of 10 °C min<sup>-1</sup> with a sample weight of ~4–8 mg under N<sub>2</sub> atmosphere. Differential scanning calorimeter (DSC) studies were carried out using a Mettler Toledo DSC1 STARe at 10 °C min<sup>-1</sup> heating rate with sample sizes of ~3–6 mg in N<sub>2</sub> atmosphere. During DSC study, polymers were first cooled from room temperature to –70 °C and then heated to 150 °C and again cooled to –70 °C at 10 °C/min heating rate. The glass transition temperature (*T<sub>g</sub>*) was determined from the third scan, i.e. from 150 to –70 °C, as the solvent or other volatile impurities would have evaporated upon heating from –70 to 150 °C.

### 2.3. Synthesis of monomers

NIPAM (5.18 g, 0.046 mol, 1.0 equivalent) was taken in a round bottom (RB) flask and dissolved in CHCl<sub>3</sub> (40 mL). The RB flask was placed in an ice-water bath and Br<sub>2</sub> (7.54 g, 0.047 mol, 1.03 equivalent) in CHCl<sub>3</sub> (20 mL) was added drop-wise under stirring for 2 h. Then, the resulting solution was stirred at room temperature for further 6 h. A saturated aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (100 mL) was added to the reaction mixture to remove the excess bromine, and washed three times with DI water. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> for 24 h, and rota-evaporated. Finally, it was purified by column chromatography (silica gel 100–200 mesh) using ethyl acetate/hexanes (1:4, v/v) to obtain pure 2,3-dibromo-*N*-isopropylpropanamide (NIPAM-Br<sub>2</sub>). Yield = 80%. <sup>1</sup>H NMR (Fig. S1, CDCl<sub>3</sub>, δ, ppm): 3.97 and 3.83 (BrCH<sub>2</sub>CHBr, 2H, d), 4.11 (BrCH<sub>2</sub>CHBr, 1H, t), 5.95 (–OCNH, 1H, d), 4.4 (–NHCH(CH<sub>3</sub>)<sub>2</sub>, 1H, m), 1.19 (–NHCH(CH<sub>3</sub>)<sub>2</sub>, 6H, dd). FT-IR (Fig. S2, cm<sup>-1</sup>): 3272 (–NH), 2958, 2918 (aliphatic –CH), 1641 (amide –C=O), 1165 (–CN), 577 (C–Br). <sup>13</sup>C NMR (Fig. S3, CDCl<sub>3</sub>, δ, ppm): 165, 46, 42, 32, 22. ESI-MS: [M + H<sup>+</sup>] = 274.06 *m/z* (Fig. S4).

Similarly, 2,3-dibromo-*N,N*-dimethylpropanamide (DMA-Br<sub>2</sub>) was synthesized from DMA and Br<sub>2</sub> (yield: 84%). See Fig. S5 for the <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, δ, ppm): 4.13 and 3.67 (BrCH<sub>2</sub>CHBr, 2H, d), 4.66 (BrCH<sub>2</sub>CHBr, 1H, t), 3.1–3.0 (–NCH(CH<sub>3</sub>)<sub>2</sub>, 6H, s). FT-IR (Fig. S6, cm<sup>-1</sup>): 2926, 2846 (aliphatic –CH), 1651 (C=O), 1123 (–CN), 604, 565 (C–Br). <sup>13</sup>C NMR (Fig. S7, CDCl<sub>3</sub>, δ, ppm): 166, 39, 37, 36, 30. ESI-MS: [M + H<sup>+</sup>] = 260.06 *m/z* (Fig. S8).

### 2.4. Synthesis of homopolymers

Main chain weak-link polysulfide homopolymers were synthesized through conventional interfacial polycondensation polymerization as described elsewhere [7]. Typically, NIPAM-Br<sub>2</sub> (0.25 g) in chloroform (5.0 mL) was added to the aqueous solution (5.0 mL) of Na<sub>2</sub>S<sub>*x*</sub> (1.2 mol, *x* = 1 or 2), wherein Na<sub>2</sub>S<sub>2</sub> is generated in situ from Na<sub>2</sub>S·9H<sub>2</sub>O (0.27 g) and sulphur (0.035 g), in the presence of CTAB (0.003 g, 0.01 mmol). The reaction mixture was stirred vigorously at room temperature for 24 h. The chloroform layer was separated from the reaction mixtures and washed with DI water (6 times), and subsequently dried overnight over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Finally, pouring the CHCl<sub>3</sub> solution into a large excess of hexanes resulted in the precipitation of the polymer. The polymer was vacuum dried to a constant weight and the yield of the resulting polymer was determined gravimetrically.

### 2.5. Synthesis of copolymers

Aqueous solution (5.0 mL) of Na<sub>2</sub>S·9H<sub>2</sub>O (432.3 mg) was mixed with NIPAM-Br<sub>2</sub> (82.0 mg) and DMA-Br<sub>2</sub> (310.0 mg) in 5 mL chloroform in a 100 mL RB flask. Then, catalytic amount of CTAB (0.006 g) was added to the reaction mixture and stirred vigorously

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