



# Well-defined second-order nonlinear optical polymers by controlled radical polymerization, via multifunctional macromolecular chain transfer agent: Design, synthesis, and characterizations



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## ABSTRACT

To address the issue of the aggregation in second-order nonlinear optical (NLO) polymers we developed an approach based on the synthesis of a multifunctional macromolecular chain transfer agent. The controlled monomer insertion polymerization into the main chain by a 'reversible addition-fragmentation chain transfer' (RAFT) mechanism allows the spatial arrangement of the NLO chromophores along the polymeric chain in order to obtain sequence-ordered polymers. In a first step, a novel trithiocarbonate based macroinitiator containing the disperse red 19 (DR19) units in the main chain was synthesized by polycondensation; in a second step, this polymeric precursor was applied to the synthesis of a sequentially ordered polymer by controlled insertion radical polymerization of styrene. Size exclusion chromatography (SEC), nuclear magnetic resonance (NMR) data revealed that, (i) for the first time, polystyrenes (PS) bearing DR19 dyes covalently bounded were obtained, and (ii) both the insertion reaction and the length of the polystyrene segments were accurately controlled. Whatever the incorporated dye amount, all the copolymers were soluble in common solvents. Second-order optical nonlinearity in corona-poled thin films was evaluated, and second harmonic coefficients up to 80 pm/V were determined for loading ratio lower than 10 wt-% (DR19/PS). This approach opens up opportunities for the incorporation of more efficient chromophores even in apolar matrices.

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## 1. Introduction

Organic second-order nonlinear optical (NLO) polymers have attracted considerable attention in the past two decades for their potential applications in information processing and telecommunications [1,2]. The interest in these materials derives from the high electro-optic (E-O) coefficients ( $r_{33}$ ) measured with NLO chromophore-containing polymeric materials [3,4]. In general, an E-O polymer system consists of NLO chromophores dispersed in a host matrix (guest-host system) or covalently attached to a

polymer backbone (side-chain polymer, main chain polymer), the second-order nonlinear effect resulting from an asymmetric alignment of the chromophores using electric field poling.

Currently, one of the most challenging task in the 2nd order NLO polymeric material development is to efficiently translate molecular optical nonlinearity ( $\beta$ ) into macroscopic second-order NLO activity (second harmonic generation, electro-optic modulation, optical rectification etc, that is to say to reduce chromophore–chromophore interactions in the bulk state) [5,6]. First, a majority of the efforts addressing the improvement of the E-O polymer performances have concentrated on the systematic design of chromophores with large hyperpolarizability ( $\beta$ ) [7]; second, beside increasing the number and efficiency of chromophores, efforts were mainly devoted to improve poling efficiency.

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In this purpose, several strategies have been proposed, such as either optimization of the guest–host interactions in the case of doped polymers [8,9], or matrix/chromophore compatibility improvement, or self-assembly, and/or shape engineering of the chromophores [10–13]. The latter approach has been intensively studied through the nanoscale tailoring of NLO chromophores and polymers leading to dendritic modified NLO chromophores [10,14–17], side-chain dendronized NLO polymers [18,19], pendant diazobenzene NLO linear polymers [20,21] or crosslinkable polymers via Diels–Alder type reaction for lattice hardening [22–26]. In the latter case, the poled/cured polymers showed very large E-O coefficients (up to 263 pm/V at the wavelength of 1.31  $\mu\text{m}$ ).

Here, we propose an alternative complementary way to minimize the chromophore–chromophore interactions, based on controlled radical polymerization. To validate this approach, we will use a non-polar matrix (polystyrene, PS) which usually leads to poor solvation of highly polar chromophores, resulting in very low electro-optic (E-O) coefficients ( $r_{33}$ ) (0.5 for 10% wt chromophore ratio) [8]. This strategy enables us to expect the synthesis of polystyrene containing NLO chromophore groups distributed homogeneously along the polymer chain and separated by PS blocks with narrow dispersity.

Since their emergence in the nineties, the controlled radical polymerization (CRP) methods [27], recently named by IUPAC reversible deactivation radical polymerization (RDRP) [28], have known an increasing interest as they proved to be efficient methods to control the macromolecular architectures (molar masses, narrow chain length distribution and topology) while preserving the versatility and the easy implementation of radical polymerization. The design of various polymers with complex topologies has been possible by the development of different CRP techniques: nitroxide-mediated living free-radical polymerization (NMP) [29,30], atom transfer radical polymerization (ATRP) [27,31,32], reversible addition fragmentation chain transfer (RAFT) [33,34], cobalt-mediated radical polymerization [35] and organotellurium-mediated living radical polymerization (TERP) [36]. Among these methods, RAFT and NMP allowed the synthesis of multisegmented polymers via the vinylic monomer insertion into either a multifunctional polyalkoxyamine macro-initiator [37–39], or a multifunctional macromolecular RAFT agent [40–48]. Well-defined multiblock copolymers were successfully prepared by this way [36–40,46,49]. Multisegmented polymers have also been prepared by consecutive radical addition-coupling reaction of  $\alpha,\omega$ -macroradicals onto nitroso compound [50], dithioester [51], dinitroxides [52] or by click chemistry of telechelic polymers synthesized by RAFT and ATRP polymerization [53,54]. A theoretical study highlighted that multiblock copolymers of higher homogeneity are rather prepared with RAFT strategy through a polyfunctional chain transfer agent than with the commonly used coupling of functionalized prepolymers [55]. The originality of the present study lies in the synthesis of a chromophore based polyfunctional RAFT agent to implement the synthesis of a multisegmented polymer with the block interconnected by the functional group.

## 2. Experimental section

### 2.1. Chemicals

All commercially available chemicals were used without further purification. Solvents were carefully dried and distilled prior to use. All glassware was also heat-dried under vacuum with a hot air gun before using. Reactions were performed under an inert atmosphere. Column chromatography was performed on Geduran Silica 60 (40–63  $\mu\text{m}$ , Merck). Styrene (Acros, 99%) was distilled under vacuum before use. Carbon disulfide (Acros, 99%), nonahydrated

sodium sulfur (Extra pur, Acros), methyltributylammonium chloride (Aldrich, 75 wt-% in water), 2-bromopropionyl bromide (Aldrich, 96%), Disperse Red 19 (Aldrich, 96%), triethylamine (Acros, 99%), tetrabutylammonium hydrogensulfate (TBAHS, Aldrich, 97%), azo-bis-isobutyronitrile (AIBN, Fluka, 98%) were used as supplied.

### 2.2. Monomer synthesis

*Synthesis of trithiocarbonate disodium in aqueous solution (1).* Carbon disulfide (6.6 g, 0.087 mol) was slowly added to a mixture of nonahydrated sodium sulfur (0.083 mol), methyltributylammonium chloride (0.42 g, 1.8 mmol) and water (28 mL). After stirring for one night at ambient temperature, a red aqueous solution was recovered and stored at 4 °C.

*Synthesis of DR19-di-2-bromopropionate (2).* 2-bromopropionyl bromide (13 mL, 0.121 mol) in anhydrous tetrahydrofuran (50 mL) was added dropwise under stirring to a cooled solution containing Disperse Red 19 (6.1 g, 0.018 mol) and triethylamine (17 mL, 0.121 mol) in 100 mL anhydrous tetrahydrofuran. The solution was stirred at room temperature for 48 h. Additional water (100 mL) was added to dissolve the triethylamine bromohydrate salts. The organic phase was extracted with diethyl ether, washed with a saturated aqueous solution of  $\text{NaHCO}_3$  (50 mL), and water ( $3 \times 50$  mL) until neutral pH of the aqueous phase was reached, dried over  $\text{MgSO}_4$ , filtered and solvent was evaporated. The crude product was purified by column chromatography on silica gel, using dichloromethane as an eluent, to give 7.5 g of a red solid (yield = 68%).

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ; 200 MHz)  $\delta$  (ppm): 1.79 (d, 6H,  $^3\text{J} = 7.0$  Hz,  $\text{CH}_3$ ), 3.83 (t, 4H,  $^3\text{J} = 6.2$  Hz,  $\text{CH}_2\text{-N}$ ), 4.43 (m, 6H,  $\text{CH-Br}$ ,  $\text{CH}_2\text{-O}$ ), 6.87 (d, 2H,  $^3\text{J} = 9.2$  Hz,  $\text{CH}_{\text{arom}}$ ), 7.93 (d, 2H,  $^3\text{J} = 9.2$  Hz,  $\text{CH}_{\text{arom}}$ ), 7.95 (d, 2H,  $^3\text{J} = 9.2$  Hz,  $\text{CH}_{\text{arom}}$ ), 8.35 (d, 2H,  $^3\text{J} = 9.2$  Hz,  $\text{CH}_{\text{arom}}$ ).

### 2.3. Multifunctional Macromolecular RAFT Agent (MM-RAFT): synthesis of DR19-based polytrithiocarbonate (3)

The DR19-di-2-bromopropionate and the crude aqueous solution of disodium trithiocarbonate were used for the synthesis of the desired DR19-based polytrithiocarbonate by step polymerization. DR19-di-2-bromopropionate (2.08 g, 3.5 mmol), tetrabutylammonium hydrogensulfate (240 mg, 0.7 mmol) as phase transfer catalyst, toluene (14 mL), and the solution of sodium trithiocarbonate in water (12 mL, 3.5 mmol) were introduced into a round-bottom flask. The mixture was stirred at 60 °C for 72 h. The organic phase was extracted with diethyl ether, washed with water ( $4 \times 50$  mL), dried over  $\text{MgSO}_4$ , filtered and solvent was evaporated. The crude product was purified by column chromatography (diameter = 15 cm; height = 1 m) on silica gel, using a 1:1, v:v, cyclohexane:dichloromethane mixture, then pure dichloromethane, then a 1:3, v:v, ethyl acetate:dichloromethane mixture as an eluent, to give several fractions, one consisting in 1.2 g of a red solid (yield = 47%). The fraction of DR19-based polytrithiocarbonate recovered for subsequent RAFT polymerization of styrene displayed the following macromolecular characteristics:  $M_n, \text{MM-RAFT} = 2690 \text{ g}\cdot\text{mol}^{-1}$ ,  $M_w/M_n = 1.20$ .

### 2.4. RAFT polymerization of styrene (4)

A mixture of the prepared multifunctional macromolecular RAFT agent (515 mg,  $1.92 \times 10^{-4}$  mol,  $M_n = 2685 \text{ g}\cdot\text{mol}^{-1}$ ,  $M_w/M_n = 1.20$ ) and AIBN in solution in dichloromethane (3.84 mL,  $5.19 \times 10^{-5}$  mol) was stirred for 5 min. After evaporating the dichloromethane, distilled styrene (51.9 mL,  $4.54 \times 10^{-1}$  mol) was added. The mixture was stirred for 30 min and subsequently poured into six tubes sealed with Rotaflo<sup>®</sup>. Oxygen was removed by

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